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REPRINTS

DEPARTMENT OF CHEMICAL ENGINEERING,

UNIVERSITY OF WISCONSIN

Volume 2

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THE EFFICIENCY OF COLLEGE TRAINING OF MEN FOR THE CHEMICAL INDUSTRIES.

By Charles F. Burgess.

An estimate of the efficiency of college training of men for the chemical industries must necessarily be based upon the qualifications which the men possess during the first years immediately following their college course, and not upon the work done either by undergraduate or graduate students.

According to observations of the writer, fully 90 per cent. of college graduates who enter the industrial chemical field make their beginning in analytical chemistry, and of these men an even greater percentage are ambitious to get beyond this stage into the works where they may have charge of productive operations.

As a typical example of the graduate who achieves success, let us follow one for a few years after graduation. His career began with an appointment as chemist in the analytical laboratory of one of the branches of a large chemical industry operating a number of plants throughout the country.

On a salary of $12 per week, and his bare living expenses being thereby assured, he gave his undivided attention to the chemical work constituting his assignment. This consisted of sulfur determinations in each of a large number of samples of ore supplied daily to the laboratory. No freedom was allowed in the choice of methods, but he was given careful instruction in a method, new to him, which had been adopted as the standard of this department. As he grew proficient, he became weary of this task, but through constant repetition he found opportunity for reflection and observation. It was a revelation to contrast the number of analyses which could be made in a given time with the determinations obtained in like time in the college laboratory.

The head of the laboratory, who held the title chief chemist, was his instructor, and was far more insistent upon accuracy and despatch than had been any of his college instructors. He was evidently a man of long years of experience in analytical chemistry, who had acquired the knack of handling a laboratory force so that it could turn out analyses at a remarkably low cost per determination. Although college bred himself, he did not hold this to be an essential requirement for analysts, since he had taken young apprentices from the shop and offices and successfully trained them to perform their daily duties of analytical determinations with accuracy and speed.

As diversion from the daily routine grind, new materials were occasionally submitted for analysis, and these required the use of new methods and an examination of the very limited literature available in the laboratories. This new work was turned over to those of the laboratory force who had received college training, their results being checked carefully by the head chemist. Presently it was rumored that the accuracy of some of the analytical results turned out in the laboratory was being questioned at the head office, where a lack of agreement between figures obtained in the company's different laboratories had been detected. This resulted in an uneasy feeling until the arrival of a representative from headquarters known as the chemical auditor. He was a man of national reputation as an analytical chemist, the owner of a Ph.D. degree, and his duty consisted in gleaning the results of research work appearing in the chemical journals, in working out and standardizing methods best adapted to use in the branch laboratories, and in a general supervision of these analytical laboratories to insure that they were all working in harmony and coöperation. He began a careful inspection of the details of the methods employed in this laboratory, and soon found some causes for discrepancies.

His acquaintance with this noted authority gave our young student his first contact with a chemist whose position he envied, but his envy was tempered by the reflection that there were few positions of this rank and responsibility in the country, while a large army of analytical chemists were competing for them. This did not discourage him, however, but he had his moments of discontent. One of these came one day when he was seated at a balance, making a moisture determination. On one side of him sat a former office boy making an ash determination, and on the other a man recently taken from a labor gang was weighing an ore sample. An official of the company looked in upon them, commenting jocularly on the "three little chemists sitting in a row." Our young man saw the joke, but that night he wrote to his former friend and adviser, the Professor of chemistry of his Alma Mater, as follows:

> I have been in this laboratory to which you recommended me for nearly a year, and have now come to the conclusion that it will be advisable to make a change. Can you advise me of an opening? All of the employees of this department are ranked on the pay-roll as chemists, though less than half of them have had any chemical training whatever before coming here. There seems to be no opportunity for advancement. The four other college graduates with whom I am working are likewise discouraged. Delay in promotion does not come from mediocre ability; the head of the laboratory is one of the ablest chemists I have known. He has been here for eleven years, and is now getting but $125 per month. I have had a good training in general and analytical chemistry, but even if I had spent my entire college course in the study of this branch, my opportunities would be no better than they are at present. All of the real thinking is done for us by a few men whom we seldom see.
>
> "In contemplating the numerous uneducated men in the laboratory who are called chemists, I do not take as much pride in holding that same title as I had expected to while in college. It seems to me that if it were only possible to get into the works as assistant to a department superintendent, the chances for advancement would be greatly improved, but such opportunities are seldom presented.

All his old professor could say in encouragement was to assert that the majority of college graduates in chemistry get into analytical work as a stepping stone to something better; that in the analytical laboratory the employers practice a weeding-out operation, separating the men of ordinary ability from those possessing enterprise, persistence, resourcefulness, and other qualities contributary to success; that although this process is frequently a slow one to a man really deserving, promotion is bound to come; and that, therefore, he should not resign, but try to make himself so proficient that when an opportunity presented itself, he would be ready to make the most of it.

Not entirely convinced that his professor really understood the situation, the young man determined to prepare himself for opening the door for opportunity when it should knock. First he took up a general study of the manufacturing business in which the company was engaged—the economic factors which had determined the location of his branch at that particular point, such as labor conditions, transportation facilities, source of raw material supply; the costs of generating steam and power. He further studied the details of the manufacturing operations as far as he could get to them; the relation of the analytical laboratory to the works at large, etc.

He found that the library facilities were decidedly inadequate for this study, consisting of a few books and several scientific publications, and that none of his associates, not even the head chemist, was familiar with the works operations. They had no interest in their work after the results had been recorded and sent to the office, and the significance of analyses upon the larger problems of the company did not concern them.

Thrown, therefore, upon his own resources, he made a survey of his college training, hoping to determin what portion of it might now be of assistance. Because of his meager salary, he could not afford to subscribe for the best scientific and technical publications, but he had learned that a large amount of useful literature was available for the asking, and so appealed to such agencies as the census bureau, various other government departments and laboratories, the state geological surveys, the bureau of labor and industrial statistics. Using what they sent him he resumed the course in economics which he had taken at college. He reviewed his work in steam engineering and power generation in the light of application to the conditions of his plant. His old work in mechanical drawing and machine design enabled him to produce working drawings of a labor- and time-saving laboratory device. Metallography had taught him the value of the microscope in the study of materials, and getting out the dust-covered microscopic equipment, he found he could determin quickly some of the properties of the materials which the slower chemical analyses were revealing. This study of costs of chemicals and other materials received and manufactured, not from laboratory supply lists but from wholesale quotations of trade publications, gave him an idea of opportunities for manufacturing profits. Out of such diversified lines of studies as these came a gently increasing interest in his routine work.

Finally opportunity knocked at his door, and he was placed in charge of the filter-press room, where a comparatively simple operation was kept going night and day. This consisted in treating a ground ore with a chemical solution yielding an insoluble, valueless filter cake and the valuable filtrate. This new foreman found that the principal item of cost was the renewal of filter cloths, amounting to a total of $1.50 per ton of ore treated, and he began a study of the possibilities of decreasing this item. The rapid wear on the cloths was due to the action of the solution on the fibers, and more especially to the wear on the upper edges of the plates where they were pulled apart for dumping. He satisfied himself by a study of the action of this chemical solution on various kinds of fibers that they were employing the best material. By subjecting the cloth in different directions to a strength-testing machine, he found that a stress elongation diagram was obtained which taken in one direction of the cloth was similar in shape to that for mild steel, and in the other direction to cast iron, as he had obtained these curves in his college testing laboratory. This yielded a method of drawing specifications for cloth best suited to the requirements, and resulted in some small reductions in cost, but not enough to be satisfactory. Since the wear was directly proportional to the time, and to the frequency of dumping the presses, it was evident that this could be reduced per ton of ore only by more rapid working, and by making a thicker filter cake. To this end the pressure of the feed was increased by changes in the pumping machinery. The principal hindrance to more rapid working was found to be the hard, flinty precipitate which formed on the plates and filled up the grooves. It was the custom to remove this coating by a pneumatic chipping hammer, requiring several hours of labor per plate. An attempt was then made to find a labor-saving solvent, but solubility tables gave our young man no assistance. Solvents which would dissolve this precipitate were either too costly, or would attack the iron as well as the scale. He discovered, however, that a caustic soda solution of certain strength, while not dissolving the scale, would in four days' time soften it so that it could be brushed off readily. A calculation of the interest and depreciation on investment in plates tied up while under this treatment showed the sum to be far less than the labor involved in the older method, which method was then discarded. The cleaner plates, higher pressures, and better cloths enabled the filter cake to be doubled in thickness in equal time, and the cost of cloths per ton of ore treated was reduced one-half, resulting in a daily saving of $50.00 in this one item alone.

With such a record of reducing cost, it naturally followed that our young man was given other opportunities to exercise his abilities. He was transferred to a branch plant, where sulfuric acid was being made by a newly developed contact or catalytic process. His problem now was to assist in the determination, if possible, of some way to prolong the life of the contact mass, upon the solving of which was dependent the commercial success and, therefore, the continuance of the use of the process.

In undertaking this problem, our protegé recalled his college thesis work, in which he had been trained in systematic procedure beginning with a statement of the problem, a summary of the state of knowledge based upon the literature and other sources of information, an outline of proposed experimentation, the execution of the work, the significance of the results in application to the problem in hand, and conclusions or recommendations based upon the investigation.

In applying this method to the new problem in hand, he found himself involved in work of a highly scientific order, comparable with the best of that done in university laboratories. He became as deeply interested in it, through an appreciation of its practical importance, as any pure scientist can become in his labors, even though appreciating that his results would not, on account of the company's policy of secrecy, be given out for publication.

Such is a narrative typical of the progress of a successful industrial chemist who benefits by his college training. The industrial people claim that the colleges are not doing all that is possible to fit men for industrial work. The educational chemists are divided in opinion as to what methods they should pursue in meeting these demands. The majority of them believe that more of a student's time should be devoted to chemistry; that they should turn out men more skilled in analyses, while others hold that it is no more the function of a university course to turn out skilled analysts than it is that of a mechanical engineering course to turn out skilled machinists or draughtsmen, or of an electrical engineering course to graduate proficient electricians. The recent introduction and present multiplication of courses in chemical engineering is in line with the views of the latter class of educators who are designing a course of study which will give to its graduates numerous viewpoints from which to regard chemical work; to acquaint them with the most useful tools for attacking industrial problems; and to qualify them not as skilled engineers or chemists upon graduation, but as men capable of learning and progressing after getting into industrial work, so that they may earn the title which is too frequently bestowed upon the graduate at commencement time.

Shall college training for chemists be intensified or diversified? Shall the training in chemistry be such as to entitle its possessor to call himself an analytical or organic, or metallurgical chemist upon graduation and limit him to pursuit in his already chosen field; or shall the training in chemistry be reduced in quantity and supplemented by study in allied subjects, so as to give a broader training, a greater versatility, and a wider range of opportunities for employment?

There are few teachers of chemistry who will deny that a broader scope of study is desirable, but there are equally few who will agree to any reduction in the amount of attention to their particular subjects. This is the basis of the growing sentiment favoring a five-year college course for industrial chemists. The writer is unable to see a solution of the problem through a lengthening of the course of study, and believes that if the fields of the technical applications of steam, electricity, hydraulics, mechanics, and the like, can be occupied successfully by men having four years of college work, there is no fundamental reason for requiring a longer course for men for industrial chemistry. The remedy for apparent crowding should come, therefore, through redesign or improvement of the four-year courses. One way of accomplishing this is through less intensification in purely chemical studies, and the time-consuming laboratory practice accompanying them. While proficiency in some particular lines might thus be sacrificed, the student could be given an interest in and knowledge of the basic principles of those lines which will enable him to continue his studies after graduation; and in the additional studies thus made room for, his total efficiency may be materially increased.

It is a fundamental error to introduce courses in industrial chemistry, or chemical manufacture, in the belief that they will give a man a working knowledge of the technical details of some particular manufacturing business which he may enter. Should a student know that he is going into the cement business, it would be time poorly spent in his college course to devote part of it to a study of technical details of cement manufacture. The manager of a large telephone company employing many college graduates each year specifies that he wishes men broadly trained rather than those who have spent time in studying the details of telephone practice, since instruction of the required kind can be given most efficiently while in the pay of the employer.

There are, however, other and good reasons for giving courses in industrial chemistry, and especially if they can be given in such manner as to increase a student's interest. The work should give him a general view of the field of technical chemistry, and of the interrelationship between the important chemical industries. It should give him the beginning of an appreciation of the commercial factors which are inevitably linked with the production of chemical materials. Such a course should teach how and where to find information as to chemical processes rather than aim to impart information about such processes. The books used should be reference rather than text-books. The student of chemistry usually finishes his course with but little appreciation of costs and values. The price lists with which he may have become familiar are those of the dealers in supplies for chemical laboratories. "The introduction of the dollar sign into the chemical equation," and the necessity of keeping the balance upon the right side of the equation, opens to the student an entirely new and a most interesting view of the field of chemistry. Frequent reference to lists of wholesale prices of chemicals such as are given in the *Oil, Paint, and Drug Reporter*, and other similar trade publications, with explanation of trade usages in making trade quotations, the influence of freight rates, the method of packing as influencing rates, import duties, insurance risks, and the like, may well constitute an important part of the teaching of technical chemistry.

The differences of opinion of the chemistry teachers and the industrial men on educational methods are due in large part to the attitude of the former toward industrial work. There is undoubtedly a tendency for the college chemist to regard his technical brother as one immersed in routine work and to whom chemistry has become a trade rather than a profession. A statement of significance in showing the attitude of the one class of chemists toward the other is taken from a presidential address which concerned the welfare of the American Chemical Society and the publication of its Journal:

> Those engaged in industrial pursuits must always remember that although they equal in number the educators and other students, or may even form a majority of the society, it is none the less true that the former are, and no doubt will continue to be, the greater producers of new and original matters, and hence deserving of greater consideration in proportion to their numbers than those who are less productive.

Any one who has had an opportunity to review the new and original work being done in industrial fields cannot help but feel a profound admiration and respect for the high-grade research work which forms the basis and the immediate means of realization of much of the industrial progress on which the present age prides itself. While the writer does not assume authority to reply for all industrial chemists, he believes that if they were not restricted by commercial policies of secrecy, their publications of new and original scientific work would be just as numerous, and quite as valuable, as those of their unrestricted brothers in the educational laboratories. Investigation work carried out to meet industrial needs may be, and frequently is, as distinctly scientific as that which is done to fulfil the requirements of a doctor's thesis.

This attitude of chemistry teachers toward the industrial field is shown by the fact that a large majority of students taking advanced graduate work have done so in preparation for teaching positions. But that graduate work is not merely a means of getting into educational work is demonstrated by the large and increasing numbers in the graduate departments of our engineering schools, who are looking forward to industrial pursuits.

In conclusion, the writer asserts his belief that there is in general an inefficiency in the college training of men for industrial chemistry; that this training is largely in the hands of men who have an insufficient acquaintance with and appreciation of the requirements of the industrial workers; and that when educational chemists and industrial chemists finally come together on common ground, some of the present difficult educational problems will disappear.

DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF WISCONSIN.

A paper read at the meeting of the Chicago Section of the American Electrochemical Society, January 20, 1911. Called up for further Discussion at the Nineteenth General Meeting of the Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

ELECTROLYTIC REFINING AS A STEP IN THE PRODUCTION OF STEEL.

By Charles F. Burgess.

During the past five years a lengthy investigation has been carried on in the Chemical Engineering Laboratories of the University of Wisconsin dealing with electrolytic refining of iron and its use in the production of alloys. About three tons of iron has been refined and over one thousand alloys produced and tested.

While this experimental work has been on the "test tube" or laboratory scale, it is believed that some of the results indicate the feasibility of enlargement to a commercial scale, and a short discussion is submitted here bearing on the question, "can electrolytic iron be made an industrial product?"

Many old text-books on electrochemistry give descriptions of methods of depositing iron electrolytically, implying therefore that electrolytic iron is not a new product. The only use suggested, however, is for facing engraved plates used for printing. By following any of these earlier processes it is seen that only very thin layers of iron can be deposited, the coating tending to become dark, rough, and powdery. It is to overcome this limitation that the work at the University of Wisconsin was undertaken, and that this has been successful in a measure is indicated by the production of an iron cathode nearly two inches in thickness.

The manner in which electrolytic refining has revolutionized the copper industry is now an old story, and electrolysis has likewise become an industrial agent in the metallurgy of silver, gold and lead. Now that it has been found that iron can be refined electrolytically almost as easily as can copper, it is pertinent to inquire whether there is a field of usefulness for such iron. This depends upon whether electrolytic iron has superior qualities due to purity or physical condition, and whether it can be procured at low cost.

From the standpoint of purity it must compete with some notable metallurgical developments which have resulted in the product such as is being made by the American Rolling Mill Company in a basic open-hearth process. For this material a purity of 99.94 percent is claimed, and justifiably so, as some of our analyses show. The electric furnace is another factor which is contributing largely to the control of the composition and purity of iron alloys, and the striking possibilities which are offered in this developing field cannot be overlooked in advocating the development of an electrolytic iron process.

The chief source of commercially pure iron has been, and perhaps now is, the high grade Swedish and Norway iron, used largely as a base material for high-grade crucible steel. The analyses of this material usually indicate a high purity, though frequently and erroneously calculated by difference after determining carbon, sulphur, silicon, phosphorus and manganese. It is not uncommon to find oxides and slag to the extent of two percent in this material, and this impurity undoubtedly may have an influence on the resulting alloys made from it.

We have found that electrolytic iron can be produced with a purity as high as 99.97 percent and perhaps even better, using extraordinary precautions. This record has been made by using the best commercial grades of pure iron as anodes. A few hundredths of a percent of purity must be sacrificed in using anodes of mild steel or other less pure materials. Electrolytic refining offers a means of reducing or screening out most of the impurities commonly found in iron, and of producing a material not only of high purity but of great uniformity. Even though it may be shown eventually that electrolytic iron may not have a higher purity than that attainable by other methods, the uniformity of its composition should make it a valuable material as a means of eliminating many of the variables with which the crucible steel maker has to contend.

Using an electrolyte containing 40 grams of iron per liter in the form of ferrous sulphate together with 40 grams of ammonium chloride, it has been found possible to conduct a continuous refining operation for many months at a current density of 6 to 10 amperes per square foot of cathode surface, and at a potential difference of about one volt. The current efficiency is very close to 100 percent, as it is in copper refining.

This leads to the calculation that one kilowatt hour will refine two pounds of iron; or a cost for power of ½ cent per pound is attainable. The cost for labor, solution maintenance, and fixed charges are estimated to be not greater than the power costs, making a cost of refining of about $20 per ton. Assuming the anode material to be mild steel costing $35 per ton, the cost of electrolytic iron would be in the neighborhood of $55. These approximate calculations indicate that this material might well compete on price with high-grade Swedish iron.

Among the properties of electrolytic iron which may give it some added usefulness is its content of hydrogen and the brittleness which results from this occluded gas. This hydrogen may be of some service in reducing oxides in a melt. The brittleness of the electrolytic iron before the hydrogen is driven off makes it easy to break it up into pieces suitable for introduction into the steel crucibles.

DISCUSSION.

(At Chicago, January 20, 1911.)

MR. F. T. SNYDER: I would like to ask Professor Burgess whether he ever used the molten condition in producing iron electrolytically.

PROF. C. F. BURGESS: Only to a very slight extent. We got no encouraging results.

MR. G. H. JONES: One point I consider very important is the cost of the current. Using it during the off months or at the off times of the day, the rate of the ordinary charge for the refinery will be almost one-half of the ordinary price, and that will make it very low indeed and ought to help out a great deal in this business.

PROF. H. N. MCCOY: At what times in the day, Mr. Jones?

MR. JONES: From four o'clock to eight o'clock in the afternoon during the months of December, January and February.

All the other months you can use it all the time, but not during those four months,—those are the off months.

MR. C. E. BAKER: I would like to ask Professor Burgess if he ever tried electrolyzing iron from chloride solutions.

PROF. BURGESS: You cannot get deposits of iron from chloride solutions as satisfactorily as from sulphate solutions. However, it is simply a question of adjusting your electrolyte so you can build up a big deposit, and which will be cheaper. Other experimenters have reported satisfactory results from chloride solutions, but we have not succeeded in getting satisfactory results.

MR. W. BENTLY: I would like to ask Professor Burgess if he has the electrodes in motion in depositing the iron; whether they are moving while the iron is being deposited or whether they are stationary in the solution.

PROF. BURGESS: Everything is perfectly quiet in the tank. We have tried the effect of rapid circulation and slow, and find little if any change in it and, in fact, the tanks are left for several months without cleaning out, that is, without cleaning out the deposits at the bottom; but once a week the solution is circulated through a series of tanks, just circulating two or three times.

MR. BENTLEY: The reason I asked that question is because I believe in certain plating work, by rotating the electrodes quite rapidly a deposit which is more uniform and which is smoother and freer from crystals or crystalline structure is obtained, and I was wondering whether it might not have some effect with iron.

PROF. BURGESS: Of course, what we tried to do was to work out a process for doing this as economically as possible and if you figure the cathode investment in moving the electrode throughout your entire plant, it would be a very expensive proposition. We have tried to deposit iron tubes by rotating the cathode, but never got any better deposits than when having them quiet.

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A paper presented at the Nineteenth General Meeting of the American Electrochemical Society, in New York City, April 7, 1911, President Wm. H. Walker in the Chair.

POLARIZATION IN ITS RELATION TO THE DECOMPOSITION PRESSURE OF ELECTROLYTES.

By Oliver P. Watts.

One of the properties which distinguishes electrolytic from metallic conductors is the relation between the impressed electromotive force and the current which is produced thereby. In a metallic wire, the resistance of which is known, the current may be calculated by an application of Ohm's law. This is not so for electrolytes when "direct current" is used, except for a few combinations of special electrodes and a particular electrolyte.

If a gradually increasing E. M. F. is applied to the ends of a wire and simultaneous readings of the current and pressure are made, the current increases in the same ratio as the E. M. F.

When an electrolytic conductor with electrodes of platinum, carbon, or some other material, insoluble in the particular electrolyte chosen, is substituted for the wire, it is found that for small values of pressure no permanent current flows. The E. M. F. must exceed a certain minimum value before a permanent current is obtained. This minimum value is the so-called decomposition pressure.

In Table I are given the values of current corresponding to the indicated E. M. F. applied to two feet of No. 26 "ni-chrome" wire.

TABLE I.

Impressed E. M. F. Volts	Current Milli-amperes	Impressed E. M. F. Volts	Current Milli-amperes
0.25	48	1.75	344
.50	95	2.	390
.75	143	2.50	490
1.00	190	3.	586
1.25	242	3.50	680
1.50	292	4.	775

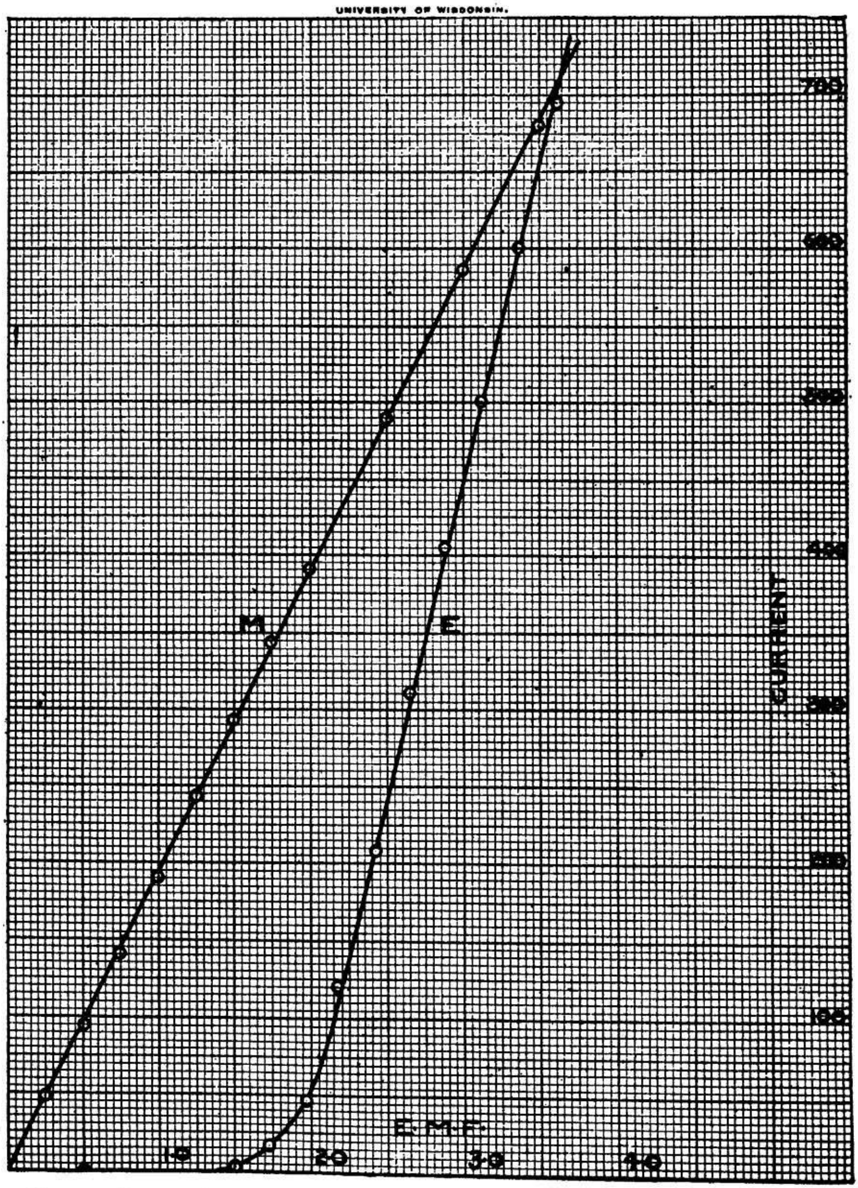

FIG. 1. Current-E. M. F. Curves for a Metallic (M) and for an Electrolytic (E) Conductor.

Figure I shows graphically the relation between current and E. M. F. for the wire, and for a 10 percent solution of zinc bromide with carbon electrodes. The numerical data for the latter are given in Table VI.

It is of interest to review the explanations which have been offered for this peculiar behavior of electrolytes. First in point of time was Grotthus' hypothesis, which was proposed in 1820. According to this, the reason why any pressure, however small, does not send a current through an electrolyte as it does through a metal is because a definite E. M. F. is required to break up the molecules of each particular compound, and therefore no current can pass below that E. M. F. These "decomposition pressures" have been determined experimentally for many different solutions, and it has been found that the more stable a chemical compound is, the greater its decomposition pressure. From the values of the heats of formation and of solution of compounds, it has been found possible to compute values for the decomposition pressures, which agree closely with those obtained experimentally.

Into this seemingly satisfactory agreement of theory with experimental observation, there was projected a disturbing fact. It is possible for an E. M. F. far below the decomposition pressure to produce a considerable momentary current, or a very minute steady current in an electrolyte. To harmonize theory and fact, Clausius, in 1856, suggested that the molecules of a dissolved compound which is capable of conducting an electric current are not firmly locked together, but that the atoms are continually changing partners with their neighbors, and that the E. M. F. is not called upon to disrupt molecules, but only to give direction to the movements of the atoms or radicals during their moments of freedom. It should thus be possible for any E. M. F., however small, to produce a flow of current in an electrolyte.

In the more recent theory of "electrolytic dissociation," advanced by Arrhenius in 1887, it is assumed that by the mere act of dissolving, a large proportion of the molecules of all dissolved substances which yield conducting solutions are broken up into two or more parts.

Thus each of the later theories of the mechanism of the process of electrolysis has been formulated in such a way as to eliminate any "decomposition pressure," yet in every case of electrolysis with insoluble electrodes no permanent current of any magnitude is obtained until a certain voltage has been exceeded. Theoretically the phenomenon of the decomposition pressure has been eliminated; practically, it is still with us.

Although the cause of this phenomenon has been clearly set forth in some of the texts on electrochemistry, there still seems to be considerable misapprehension upon this point.

One view of the cause of the different behavior of metallic and of electrolytic conductors is indicated in the two following quotations:

[1] "The advantages of soluble anodes over insoluble anodes is that a very much smaller E. M. F. is required to produce the same result. * * * This is due in the two cases to a difference in the contact resistance to the current, as it leaves the electrode and enters the solution, which is sometimes called "transfer resistance." This is undoubtedly a physical effect, which must not be confounded with the phenomena of polarization. With insoluble anodes, *this resistance is said to be largely due to a condensed film of gas,* which is only slightly removed by agitation of the liquid, but it is also accounted for by other actions of a more complex nature."

In a very valuable and suggestive paper[2] upon the corrosion of metals, it is pointed out that the rusting and corrosion of iron is an electrolytic process and that the speed of rusting depends upon the rate of removal of a protective film of hydrogen which forms upon the metal. Thus we find:

"One fact regarding the corrosion of iron appears to be undisputed, *viz.,* that oxygen is necessary for a continued action. This corrosive action can cease from two causes, viz., * * * or the action may be stopped by a film of molecular or gaseous hydrogen upon the metal, which, owing to its resistance, prevents the flow of an appreciable current."

It is the purposes of this paper to show clearly that the principal factor in causing the phenomenon of the decomposition voltage as observed in electrolysis is not the *resistance* of a gas or other film upon either or both electrodes, but that it is due to a counter-electromotive force which is produced at the electrodes as a result of the action of the impressed E. M. F. This counter-E. M. F. will hereafter be referred to as polarization.

Let a voltmeter and a milli-ammeter be suitably connected to two platinum electrodes immersed in dilute sulphuric acid or

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[1] Cyaniding of Gold and Silver Ores. Julian and Smart, p. 137.

[2] Tr. Amer. Electrochem. Soc., **14**, 179 (1908).

sodium chloride, and readings of current made as the impressed E. M. F. is increased. If the circuit is opened from time to time for the purpose of reading the polarization, great difficulty will be experienced, if it be not found utterly impossible, to get satisfactory readings when the electrodes are the small ones of one or two square centimeters area, such as are commonly used for these experiments in the laboratory. The polarization is there, but the voltmeter requires a greater current for its action than this tiny storage cell can furnish.

TABLE II.

Electrolyte, Normal NaCl. Electrodes, carbon.

Impressed E. M F. Volts	Current Milti-amperes	Polarization Volts
0.1	0	0.075
0.2	0	.16
.45	0	.40
.62	0	.58
.84	0	.80
.96	0.25	.88
1.09	0.25	1.03
1.26	0.4	1.18
1.51	1.0	1.38
1.96	5.	1.57
2.21	10.5	1.80
2.51	22.	1.84
2.80	60.	1.84
3.00	105.	1.83

In Table II and Fig. 2 are given the results obtained when the potentiometer is substituted for the voltmeter. The electrolyte was normal sodium chloride and the electrodes were of carbon, 6 x 9 mm., immersed about 37 mm. The curves indicate the reason for no permanent current up to 1.5 volts. With each increase of applied pressure there is developed a counter-electromotive force equal to it, so that no current can flow, and the only reason there is ever any permanent current through an electrolyte when using insoluble electrodes is because there is a limit beyond which the polarization no longer increases in the same ratio as the impressed E. M. F. At about 1.5 volts the polarization lags behind the impressed E. M. F., and at this point the flow of current begins. At about 2.5 volts the polarization has reached its maximum value, so beyond this pressure the current varies directly as the impressed E. M. F.

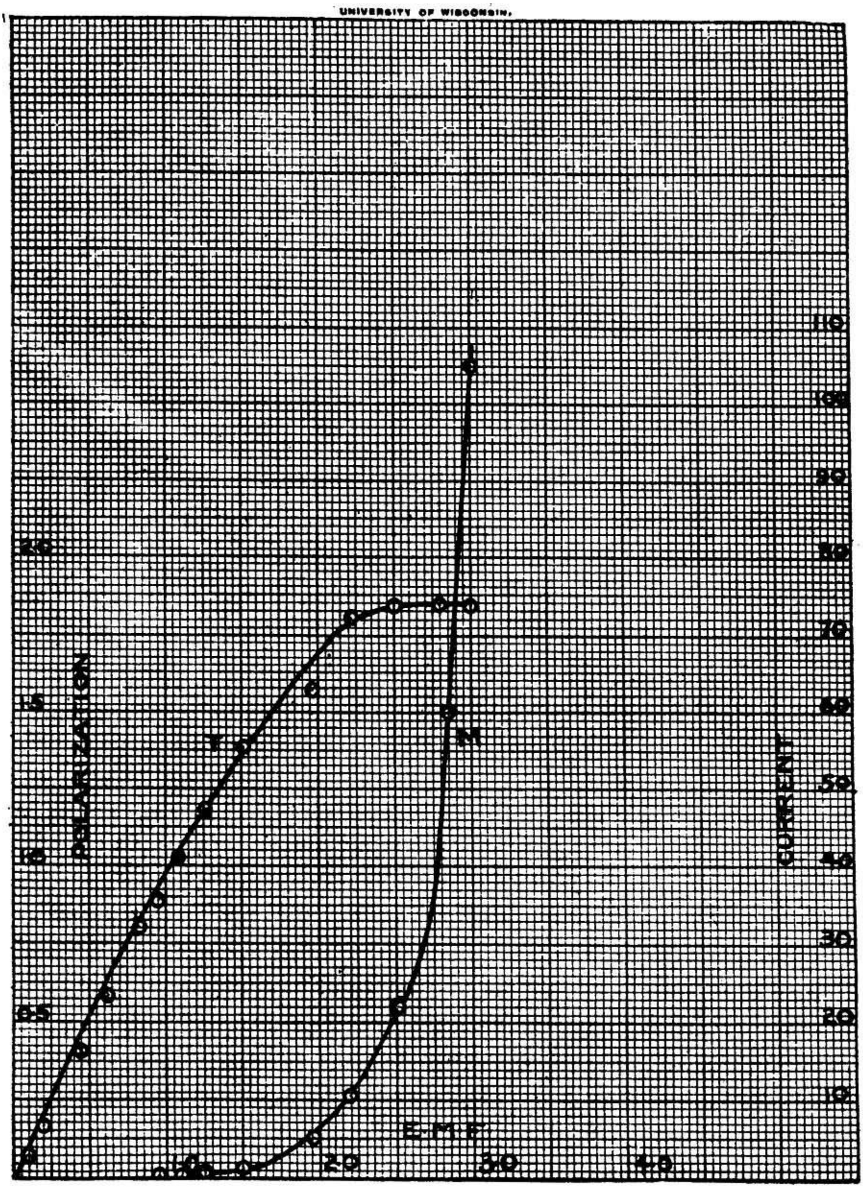

FIG. 2. Electrolysis of n.NaCl.—Carbon Electrodes.

The only possible part that the resistance of a gas film can play is to that small extent by which the polarization falls short of equaling the impressed E. M. F. The method of reading the polarization consisted in opening the line switch with one hand

and afterward closing the key of the galvanometer with the other, so that an appreciable interval elapsed between the breaking of the circuit and the reading of the galvanometer. It is therefore probable that the actual values of the polarization are slightly higher than the values recorded.

TABLE III.

Electrolyte, Normal $CuSO_4$. Electrodes, platinum.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization Volts
0.25	0	0.25
.50	0	.43
.75	0	.71
1.00	0	.90
1.25	0	1.13
1.50	1.	1.30
1.75	7.	1.36
2.0	11.	1.40
2.25	37.	1.40
2.50	53.5	1.40
2.75	70.	1.39
3.00	85.	1.41
3.25	102.	1.41
3.50	119.	1.43
3.75	130.	1.43

Table III and Fig. 3 show similar observations for normal copper sulphate with electrodes of sheet platinum one centimeter square. The general character of the curves is the same as for sodium chloride. It is to be noted that in this case gas is liberated only at the anode, and if it were the resistance of a gas film which prevents the passage of the current below 1.25 volts, this action would be confined to the anode, and the single gas film there would have to be quite as effective as the two films, one at each electrode, in the case of common salt.

The cause of the polarization is indicated by the behavior of the ammeter needle. When the E. M. F. is 0.5 volts, or any other value below the decomposition point, if the circuit be opened for a minute, and then closed again, at the instant of closing there is a considerable rush of current, which in a second or two dies away to zero, the value of the permanent current for the E. M. F. applied. When the circuit was open there was little or no polarization at the electrodes, and on closing the circuit a flow of

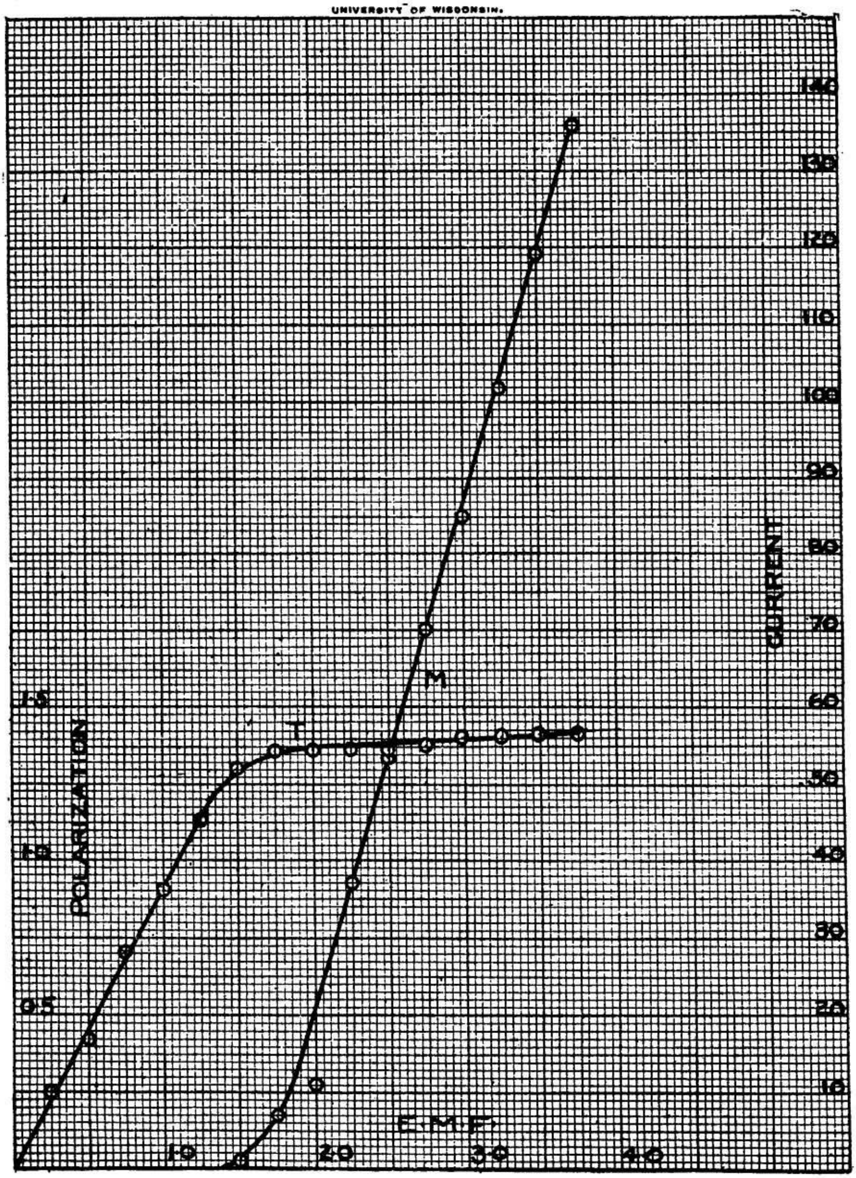

Fig. 3. Electrolysis of n.CuSO$_4$—Platinum Electrodes.

current began according to Ohm's law, just as it would flow through a wire, but, as a result of the deposition of the products of electrolysis at the electrodes, an increasing counter-electromotive force was produced, which finally attained the value of the impressed E. M. F. and stopped the flow of current.

The "residual current," that permanent current, normally so small as to escape notice, which flows through electrolytes at any constant E. M. F. below the decomposition pressure, is only the current required to deposit products of electrolysis equal in amount to those dissolved by the electrolyte or otherwise removed.

By the introduction of a third electrode and the measurement of the differences of potential between this and the anode and cathode, it is possible to ascertain what proportion of the total polarization is contributed by the anode and what by the cathode. The most satisfactory reference electrode to use for this purpose is the "normal calomel electrode," so well known that a description of it is unnecessary.

TABLE IV.

Electrolyte, normal $CuSO_4$. *Electrodes, platinum.*

Impressed E.M.F.Volts	Current Milli-amperes	Polarization		Total volts
		Anode volts	Cathode volts	
0.05	0	—0.882	—0.839	0.031
.25	0	—.903	—.689	.236
.48	0	—1.118	—.646	.460
.72	0	—1.355	—.646	.709
.96	0	—1.591	—.642	.962
1.20	0	—1.763	—.581	1.185
1.44	0.5	—1.883	—.560	1.344
1.68	5.	—2.020	—.560	1.460
1.92	18.	—2.012	—.560	1.452
2.17	33.	—2.020	—.560	1.460
2.42	49.5	—2.020	—.560	1.460

Table IV and Fig. 4 show the results of repeating the electrolysis of normal copper sulphate and determining the polarization at each electrode. The current curve, M., and the curve of the total polarization, T, are as in the previous experiment. The curves of polarization of the anode, A, and of the cathode, C, are especially interesting. The initial readings of polarization at anode and cathode, before any external E. M. F. was applied to them, was omitted by the student who performed this experiment, but if curves A and C were extended backward to obtain the value of the polarization at zero E. M. F., both electrodes would show about 0.77 volts, the single potential of platinum in this electrolyte. As the E. M. F. impressed upon the electrodes is increased, the curves A and C separate, the potential of the cathode increasing to

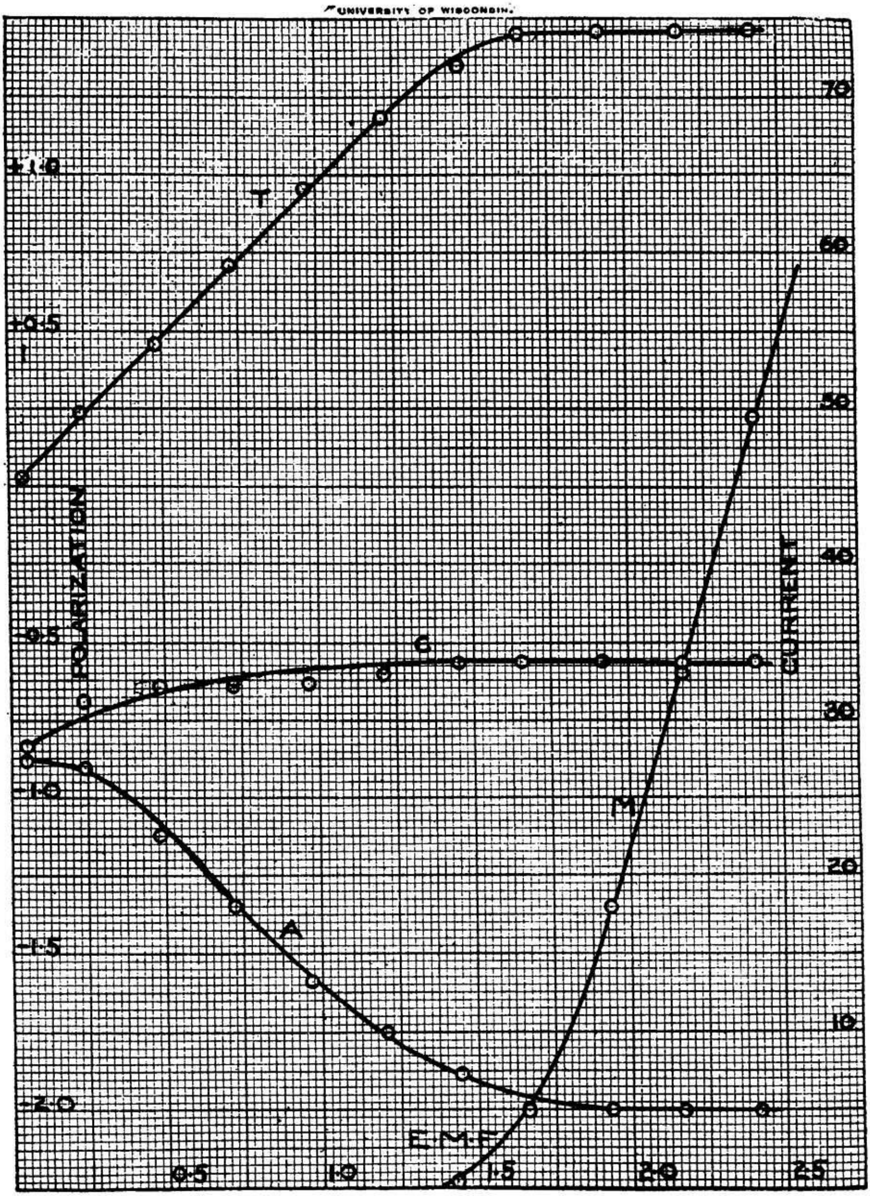

FIG. 4. Electrolysis of $n.CuSO_4$—Platinum Electrodes.

that of copper as its limit, and the potential of the anode diminishing to that of platinum saturated or coated with oxygen. It is seen that the polarization of the cathode quickly reaches a maximum, while that of the anode continues to increase until the impressed

E. M. F. reaches 1.75 volts. The cathode contributes only 22 percent to the total maximum polarization, the remainder being due to the anode. A comparison of the distances between curves A and C at various points, with values shown on curve T for the same E. M. F., shows how closely the separate potentials of anode and cathode agree with measurements of the total polarization.

TABLE V.

Electrolyte, zinc bromide. Electrodes, carbon.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization Anode Volts	Cathode Volts	Total Volts
0	0	—0.995	—0.992	0.009
0.05	0	—1.004	—.960	.037
.15	0	—1.050	—.951	.102
.25	0	—1.137	—.919	.215
.48	0.5	—1.245	—.809	.429
.72	0.7	—1.251	—.575	.667
.96	0.7	—1.253	—.342	.893
1.20	0.8	—1.271	—.148	1.122
1.44	2.5	—1.285	+.026	1.311
1.68	18.	—1.315	+.165	1.479
1.92	43.5	—1.323	+.368	1.654
2.17	119.	—1.362	+.456	1.816
2.42	209.	—1.372	+.461	1.833
2.65	310.	—1.372	+.472	1.845
2.88	405.	—1.372	+.484	1.856
3.13	500.	—1.372	+.484	1.856
3.38	600.	—1.372	+.484	1.856
3.62	695.	—1.401	+.461	1.862
3.86	795.	—1.401	+.461	1.862
4.11	925.	—1.401	+.461	1.862

Table V and Fig. 5 are the results of the electrolysis of a solution of zinc bromide with carbon electrodes. The cathode contributes 78 percent of the 1.86 volts total polarization, while the anode supplies the remaining 22 percent. The electrolysis of zinc bromide effectually disposes of any claim that the failure to obtain a visible current with the first application of E. M. F. to electrolytes is due to the resistance of a gas film at either electrode. No gas is evolved in this case, except that at a very high current density a little hydrogen may be deposited along with the zinc at the cathode.

The curves for the cathode in figures 5 and 6 show a gradual change from electrodes of platinum to copper and zinc, respectively. Similarly, the anode curves represent the change from a

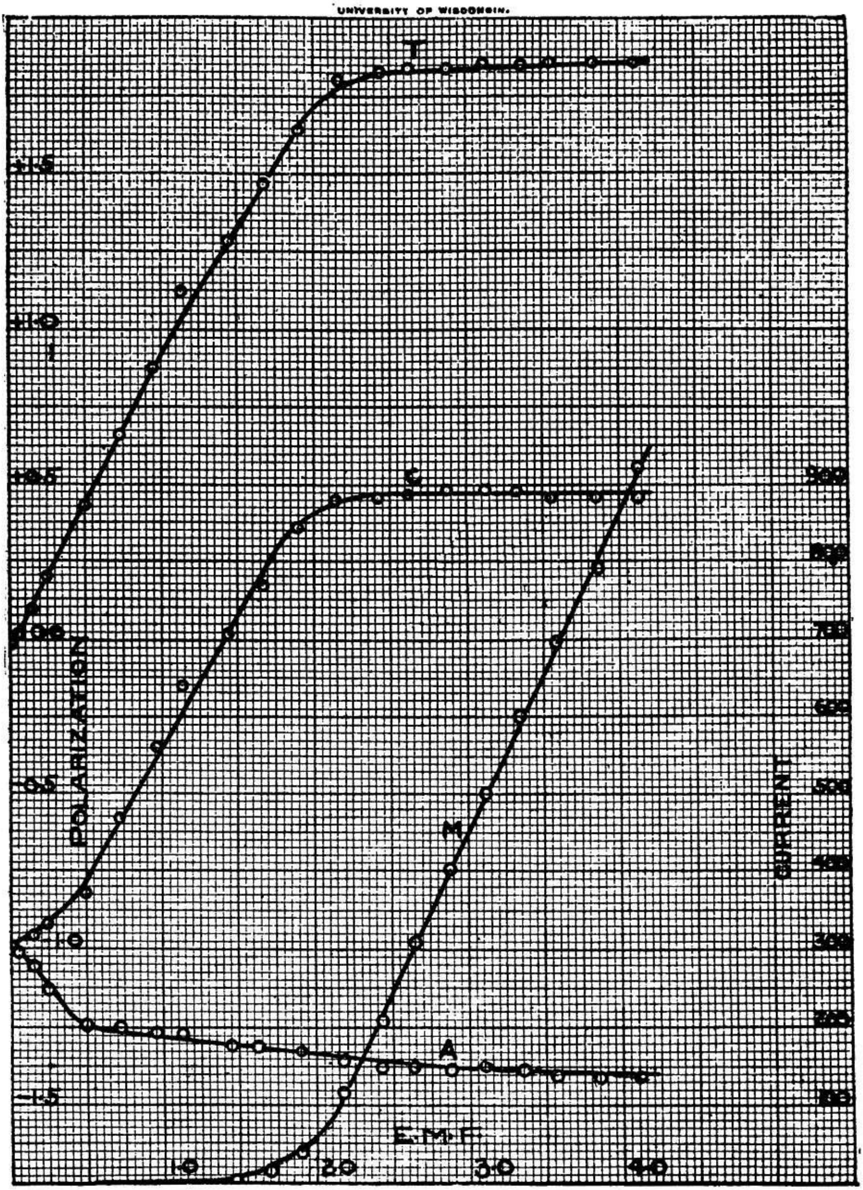

FIG. 5. Electrolysis of $ZnBr_2$—Carbon Electrodes.

platinum electrode making contact with the original solution, to platinum saturated or alloyed with oxygen and with bromine, respectively, making contact with an electrolyte saturated with these products of electrolysis. The source of the counter-electromotive force, then is of the same nature as the E. M. F. of any primary, or storage cell, viz., it is the result of an unsymmetrical electrochemical system, consisting of two electrodes in one or more electrolytes. Before electrolysis the electrolytic cell was symmetrical consisting of like electrodes in an electrolyte of uniform composition, concentration and temperature, and therefore the E. M. F. of the cell was zero. With copper sulphate the application of an E. M. F. causes the system to become unsymmetrical, by the deposition of copper at the cathode and oxygen at the anode. The E. M. F. of this little copper-oxygen storage cell, which, as in all storage cells, is opposite in direction to the charging E. M. F., continues to increase in magnitude, as more and more copper and oxygen are deposited, until its E. M. F. equals the impressed E. M. F., when the flow of current ceases. All this may occupy one or two seconds. With each increase of impressed E. M. F. this process is repeated, until the value of the impressed E. M. F. exceeds that attainable by the little storage cell; then a permanent current flows.

Having considered several cases of electrolysis with insoluble electrodes, it will now be of interest to use a soluble anode.

TABLE VI.

Electrolyte, acid $CuSO_4$. Electrodes, copper.

Impressed E.M.F. Volts	Current Milli-amperes	Polarization		
		Anode Volts	Cathode Volts	Total Volts
0	0	—0.553	—0.563	0.001
0.15	2.9	—.556	—.538	.017
.25	10.7	—.556	—.545	.015
.50	31.	—.560	—.545	.020
.70	50.	—.560	—.545	.017
1.00	82.	—.563	—.543	.022
1.25	105.	—.567	—.538	.025
1.50	130.	—.560	—.531	.030
1.75	152.	—.567	—.531	.032
2.25	182.	—.567	—.519	.045
2.75	232.	—.571	—.512	.060
3.25	295.	—.574	—.502	.076
3.75	350.	—.579	—.499	.087
4.75	325. (*a*)	—.574	—.487	.087
5.00	380.	—.574	—.487	.089

(*a*) The current varies between 250 and 400.

Table VI and Fig. 6 show the action of copper electrodes, 1 x 2 cm., with only one side exposed, in the acid copper sulphate solu-

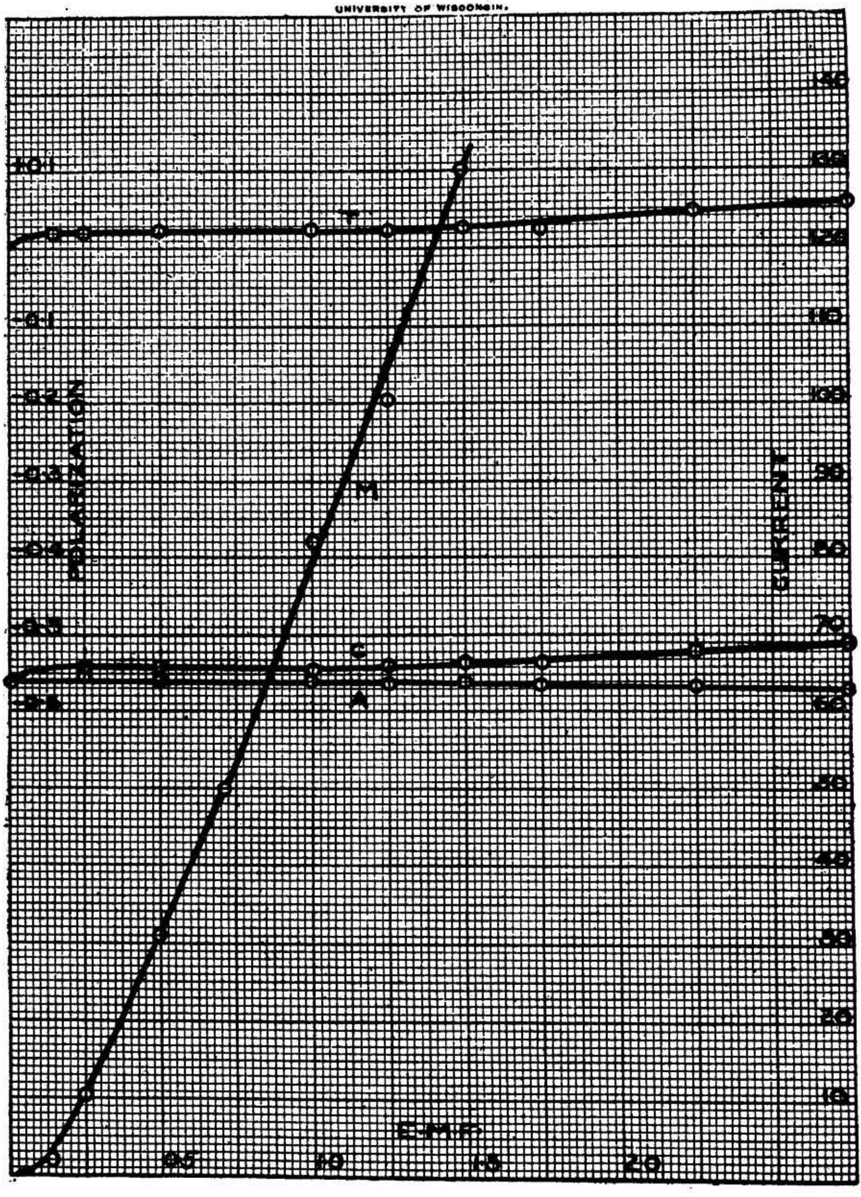

FIG. 6. Electrolysis of Acidified $CuSO_4$, Electrodes Copper, 1 x 2 cm., one side only exposed. Current Density: A. per Sq. foot = milliamperes used ÷ 2.

tion as used for electro-plating. The current-E. M. F. curve is almost like that for a metallic conductor. The reason for this is seen on examining the polarization curves. The greatest value for the total polarization was 0.06 volts instead of 1.46 obtained for copper sulphate when platinum electrodes were used. It is this failure of the polarization to rise to any considerable value, which makes the current-E. M. F. curve so different from those of the other electrolytes. At the lowest E. M. F., 0.15 volt, the total polarization had already attained to 20 per cent. of its highest value. Eighty-five percent of the greatest total polarization is found at the cathode. It is to be noted that the polarization shows no evidence of having reached a maximum, as it did with the insoluble electrodes. It is evident that had a greater E. M. F. been applied, a still larger polarization would have resulted. It might well be asked how there can be any polarization when at the outset, and also at the end, the system consists of two copper electrodes in a solution of copper sulphate. If such an electrolytic cell as this is projected on a screen by means of a stereopticon, the reason for polarization appears. At the cathode there is formed, as a result of the deposition of copper, a layer of dilute solution in contact with the cathode. It is well known that the value of the potential set up by a metal making contact with a solution is affected by the concentration of the solution. Copper in copper sulphate is no exception to this rule. Diffusion and the circulation caused by differences in density tend to destroy this film of dilute electrolyte bathing the cathode, so that the degree of dilution attained may be expressed as a state of dynamic equilibrium here between the electric current which produces it and the above forces which would destroy it. It is evident that the higher the current density at the cathode, the more dilute will be the electrolyte which is in immediate contact with it. The anode, on the other hand, is surrounded by a layer of electrolyte which is more concentrated than the original solution; but as this dense electrolyte rapidly streams down and collects as a layer across the bottom of the cell, it might be expected that increase of current would have less effect upon anode polarization than upon that at the cathode, and this is shown to be the case.

The examples of electrolysis so far considered show that:

1. Polarization is responsible for the phenomenon of decomposition pressure in electrolytes.

2. The total polarization may be resolved into two components, the one at the anode, the other at the cathode.

3. Since it is polarization which prevents the flow of current in accordance with Ohm's law, the residual current is the equivalent in current of the rate of depolarization of the electrodes by the electrolyte.

Moreover, if electrolysis causes a change in the material of an electrode, or of the electrolyte in immediate contact with it, the polarization at the electrode is large. This is the case with an insoluble anode, and usually so for a cathode whose position in the electrochemical series is far from that of the element which is deposited upon it by the current.

If the chemical composition of the electrode and of the electrolyte in contact with it are not changed, the polarization will be small. This occurs with a soluble anode and with a cathode of the same material as that deposited by the current.

The data in the tables was, in the main, secured by students in the regular laboratory experiments in electrochemistry, and this paper is presented with the hope that it may prove useful to students who are engaged in similar work. For the plotting of the curves, the author is indebted to Mr. W. B. Schulte.

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University of Wisconsin.

DISCUSSION.

Prof. J. W. Richards: I think this is largely a very careful repetition of work which has already been done, and does not carry with it any disclosures or any new principles. I think, however, that the data and the curves given will furnish a good basis for careful discussions of the phenomena of back-electromotive force.

Mr. Carl Hering: It seems to me that Dr. Watts merely gives this phenomenon a name; giving a thing a name is not giving an explanation. It is a fundamental principle that a current multiplied by an electromotive force represents energy. If a current is passed against a counter-electromotive force, it must represent energy, and energy which is not in the form of heat; in an electric motor it is in the form of motion; in a cell it is in the form of chemical energy. It seems to me the explanation of this counter-electromotive force, which the author calls polarization, is simply that some chemical energy is being stored up somewhere; electrical energy is being changed into chemical energy of some kind.

In connection with the latter part of the paper, where Dr. Watts compares the two electrodes with the calomel cell, I recall a method I used a good many years ago in testing accumulators. It consists in having in the cell two other plates, which are exactly like those that you are testing except that they are not in circuit and may be quite small. For instance, I used two small, fully charged accumulator plates, one positive and one negative, which I inserted in the accumulator and then measured the voltage between each of the test plates and the corresponding accumulator plate. In that way I obtained an indication of the condition of the large plates with reference to the normal test plates, which were not in circuit. The results were quite instructive.

In connection with this subject, although not bearing on it directly, I would like again to bring up the question of the origin of the energy of the expansion of the gases set free. When gas is liberated in electrolysis there is an expansion of, I think, about 1,600 times the volume; that is, the gases, oxygen and hydrogen, after they are set free, have a volume about 1,600 times that of the water from which they are formed. Hence there has been a very great expansion against atmospheric pressure, and that requires energy. The question is, where does that energy come from; does it come from the current or from the heat of the liquid? I think an investigation of this question might lead to some interesting results.

PROF. RICHARDS: In most of these tables there is given a statement of the first-applied electromotive force, showing no current in milli-amperes. My experience has been that with almost any applied electromotive force, under similar conditions, you can find a current if you have the ammeter delicate enough to measure it. The fact of "no current" means that the milliammeter was not delicate enough to measure the current. With a micro-ammeter Dr. Watts would have gotten readings all the way down to the first-applied electromotive force which could have been put on the cell.

Dr. Watts (*Communicated*): This paper is an attempt to set forth the facts in regard to the relation between current and impressed electromotive force in several different electrolytic cells and to point out that, in those cases in which the flow of current is not in accordance with Ohm's law, there exists a counter-electromotive force which partially or completely, as the case may be, nullifies the impressed e. m. f. and so causes the phenomenon of the decomposition voltage.

While agreeing with Mr. Hering when he says that "giving a thing a name is not giving an explanation," the writer was under the impression that he had included the explanation as well as the name. On pages 94-98, 101, 103, 105 and 106 the cause of the counter-electromotive force is traced to the changes produced in the materials of the electrodes by the passage of current, and it is there stated that "the source of the counter-electromotive force is of the same nature as the e. m. f. of any primary or secondary cell." Since an explanation of any new or imperfectly understood phenomenon in nature consists in showing that it has a definite relation to other and well-known phenomena, it is hoped that the above may be accepted as an explanation of decomposition voltage.

4

8. *Über das Schmelzen von Kohle;*

von O. P. Watts und C. E. Mendenhall.

In einem der neueren Hefte der Annalen[1]) hat Herr La Rosa einige Versuche über die Krümmung von Kohlestäben bei hohen Temperaturen beschrieben und hat diese Krümmung zusammen mit gewissen von ihm beobachteten besonderen Erscheinungen an der Oberfläche als Beweis für das Vorhandensein eines wahren Schmelzpunktes für Kohle bei gewöhnlichen Drucken herangezogen. Wir waren der Meinung, ehe man die Erklärung annehme, die La Rosa für seine Krümmungseffekte gibt, dürfte es sich empfehlen, weitere Versuche zu machen und dabei besonders zwei Punkte ins Auge zu fassen, nämlich:

1. die Eigenschaften des Graphits und der Kohle bei hohen Temperaturen zu vergleichen, festzustellen, ob die Krümmung von den Spuren des Bindemateriales (irgendeines Kohlenwasserstoffes) herrührt, die in der Kohle zurückgeblieben sind, oder ob sie ebensogut am Graphit auftritt, wo man naturgemäß annehmen darf, daß das Bindematerial durch die ausgedehnte und intensive Erhitzung, der das Material bei der Herstellung unterworfen wird, größtenteils entfernt sein wird;

2. wenigstens annäherungsweise die Temperaturen zu bestimmen, bei denen die Krümmung auftritt, um zu entscheiden, ob sie wirklich ein Zeichen des Schmelzbeginns ist, oder nur ein Zeichen zunehmender Plastizität bei hohen Temperaturen.

Uns stand glücklicherweise eine Dynamo zur Verfügung, die imstande war, beständig Gleichstrom von 600 Amp. bei 110 Volt zu liefern. Wir konnten daher stärkere Stäbe benutzen als La Rosa und uns dem Krümmungsstadium all-

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1) M. La Rosa, Ann. d. Phys. **34.** p. 95. 1911.

mählich nähern, wobei wir uns reichlich Zeit lassen konnten, um an dem Stabe mittels eines optischen Pyrometers nach Holborn-Kurlbaum Temperaturmessungen vorzunehmen. Diese Beobachtungen ergeben natürlich unmittelbar nur die „schwarze“ Temperatur der Stäbe. Um diese auf die wahre Temperatur umzurechnen, haben wir von den demnächst zu veröffentlichenden Ergebnissen des einen von uns über den Zusammenhang zwischen der „schwarzen“ und der „wahren“ Temperatur der Kohle Gebrauch gemacht.[1] Wir haben zahlreiche Versuche an Stäben von 6 mm Durchmesser und 15 cm bzw. 30 cm Länge ausgeführt. Das Material war dabei: a) gewöhnliche käufliche Kohle von der National Carbon Co., Cleveland, Ohio, U. S. A.; b) eine äußerst feinkörnige hochgradige deutsche Kohle (Conradty), die vermutlich dem von La Rosa benutzten Material sehr ähnlich war; und c) der reinste von der Atcheson Graphite Co., Niagara Falls, N. Y., hergestellte Graphit. Wir brachten die Krümmung entweder dadurch zuwege, daß wir die eine Elektrode gegen die andere schoben, oder dadurch, daß wir die eine Elektrode um einen Zapfen nahe an der Mitte des Stabes drehten, oder dadurch, daß wir ein Gewicht an zwei gleiche Stäbe hingen, die nahe beieinander und parallel zueinander eingeklemmt und an ihren freien Enden verbunden waren.

Unsere Ergebnisse lassen sich kurz zusammenfassen wie folgt:

1. Amerikanische Kohle nimmt am leichtesten eine dauernde Krümmung an, demnächst deutsche Kohle, und am schwersten Graphit. Das ist die Reihenfolge zunehmender Reinheit und abnehmenden Gehaltes an Bindungsmaterial. Trotzdem erreichten wir selbst beim Graphit leicht ausgeprägtere Krümmungen als irgendeine der von La Rosa angegebenen, beispielsweise eine scharfe Krümmung von 50° in der Mitte eines 30 cm langen Graphitstabes (vgl. Fig. 1, *1*) innerhalb vier Minuten bei einer Temperatur zwischen 2700° C. und 2800° C.

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[1] Oberhalb 2000° C. erfordert die Bestimmung dieser Korrektion eine Extrapolation einer empirischen Kurve; die höchsten Temperaturen können daher um 50 bis 75° falsch sein.

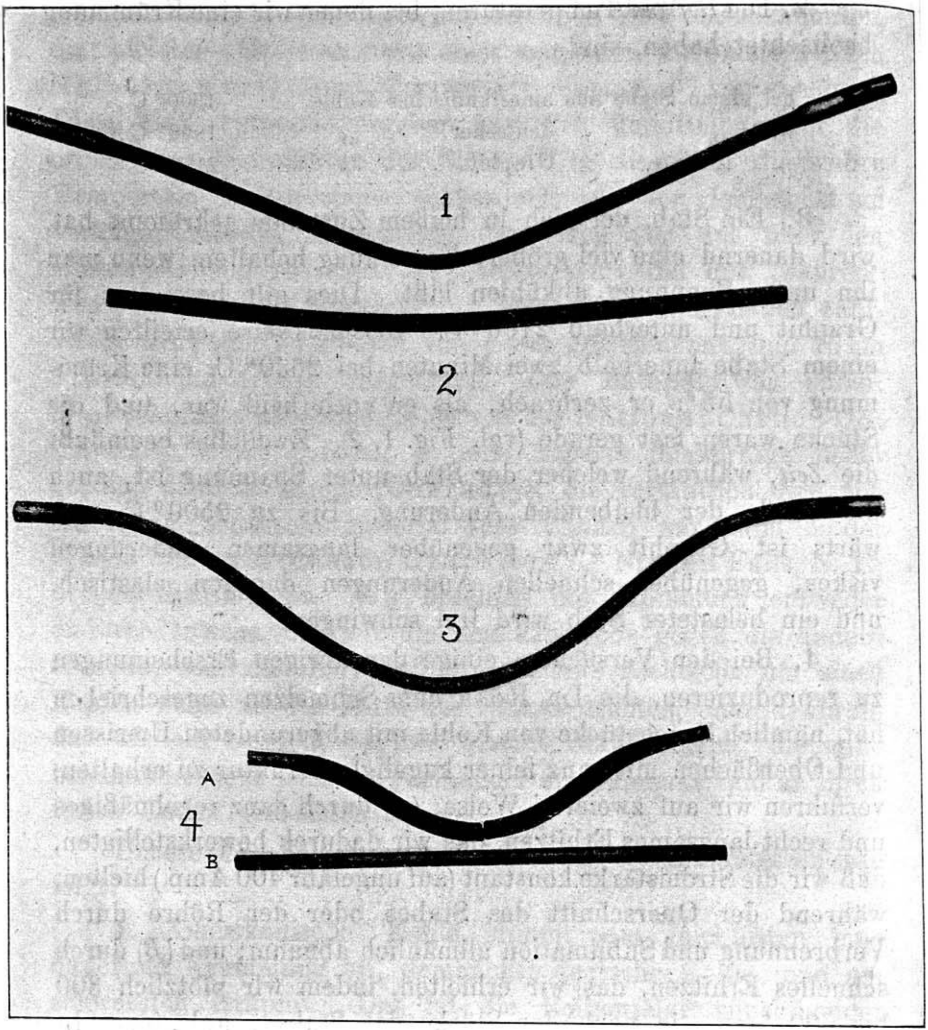
2. Die *tiefsten* Temperaturen, bei denen wir eine Krümmung beobachtet haben, sind

bei einem Stabe aus amerikanischer Kohle . . 1800° C.,
" " " " deutscher " . . 1900° C.,
" " " " Graphit . . . . 2150° C.

3. Ein Stab, der sich in heißem Zustande gekrümmt hat, wird dauernd eine viel größere Krümmung behalten, wenn man ihn unter Spannung abkühlen läßt. Dies gilt besonders für Graphit und unterhalb 2700° C. Beispielsweise erteilten wir einem Stabe innerhalb zwei Minuten bei 2630° C. eine Krümmung von 55°; er zerbrach, als er noch heiß war, und die Stücke waren fast gerade (vgl. Fig. 1, 2). Zweifellos beeinflußt die *Zeit*, während welcher der Stab unter Spannung ist, auch die Größe der bleibenden Änderung. Bis zu 2500° C. aufwärts ist Graphit zwar gegenüber langsamen Änderungen viskos, gegenüber schnellen Änderungen dagegen elastisch, und ein belasteter Stab wird frei schwingen.

4. Bei den Versuchen, einige der übrigen Erscheinungen zu reproduzieren, die La Rosa dem Schmelzen zugeschrieben hat, nämlich Bruchstücke von Kohle mit abgerundeten Umrissen und Oberflächen mit ganz feiner kugeliger Struktur zu erhalten, verfuhren wir auf zweierlei Weise: (*A*) durch ganz regelmäßiges und recht langsames Erhitzen, das wir dadurch bewerkstelligten, daß wir die Stromstärke konstant (auf ungefähr 400 Amp.) hielten, während der Querschnitt des Stabes oder der Röhre durch Verbrennung und Sublimation allmählich abnahm; und (*B*) durch schnelles Erhitzen, das wir erhielten, indem wir plötzlich 300 bis 600 Amp., je nach der Stärke des Stabes, anlegten. In allen Fällen versuchten wir die eingeschlossenen Gase durch voraufgehendes Erhitzen auf 2000° C. oder darüber zu entfernen.

Fall A. Ein $^1/_4$zölliger Kohlestab brannte 3—5 Minuten in freier Luft, während die Temperatur allmählich von $T_w = 2500^\circ$ C. an zunahm. Die Verhältnisse wurden ziemlich regelmäßig bei „schwarzen“ Temperaturen von 3080° C. bis 3250° C. („wahre“ Temperaturen schätzungsweise 3300° C. bis 3500° C.) instabil, und es bildete sich ein Bogen. Die Enden solcher Stäbe (oder Röhren) zeigten nach dem Bruch niemals irgendwelche Zeichen eines Schmelzens, abgesehen davon, daß



1 **Graphit.** Krümmung von 50°. Höchste Temperatur 2770° C.

2 Graphit. Heiß zerbrochen bei einer Krümmung von 55° in der Mitte. 2630° C.

3 Kohle. Winkel 75°. 2600° C.

4 *A* Durch Kohlendampf gedehnter Stab. 2900° C.
B Ursprüngliche Größe des Stabes.

Fig. 1.

sie zuweilen teilweise mit einer Haut oder einem Überzug von mikroskopischer tropfenartiger Struktur, wie ihn La Rosa beschrieben hat, bedeckt waren. Solche Oberflächen fanden sich beispielsweise:

1. an den *kälteren* Stellen auf der *Innenseite* einer auf etwa $T_w = 3100^0$ an der heißesten Stelle (in einem Vakuum)

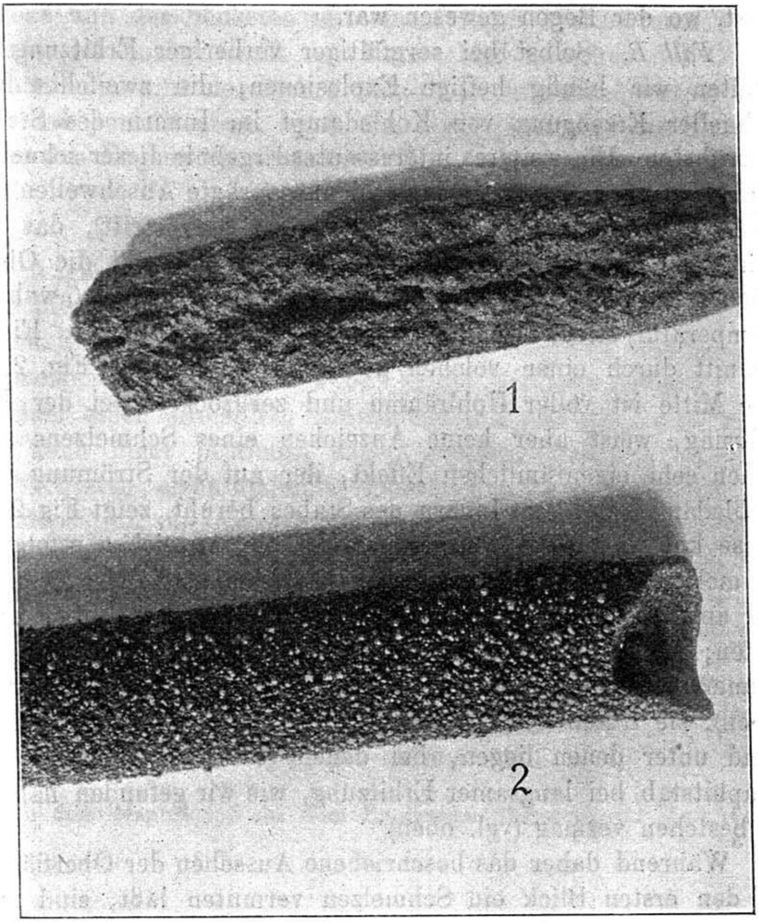


Fig. 2.

erhitzten Graphitröhre. In diesem Falle war zur Innenseite der Röhre eine 0,1 mm bis 0,3 mm dicke Schicht *hinzugekommen*, wodurch der innere Durchmesser kleiner geworden war. Diese Schicht war beträchtlich *härter* und feinkörniger als der ursprüngliche Graphit;

2. an der *Mitte* des Endes eines als negative Elektrode eines Lichtbogens benutzten Kohlestabes, bei dem der Lichtbogen den Rand des Endes umspielt hatte;

3. zu verschiedenen Zeiten als Flecken am Ende der Stäbe oder Röhren, die Lichtbogen geliefert hatten, aber nicht dort, wo der Bogen gewesen war.

Fall B. Selbst bei sorgfältiger vorheriger Erhitzung erhielten wir häufig heftige Explosionen, die zweifellos von schneller Erzeugung von Kohledampf im Innern des Stabes herrührten. Ein weiteres interessantes Ergebnis dieser schnellen Kohledampferzeugung ist das sehr ausgeprägte Anschwellen von Kohlestäben (das beim Graphit weniger hervortritt), das bei schnellem Erhitzen auftrat (vgl. Fig. 1, *4*). Obwohl die Oberflächentemperatur nicht über 3000° C. bis 3200° C. („wahre" Temperatur) stieg, war das Innere zweifellos viel heißer. Einen Schnitt durch einen solchen gedehnten Stab zeigt Fig. 2, *1*. Die Mitte ist voller Hohlräume und zerbröckelt bei der Berührung, weist aber keine Anzeichen eines Schmelzens auf. Einen sehr eigentümlichen Effekt, der auf der Strömung von Kohledampf aus dem Innern des Stabes beruht, zeigt Fig. 2, 2. Diese knötchenartige Oberfläche weist alle Anzeichen erfolgten Schmelzens auf. Trotzdem ist zu beachten, daß diese Zeichen nur an den äußeren (mithin kälteren) Stellen des Stabes auftreten; sie sind bei stärkeren Stäben ausgeprägter als bei dünneren (größere Temperaturunterschiede zwischen außen und innen); sie treten bei Temperaturen auf, die mehrere Hundert Grad unter denen liegen, bei denen ein fester Kohle- oder Graphitstab bei langsamer Erhitzung, wie wir gefunden haben, zu bestehen vermag (vgl. oben).

Während daher das beschriebene Aussehen der Oberfläche auf den ersten Blick ein Schmelzen vermuten läßt, sind wir doch überzeugt, daß es in allen von uns untersuchten Fällen auf Kondensation von Kohle an den verhältnismäßig kälteren Stellen beruht. Die höchste Temperatur, die durch elektrische Heizung von Kohle erreicht werden kann, ist durch den Sublimationspunkt bei dem angewandten Drucke festgelegt. Weitere Steigerung der Energiezufuhr über diesen Punkt hinaus geht einfach in die Sublimationsenergie der Kohle über. In einem Vakuumofen aus Graphitrohr haben wir im hiesigen Institut bei einigen Millimetern Druck eine höchste (wahre) Temperatur von etwa 3100° C. erhalten, während wir mit einem Kohlestabe in Luft bei 1 Atm. Druck bis zu 3500° C. erhielten. Mit demselben Pyrometer ergab ein Bogen von 250 Amp. $T'_s = 3500°$ C. oder $T_w = 3800°$ C. Der Unterschied zwischen der Temperatur des Bogens und der höchsten mit einem Stabe beobachteten Temperatur ist unzweifelhaft der Unterschied zwischen der Oberflächentemperatur des Stabes und seiner Innentemperatur, und der Stab zerfällt eben, wenn die *Innen*temperatur die Temperatur des Bogens erreicht.

Schlußfolgerung.

Angesichts der vorstehenden Versuche erscheint der Schluß berechtigt, daß die Krümmung von Kohle und Graphit bei hohen Temperaturen an sich nicht als Zeichen beginnenden Schmelzens angesehen werden kann, sondern vielmehr als Zeichen einer allmählich zunehmenden Plastizität, und wenn wir auch nicht bestimmt sagen können, daß die von uns beobachteten eigentümlichen Oberflächeneffekte, die wir der Kondensation von Kohledampf zugeschrieben haben, dieselben sind wie die von La Rosa beobachteten, so dürfte uns doch ihre große Ähnlichkeit zu der Annahme führen, daß die von La Rosa beschriebenen Erscheinungen wahrscheinlich auf Kondensation beruhen und nicht auf Schmelzen.

Universität Wisconsin, Madison, April 1911.

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(Nach dem Manuskript aus dem Englischen übersetzt von Max Iklé.)

Electrolytic Corrosion of Iron in Concrete

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ELECTROLYTIC CORROSION OF IRON IN CONCRETE.

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Presented February 22, 1911.

This paper has for its purpose the presentation of results of experimental work dealing with a study of the extent to which concrete may act as a protective agent against the electrolytic corrosion of iron imbedded in it.

Mr. A. A. Knudson, *Transactions American Institute of Electrical Engineers,* March, 1907, appears to be among the first to have conducted investigations of the electrolytic corrosion of iron in concrete. His conclusions were somewhat sweeping in that they contained a statement that where but a small current passes from iron to concrete or masonry there will be a corrosion of the metal and disintegration of the concrete or masonry. He called attention to the calamities which may result from this fact; but the justice of his conclusions were questioned by those who took part in the discussion of his paper. Other contributions on this same subject have been offered by Professor A. S. Langsdorf, *Journal of the Association of Engineering Societies,* Vol. 42, 1909, and by Mr. W. J. Nicholas, *Engineering News.* Vol. 60, 1908. These papers were in a measure confirmatory of the views offered by Mr. Knudson.

The principal basis of objection to the conclusions of this first paper appear to be that the experiments were not illustrative of what may occur in practice, in that a constant current of 0.1 ampere was passed through a concrete block from an imbedded iron pipe, the voltage being raised continually to maintain the current at a constant value. This required in some cases a high voltage and liberation of heat, which resulted in a cracking and softening of the concrete within a 30-day period of exposure to the action of the current.

In view of the fact that reinforced concrete has become one of the most important structural materials, it is reasonable that the charge made against this material, that a very small electric current will result in its destruction, should be accepted with caution. The importance of the question merits far more attention than has been given to it, and in offering the results of further study it is appreciated that there is still much analytical work to be done before an exact quantitative idea may be had of the depreciation caused by electrolytic corrosion.

In a publication of the Carnegie Library of Pittsburg, entitled "Metal Corrosion and Protection" there is an extensive

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bibliography, a portion of which deals with literature on cement and concrete as a protection against corrosion, there being forty-eight articles and papers included under this division. Comparatively few of these, however, relate to the electrolysis factor.

During the past three years there have been carried on at the Chemical Engineering Laboratories of the University of Wisconsin, two series of tests on the quantitative effect of electrolysis on iron in concrete, and some of the results of this work have been drawn upon in presenting this report. More detailed descriptions are given in theses prepared by F. F. Farnham, in 1909, and A. B. Chadwick, Jr., in 1910.

It has become a generally appreciated fact that concrete absorbs water and aqueous solutions and thereby becomes electrolytically conductive. The conductivity varies through a wide range, depending upon the nature of the concrete itself as to physical and chemical composition, and to the composition of the impregnating solutions. From various sources of information it appears that the resistance of cement and concrete may be anywhere from 30 ohms to several thousand ohms per foot cube, values which are comparable to the specific resistance of earth materials.

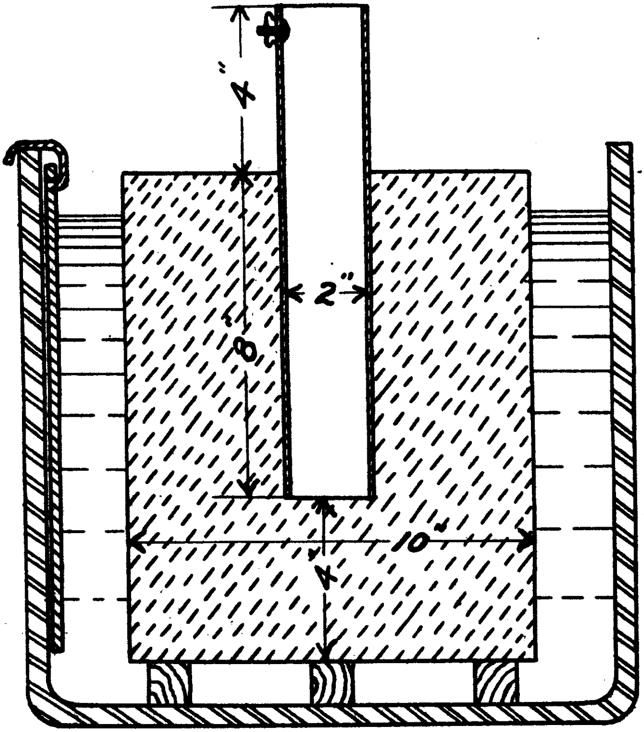

Fig. 1—Dimensions of Specimens Used in First Set of Tests.

In carrying out the experiments to be described the purpose was to employ conditions typical of those which may be met with in actual practice. A constantly applied pressure of 8 volts was employed as being a value which, although somewhat high, is occasionally encountered and even exceeded in existing structures. Although this value is higher than the average, it was necessary to choose such pressure as would give distinct results in reasonable time. Two sets of tests were made, the first covering a period of 180 days and employing concrete moistened with water, and the second covering a period of 64 days, using salt solutions. The dimensions of specimens used in the first set of tests are illustrated in Fig. 1, and in the second set of tests by Fig. 2.

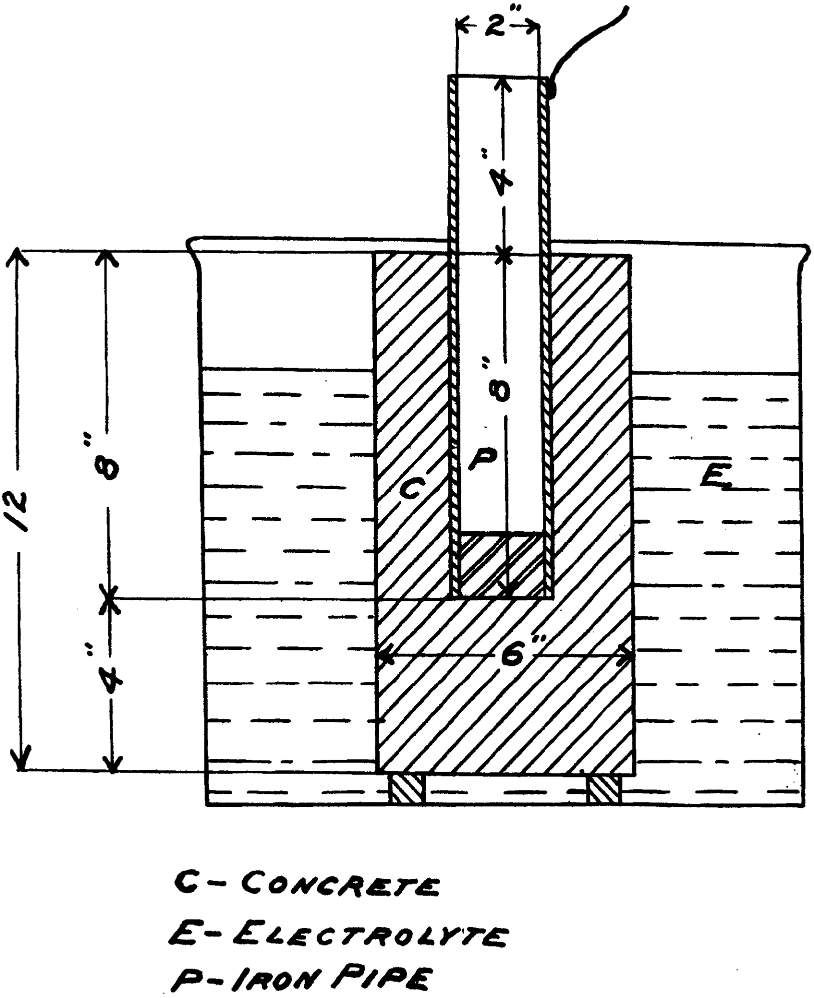

Fig. 2—Dimensions of Specimens Used in Second Set of Tests.

The first ten test specimens were made of various brands of cement and in various mixtures. In some cases the cement was poured into the mold moist and in others wet. The imbedded iron consisted of a 2 in. wrought iron pipe which had been previously washed carefully, the lower end being closed by a paraffined wooden block to exclude moisture. Specimens were set in a mold for 48 hours, at the end of which time they were put into earthen jars containing lake water, where they remained for 12 days before electrical pressure was applied. The cathode consisted of an iron plate hung from the side of the jar. The cells were electrically connected in parallel, Fig. 3, current being supplied by storage cells through a rheostat by which a fairly constant pressure value was maintained throughout the test. By taking frequent measurements of current, applied pressure, and polarization pressures, the principal records of the tests were obtained. The summary for this series is given in Table 1. The loss in weight was determined by preliminary weighing, and another weighing at the end of the test after the samples had been scratch-brushed to free them from adhering rust. By integration of the current values the number of ampere hours which flowed from each of the specimens was obtained. Assuming 1.05 grams per ampere hour as the electrochemical equivalent of iron, the theoretical corrosive action of the current was obtained and by comparison of this value with that actually obtained by loss of weight, the figures in the column headed "current efficiency" were calculated.

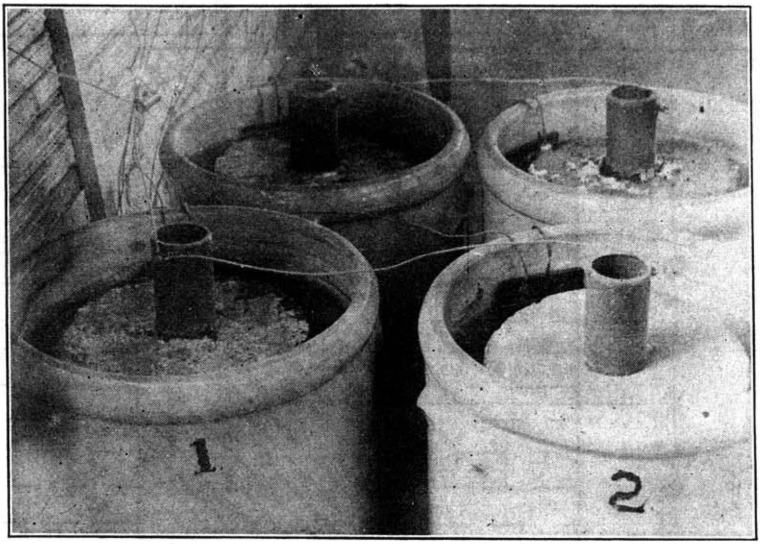

Fig. 3—Cells Electrically Connected in Parallel.

In view of some of the previous publications it was a matter of some surprise that current efficiencies were found to be of low value. These indicate that concrete may have some protective action other than that offered by its questionable insulating property.

In this first series of tests there was little evidence of cracking or softening of the cement. Samples employing neat cement showed some slight cracking at the beginning of the test, but this was evidently apart from the influence of the electric current.

The examination of the pipes after cleaning at the end of the test showed that corrosion had taken place in the form of pitting, Fig. 4, the pitting being the more marked at the top.

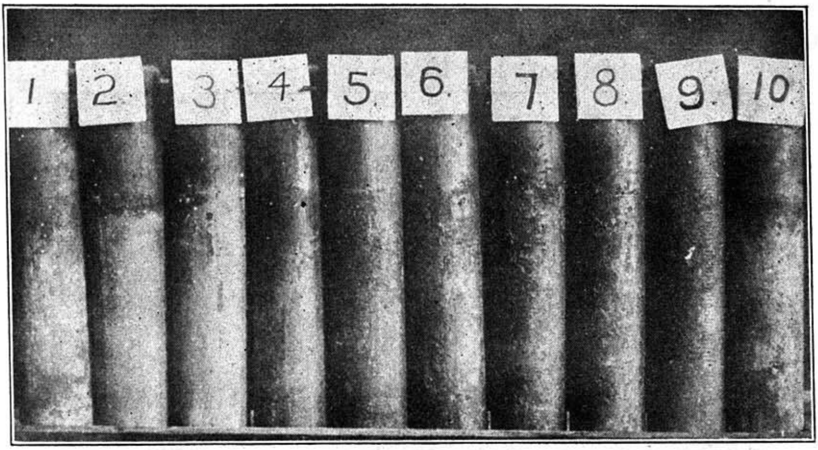

Fig. 4—Corrosion in Form of Pitting.

That the observed rusting and pitting was due to electrolytic action was evident by comparison with a check sample, from which no current was passed and which at the end of the test was found to be in a bright uncorroded condition. The low current efficiency of corrosion indicates that the current under these conditions expends itself in the liberation of anode products other than the formation of iron compounds. This is evidenced further by the frothing and the liberation of gas which appeared at the top of the concrete block near the iron anode.

The second series of tests was undertaken to determine in what measure the addition of salt to the water would influence the current efficiency of corrosion. For this purpose 3% salt solution was chosen as being typical of the conductivity of sea water and possibly of solutions which may be found under soil conditions.

The specimens were similar to those of the first series with the exception that the cement blocks were 6 in. instead of 8 in. in diameter, thus leaving a wall of cement about 2 in. instead of 3 in. for the current to pass through. This offered a lower electrolytic resistance, and therefore a means of decreasing the duration of the tests.

Concrete was taken from a concrete mixer handling material in proportion of 2 parts of cement, 4 of sand, and 6 of crushed stone. Two mixes were employed, one using Marquette cement and one the Medusa brand. This concrete was tamped around the iron pipes as in the previous tests, and the resultant blocks allowed to set for 28 days before being placed in the electrolyte in stoneware jars.

The 3% sodium chloride solution was used for seven of the specimens, ordinary lake water being employed for the other three, as a means of comparing this series with the former one.

The measurements of current, pressure, and polarization were taken almost daily for 64 days, the duration of the run.

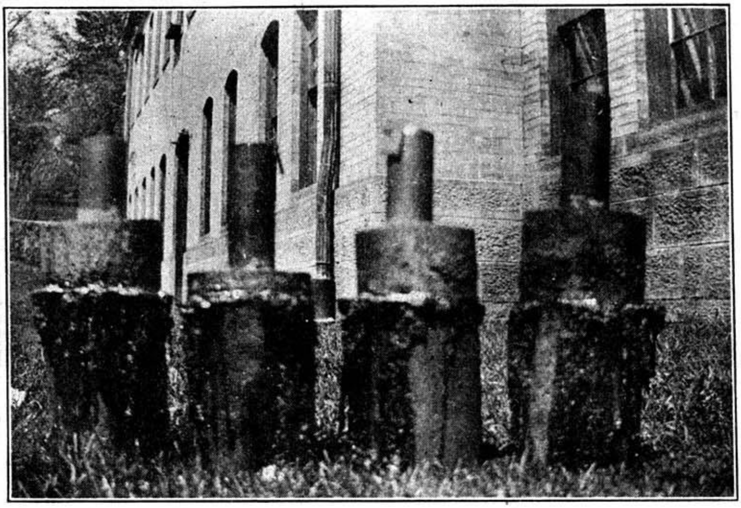

Fig. 5—Appearance of Blocks from Use of Salt Solution.

The pressure applied to each of the specimens was kept close to eight volts. The electrolyte was kept at constant level by occasional addition of water.

A ferric hydrate precipitate formed in all of the salt solutions; this crept up the surface of the exposed concrete and gave a rusty appearance to it. At the termination of the test the concrete blocks were removed from the solutions. Those from the salt solution had large and irregular adhering deposits of iron hydrate; these deposits apparently started at the surface of the solution and grew downward in large stalactitic formations.

Fig. 5 shows the appearance of the blocks from the use of salt solution, and Fig. 6 from the use of lake water. The blocks were broken by a hammer. In no case was the concrete softened, the only defects being the cracking noticed in blocks 11, 12, 13 and 14. The concrete had little rust or iron deposit in it except along the cracked surfaces. It is not certain that the cracking was caused by the electric current.

An examination of the pipes showed those exposed to salt water to have been corroded far more than were those of the previous test, or of those in lake water. The corrosion of the pipes started not at this surface level of the electrolyte but at the upper surface level of the concrete block. This is naturally the case on the basis that the solution works up into the concrete and renders it electrolytically conductive. The corrosion was found to be most marked at the locations of the cracks, the pipes having been entirely perforated at these places, but even in those specimens which had not developed defects in the concrete the corrosive pitting was very marked.

Fig. 6—Appearance of Blocks from Use of Lake Water.

Fig. 7 shows the appearance of the corroded pipes.

After brushing and cleaning the pipes they were weighed and the losses determined. By comparing these losses with the loss determined by averaging the current readings the percentage corrosion efficiency was determined.

Data concerning this test are given in Table 2. The deductions from this table are that the corrosion efficiency where salt is used in most cases is about 60%.

It appears from this table that there may be some relationship of polarization pressure to corrosive action, as those specimens showing greatest corrodibility by the current have the higher polarization pressures. This is contrary to what migh be expected, on the supposition that low current efficiency means the setting free of products of decomposition of the electrolyte and the setting up thereby of higher polarization pressures.

These tests show in a decisive manner the fact that salt in solution greatly increases the conductive power of concrete above that produced by ordinary water. They also show that the electrolytic corrosion of iron is thereby greatly enhanced by the presence of salt. There was no evidence, however, that the concrete itself undergoes any chemical deterioration by electrolysis. While some of the test samples cracked during the test, it is not believed that we have shown conclusively that this cracking is connected either directly or indirectly with the flow of current.

Table 3 is a compilation of data and deductions intended to get a quantitative idea of the corrosive action of the current. In the third column are given the average values of current flowing throughout the test on each of the specimens. The current is at a maximum at the beginning of the test and decreases to a more or less constant minimum value after a certain lapse of time. It was found that the minimum values had been reached during both of these two series of tests, and it is probable that these minimum values should be used rather than the average values where calculating what may happen under field conditions. These values of minimum current are therefore given in the fourth column. The average current of the tests is reduced to current per square foot of iron surface in column five, and the experimentally determined corrosion efficiencies in column six.

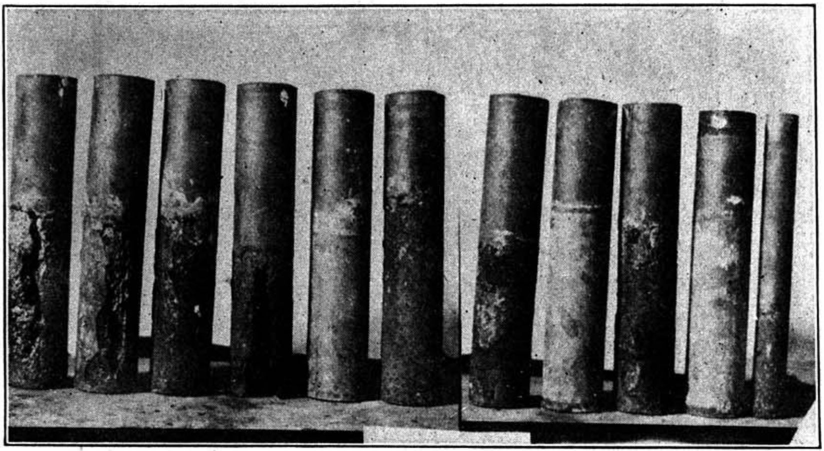

Fig. 7—Appearance of Corroded Pipe.

Using 20 lb. of iron per ampere year as the electrochemical equivalent of iron, the amount of iron to be corroded per year under the experimental conditions from each square foot of surface is given in column seven. Taking into account the minimum currents rather than the averages of the tests, gives column eight, which may be the really useful one for conveying a quantitative idea of the corrosion which may be encountered in practice.

A corrosion of 0.02 to 0.08 lb. of iron per square foot of iron per year is shown to be possible where concrete is subject to the action of ordinary water. This may or may not be a negligible depreciation factor, depending upon the massiveness and proportions of the encased iron. It must be borne in mind that the corrosion is not uniform, that pitting is the characteristic, and that should any cracks develop, the corrosion is concentrated at such places.

It is also seen in this column that the presence of a salt in the water increases the rate of corrosion one hundred times; due in part to the greater electrolytic conductivity but in much greater part to the increased corrosive efficiency of the current. While a 3% salt solution may give results typical of what may be expected from sea water, the seepage water of city streets is undoubtedly less harmful than the 3% salt solution. A quantitative investigation of the action of these and other solutions would be of importance as bearing on this question.

In interpreting the data above set forth, it must be borne in mind that an electrical pressure of eight volts has been assumed. This is higher than is generally found under actual conditions. Correction for lower pressures can be approximated by the application of Ohm's Law, taking into account a maximum polarization of from one to two volts.

Polarization pressure measurements were made throughout the conduct of these tests to determine, if possible, any relationship which might exist between corrosive efficiency and polarization pressures. No such relationship was established and it is not deemed essential to burden this paper with such data.

If, as shown in this paper, the possibility exists of removing 5 lb., 1 lb., or even 0.1 lb. of iron per year from a square foot of iron surface imbedded as reinforcement in concrete, it becomes a matter worthy of more attention than has been given to it in the past. It is true that comparatively few failures of structures have been attributed to electrolysis in the past, but we may not conclude from this that the time of reckoning with this factor will be indefinitely postponed.

Cement and concrete have been tried repeatedly as a protection to underground gas and water mains and services, but naturally with little beneficial results. There has been called to the attention of the writer the failure of concrete arches which is apparently attributed to electrolytic action, and we may naturally wonder how far this phenomenon may be responsible for some of the mysterious failures of concrete work which are recorded with some frequency and regularity.

The question is certainly entitled to further investigative study. This should include determinations of conductivity of concrete as influenced by composition, by different electrolytes, by methods of mixing; also the determination of the corrosive efficiency of the current as influenced by the variety of conditions met with in practice. In addition to laboratory work of this sort there should be made field observations as to leakage currents and their influence on structures.

TABLE 1.

Specimen No.	Brand of Cement	Mixture Cement—Sand—Gravel	Condition of Mix.	Loss by Corrosion —Grams	Ampere Hours	Current Efficiency of Corrosion
1	Atlas	Neat	Moist	7.2	416	1.66%
2	Chicago A-A	Neat	Wet	3.4	86.4	3.89%
3	Universal	Neat	Wet	1.2	109	1.05%
4	Universal	1-3-6	Wet	6.6	145	4.36%
5	Chicago A-A	1-3-6	Wet	7.5	134	5.38%
6	Atlas	1-1	Moist	9.8	458	2.06%
7	Atlas	1-3	Wet	11.7	163	6.88%
8	Atlas	1-3-6	Wet	6.3	131	4.61%
9	Chicago A-A	1-3	Moist	8.5	288	2.84%
10	Universal	1-1	Moist	5.2	413	1.23%

TABLE 2.

Specimen No.	Brand of Cement	Electrolyte	Loss by Corrosion —Grams	Ampere Hours	Current Efficiency	Polarization 64th day
11	Medusa	3% NaCl	210	355	55%	1.90 volt
12	Medusa	"	247	295	80%	1.90 "
13	Medusa	"	105	248	40%	1.70 "
14	Medusa	"	203	294	66%	1.65 "
15	Marquette	"	178	246	69%	1.90 "
16	Marquette	"	113	174	62%	1.80 "
17	Marquette	"	192	268	69%	1.75 "
18	Medusa	Lake Water	0	29	0	1.20 "
19	Marquette	"	0	30	0	1.25 "
20	Marquette	"	1	31.3	3%	1.30 "

TABLE 3.

Specimen No.	Electrolyte	Average Current Amperes	Current at end of Test	Average Current per sq. foot	Corrosive Efficiency of Current	Pounds Corroded per Year per sq. foot at Average Current	Pounds Corroded per sq. ft. per. Year—for Rates at End of Test
1	Water	.096	.030	.230	1.66%	.076 lb.	.0237 lb.
2	“	.020	.002	.048	3.89%	.037 lb.	.0037 lb.
3	“	.025	.007	.060	1.05%	.013 lb.	.0036 lb.
4	“	.033	.010	.079	4.36%	.068 lb.	.0200 lb.
5	“	.031	.012	.074	5.38%	.079 lb.	.030 lb.
6	“	.106	.055	.254	2.06%	.105 lb.	.054 lb.
7	“	.037	.025	.089	6.88%	.122 lb.	.082 lb.
8	“	.030	.010	.072	4.61%	.066 lb.	.022 lb.
9	“	.066	.030.	.158	2.84%	.090 lb.	.041 lb.
10	“	.096	.010	.230	1.23%	.057 lb.	.006 lb.
11	3% NaCl	.231	.190	.554	55. %	6.09 lb.	5.0 lb.
12	“	.192	.151	.461	80. %	7.42 lb.	5.85 lb.
13	“	.163	.141	.391	40. %	3.13 lb.	2.70 lb.
14	“	.191	.181	.458	66. %	6.07 lb.	5.75 lb.
15	“	.160	.135	.384	69. %	5.35 lb.	4.50 lb.
16	“	.113	.100	.271	62. %	3.38 lb.	3.00 lb.
17	“	.174	.125	.417	69. %	5.77 lb.	4.15 lb.
18	Water	.019	.011	.046	0. %	...	...
19	“	.019	.018	.046	0. %	...	...
20	“	.020	.015	.048	3. %	.029 lb.	.022 lb.

DISCUSSION.

J. G. Wray, M. W. S. E., (Chairman): We have all been much interested and instructed by Professor Burgess' paper. The results presented indicate that while electrolysis of iron imbedded in concrete does take place, the concrete itself appears not to be disintegrated by the electrolytic action nor destroyed by the corrosion of the metal. I read a paper not long since (I do not remember the name of the author) in which it was stated that electrolysis destroyed the concrete immediately surrounding the metal. This would obviously greatly reduce the strength of the reinforced concrete. Professor Burgess has already shown that electrolysis does not have this effect.

I realize my inability to discuss this paper intelligently but know that there are others here who can do so, much better than I can. Before calling for a general discussion, however, I would like to make a few suggestions, which I believe have a bearing on the subject and may perhaps explain the apparent discrepancy between the results obtained by Professor Burgess and those of other investigators. I would suggest the possibility that the porosity of the concrete or the composition of aggregate, whether of limestone, granite, gravel, etc., may have something to do with the amount of electrolytic action which takes place. It is also possible that the richness of the mixture or the age of the concrete may affect the results of the experiment.

William B. Jackson, M. W. S. E.: We are indebted to Professor Burgess for this valuable and interesting contribution to our knowledge of electrolysis of iron when imbedded in concrete. What I have to say is hardly in the line of discussion but more in the line of query.

The tests described in the paper show, other things being equal, a greater electrolytic action upon iron imbedded in concrete which is immersed in salt water than when immersed in fresh water. This suggests the thought, whether putting salt in the water used in making concrete—which is so frequently done when laying concrete in cold weather—may not have the effect of producing concrete wherein imbedded iron is abnormally affected by electrolysis. I shall be glad to have the author's opinion as to this.

The table covering the results of the tests of electrolysis upon iron in concrete immersed in lake water showed a decidedly less percentage of corrosion in the cases of concrete made with one brand of cement from that made with the other brands. This naturally raises the query as to whether there is some particular ingredient either lacking or present in this one cement which produces concrete which tends to protect the iron from electrolysis better than concrete made with the other cements.

J. N. Pierce: I am in the electric line, and as I was listening to the paper it occurred to me that there are various other things that caused this corrosion and that it was a matter of keeping the moisture out of the cement; then it occurred to me that some of the waterproofings are an iron compound mixed with the cement,—and I would ask if that would not be really very detrimental to use? I have heard a great many salesmen in connection with reinforced concrete talking about mixing this moisture-proof substance with the concrete before putting it around the iron. It seems to me that this would be more harmful than beneficial, on account of increasing the conductivity of the cement.

Professor Burgess: Do I understand that those moisture-proof materials have iron in them?

Mr. Pierce: Yes. Ironite is one of the cheap materials. I think the general idea is that these moisture-proof materials work into the pores of the concrete and expand with corrosion.

W. H. Finley, M. W. S. E.: Wouldn't it be a good idea to put current through all reinforced concrete and thereby increase the adhesion?

Wm. Seafert, AFF. W. S. E.: About 10 % more bond is obtained with rusty material than where there is no scale.

Carl A. Keller: It sometimes becomes necessary to use cinder concrete in proportions of one of cement to seven of cinders. I have seen cases where this cinder concrete had to be placed in thicknesses of 18 in., and there has been some question as to the desirability of putting the cinder concrete next to the iron beams or iron posts that may be imbedded, and in order to avoid any corrosion a cement coating had been applied to the beam before laying the cinder concrete. I wish to inquire of Professor Burgess if he can explain to us the action of the cinder concrete and the iron. I would also ask if some tests could not be made similar to those explained to us this evening, using cinder concrete around the pipe and in various electrolytes that were mentioned in the paper?

A. O. Anderson, M. W. S. E.: I was wondering how these tests were made, and whether it would not be advisable to make a similar set of specimens, put them under similar conditions, and not send any current through them. I rather think the specimens that were left in that salt solution for 108 days would show some rust without the cement, and we need not charge up all of that rust to the electric current.

Mr. Fowler: I would ask Professor Burgess about the corrosion near the surface. The electrolyte, as I understand it, was below the level of the top of the concrete. Did you take any precaution, with oil, for instance, covering the electrolyte or the concrete so that there would be no access of air? Where was the most corrosion? Then, in removing these specimens from the concrete, what precaution was taken to prevent actual scaling of the iron,—by a hammer blow, for instance?

G. T. Seely, M. W. S. E.: It seems to me that this paper is a very timely one, and one that is of considerable value for local application. It has been proposed here in Chicago that the subway be constructed of reinforced concrete. In this subway there would be railway lines carrying either single units or trains which would require heavy electrical currents. These currents, if there is much reinforcement, would tend to be carried in the structure itself, it seems to me, which would not only present the danger of electrolysis where the current would leave the reinforced structure, but also perhaps in the length of the structure. I do not think the danger is as apparent as it may seem, for the reason that the difference in the voltage between the ends of the reinforcement, if the reinforcement were not continuous, would be very small, and, as Professor Burgess pointed out, if the difference were less than the polarization voltage it would probably have no effect. It seems to me that this might be something which would be well to determine by experiment. If there is such an effect, it would have an important bearing upon determining the degree of insulation of the track rails in the subway.

Oscar E. Strehlow, M. W. S. E.: I do not know that I can say anything definite on this subject, because methods have to be tried to determine the effect. But in retaining-walls a condition sometimes exists in which the prices of the reinforcing material and cement, and the crushed stone and sand, and of back filling behind the retaining-walls, are such that a reinforced concrete wall and a gravity masonry wall are about equal. In view of this uncertain and untried question of electrolysis, it seems to me it would be a safer proposition to stick to the gravity wall.

Mr. Finley: I think that one of the valuable lessons we can learn from the experiments of Professor Burgess and those who have preceded him is that it is necessary to use great care in the construction of our concrete, particularly in the reinforced concrete; that is, to get a mixture as nearly impervious as possible, and also to see that it is thoroughly waterproof.

In 1904 I prepared an article on the necessity for waterproofing engineering structures in concrete, and called attention then to the possibility of the destruction of the reinforcing material in concrete by electrolysis. At that time I knew of no experiments having been made to determine that fact, nor could I find that the matter had really been given any attention. I am glad to see that since that time there have been experiments made in that line, and that while the question is not determined positively one way or the other, the results shown by Professor Burgess' experiments and others do indicate very clearly that we should exercise great care in building reinforced concrete.

R. H. Rice, M. W. S. E.: There are a couple of questions that I would like to ask. I understand from the paper that the results show nothing as regards the actual conductivity of the concrete itself, and the current that passes through I presume is conducted entirely by the moisture in the pores of the concrete. I would like to ask when the observations were made, whether the concrete had been immersed for a length of time sufficient to allow it to become entirely saturated with the water?

The other question was in regard to the time of the polarization. I presume that as soon as the concrete was placed in the water and became moist the polarization E. M. F. rose to its maximum value almost immediately, so that if a potential difference of 8 volts was applied, and there was a polarization E. M. F. of say 1½ volts, the actual potential difference which was causing this current flow would be then 6½ volts, and that would be the potential difference to which the concrete was subjected continuously throughout the experiment.

F. F. Fowle: This paper, it seems to me, is one of very great interest to us all. Of course it is one which is rather difficult to discuss because of the meagreness of the subject, but its present importance can hardly be overstated.

One of the interesting features in regard to electrolysis, not only in this case but in others, is the question of polarization, and I would like to ask the author what his experience has been in regard to the characteristic current flow when the voltage is diminished. It is very clear that after there had been a flow of current sufficient to establish a polarization of, say, 1½ volts, a reduction of the impressed E. M. F. would result in a diminished flow of current. It would be interesting to know whether he started out with any E. M. F. values of about 2 volts or less, and what characteristic flow was observed under those conditions. In a great many cases of electrolysis the potential difference does not exceed perhaps 2 volts, except for a very short period of the day, possibly during the peak of the load. In that case it would be very instructive to know how the current characteristic is affected. This has been a matter of some controversy in various cases of ordinary electrolysis of underground pipes, where some have contended, on the one hand, that any applied E. M. F., however small, would result in damage; while it has been contended, on the other hand, that the polarization would quickly shut off any current flow of dangerous magnitude.

Another point occurs to me, in regard to which there appears to be an entire lack of data up to this time. This concerns the question of whether or not the concrete is affected in any way by the flow of current through it or by any electrolytic corrosion that may be taking place. In Prof. Burgess' suggestions of new fields for investigation it seems that we might add several things, one of which would be tests for tensile, and compressive strength, of samples in which the current had been allowed to pass between two electrodes at opposite ends of the test piece. Such tests would embrace variation in the current density and the duration of flow; and comparisons would be made with similar test pieces not exposed to possible corrosion or disintegration.

In reinforced structures we depend, of course, on the steel for tension, and the stresses are communicated from the concrete to the steel by the resistance to shear along the junction of the two materials. This seems to be still another profitable field for investigation, which is perhaps more important than the one first suggested. Obviously many chemical changes are taking place along the plane of shear, at the junction, and any weakening of the structure at this point might be attended by disastrous results in practice.

D. A. Abrams, JUN. W. S. E.: I did not wish to speak of electrolysis, but I heard a question some time ago regarding the effect of the rust on the bond strength between the concrete and steel. I know it is well recognized that rusted steel will give a higher bond strength, but I do not believe it will necessarily follow that the rust generated after the concrete was placed around the steel would give the same result.

W. O. Hotchkiss, M. W. S. E.: It occurs to me that many of our reinforced concrete structures are not in a similar situation with the test pieces. Those with which we ordinarily deal are alternately wet and dry, or very considerably in the degree of moisture. It occurs to me, in this connection, that possibly with the sediment drying off from the entrance of air, the concrete might become filled with the oxidized iron within the concrete, and in that way become far less porous, so that the electrolytic destruction of the iron would be greatly retarded. I should like to ask the author his opinion in regard to that,—what would be the effect of the alternate dryness and wetness of the structure?

CLOSURE.

The Author: Referring to the chairman's inquiry as to the possibility of the porosity of the concrete or the composition of the aggregate having something to do with the amount of electrolytic action which takes place, there is no doubt that there is a marked influence produced by the physical character of the concrete such as porosity and perhaps its chemical condition. The free lime, for example, ought to have a retarding influence. It would appear that if a concrete could be made non-porous, it would then offer a protection against electrolytic action.

Mr. Keller brought up the question as to the use of cinder concrete. As I understand it, the objection to cinder in concrete is that the particle of carbon coming in contact with the iron forms a local couple; there is no doubt that the possibility of electrolytic action exists where such a couple is formed. This would be entirely prevented by the use of a thin layer of uncontaminated cement, as mentioned by Mr. Keller. I doubt, however, even if the cinder does come in contact with the iron, that the couple would be active on account of the polarization which is set up. The maximum voltage of that couple would be not much more than one volt. The polarization would probably be equal to that, and the current would be stopped unless the air or oxygen could get at that cinder and depolarize it, which probably would not be the case. It is my opinion that there will not be much damage to the reinforcement due to local action by the imbedded cinders.

Our chairman presented the query as to whether the formation of iron rust in the concrete did not block up the holes and therefore stop the flow of current. That would be the case if the rust formed within the concrete or at the surface of the iron, but our experiments showed that it does not so form unless air gets in, and this action of the air must be very slow, while the concrete is all wet. Rust forms on the outside surface of the concrete, the iron existing in the concrete in the form of a soluble salt as a ferrous or ferric chloride. It is only when that is oxidized that the rust forms. The presence of salt in the concrete would undoubtedly make that concrete more conductive.

Our experiments would show that salt, in addition, makes the corrosive action of the current much more marked, and it appears, therefore, that the use of salt in mixing concrete might constitute a disadvantageous factor.

The presence of iron compounds in the concrete, put there to render it waterproof, ought not to have any disadvantageous effect unless such compounds be soluble electrolytic conductors. The chemical composition of the materials referred to is not given, and opinion as to their influence cannot well be formed. As pointed out before, the matter of making concrete moisture-proof seems to be a highly important one from the standpoint of electrolytic corrosion.

Referring to Mr. Jackson's inquiry, it does not appear that our tests have been sufficiently accurate, nor the results sufficiently conclusive, to warrant the deduction that there is a material difference in the electrolysis resisting property of concrete as influenced by the particular brand of cement employed. It is probably true that there may be such difference, and especially would this be true if the deficiencies in cement make decided differences in the density and permeability of the concrete. It should be a matter of further investigation to determine if there are any constituents in cement and concrete which have a notable influence on electrolysis.

The question has been asked, whether the kind of iron itself may have a marked influence on the electrolytic corrosion. While the tests referred to were limited to but one kind of iron,—a mild steel,—I am of the opinion that the kind of iron makes very little difference, as far as the current efficiency in the corrosion is concerned.

Again, it has been asked whether there might not have been a similar amount of corrosion if the pipes had been exposed to the salt water without the flow of current. While I have not referred to the existence of check samples in this work, such samples were prepared and it was found that the salt water produced very little natural oxidation during the period of the test where current was not flowing.

In answer to another question: The corrosion takes place in the most marked degree at the surface of the concrete block. This level was several inches above the surface of the solution in the tank, but it was really at the level of the solution since the solution worked its way up into the concrete block to the surface of it by capillarity, so that the corrosion really takes place at the surface of the electrolyte.

The tubes were removed and brushed; there was no scale on them, and they were just as a piece of iron would look after taking it out of an acid solution. They were simply washed off and brushed, and the rust which is apparent on these samples —the brown rust—is the result of subsequent exposure to the air. If the air could get at the concrete around the iron reinforcement occasionally, as one of the speakers suggested, it would result in the formation of this brown rust throughout the concrete and ought to act as a retarder. It ought to fill up the pores with a non-conducting material,—the brown rust is practically non-conductive,—and make the resistance high.

The question of polarization is a really important one in the study of electrolytic corrosion, and it is one which has been given too little attention. We have under way at the present time another series of tests in which the applied pressures are 0.5 of a volt from the beginning of the test, and it is found that the polarization is somewhat less than 0.5 of a volt. There is a slight amount of current flowing, and whether that amount of current is going to produce 90% electrolytic corrosion, or 80%, or only 1 or 2%, is something that we have not as yet found out. We have found no reference in literature to other work which has been done on this polarization subject, and it is worthy of attention.

The average pressure throughout the day may be in some localities 8 volts, setting up a polarization pressure of 2 volts. When this applied pressure drops down below 2 volts, there ought not to be any electrolytic action until that polarization is diminished by the action of the oxygen of the air.

The current is carried through the cement electrolytically by the electrolyte in the voids in the concrete. The United States Government chemists have conducted a rather exhaustive investigation of the conductivity of soils,—sand and clay and other materials,—and the results are of a good deal of interest to any one studying the practical electro-corrosion phenomena. They find that the conductivity is purely a question of the electrolyte between the particles of sand or clay.

The suggested importance of studying the electrolytic corrosion, in view of the possibility of a subway in Chicago, is very interesting, but from what I have recently read in the papers that is a purely theoretical speculation.

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THE UTILITY OF THE METALLOGRAPHIC MICROSCOPE.

By JAMES ASTON.

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This article will be confined entirely to the metallographic microscope, without touching upon its use in the immense fields of geology and botany, where the examination of rock sections and vegetable products has a direct utility in engineering. Here, however, the methods are somewhat different than in metallography, since transparent sections and transmitted light (often polarized light) are used. Also, it is not purposed to dwell especially upon the technique of microscopic metallography. The methods employed are presented in good form in several books and numerous articles devoted to the subject. Again no detailed or elaborated discussion of any complex phase of the subject will be taken up. Rather, concrete examples will be brought forward illustrating what metallography has done for us, with the hope that the discussion will open suggestions of its possibilities in individual fields of endeavor.

Metallography is but a step towards the rationalizing of our study of metals and alloys. The earlier work in the study of these materials was naturally along the lines of their possible uses; it consisted of tests of these various properties and a classification according to their several fields of service. A vast accumulation of data of this kind led to the adoption of a rather empirical correlation of composition and quality. Chemical analysis later came in to give us a more exact correlation by the elimination of one big uncertainty, the composition. But chemical analysis falls short of giving us sufficient information regarding our material. Substances owe their properties solely to their make-up, or structure. Composition is but one of the determining factors; chemical analysis therefore fixes but one of the variables. The relation of these chemical elements or the make-up of the material is most vitally dependent on its history. Temperature and pressure conditions, or the proximity of disturbing influences, are of importance. In steels, for example, we consider the effects of heat and mechanical treatment; that is, for identical analyses, a steel annealed at 1200° C. would be weaker than one annealed at 800° C.; one quenched at 800° C. would be harder than the same material slowly cooled from that temperature, while cast material is weaker than that which has had subsequent rolling or forging.

Structure or make-up is therefore the first step in the interpretation of the properties of materials. An essential in this determination is the composition; chemical analysis is therefore a necessity, and it must be understood clearly that metallographic study is only an auxiliary to the other methods of test. Two lines of attack are open: by the use of the pyrometer and by the use of the microscope. The latter was developed much the earlier, having its beginning in the work of Dr. Sorbly in England in 1864 and the later independent investigations of Martens in Germany in 1875. However, the real development has come about within the last ten years; this is due to the rapid progress in physical chemistry, particularly in a better understanding of the theory of solutions. In the earlier work it was possible to develop the structure of the material under examination, but the full measure of the value of the work was missed through the inability to interpret the developments; again systematic research was handicapped by this lack of knowledge. To-day we have a rational interpretation of the results of solidification of molten mixtures and a consequent explanation, more or less developed, of the variations in the structure of alloys occasioned by changes of composition or treatment.

It will be impossible in this paper to dwell upon the use of the pyrometer in the study of the structure of alloys. Cooling curves obtained by its use undoubtedly furnish the most rational basis for the theoretical deductions of the results to be expected on solidification of the melt. But outside of its very direct practical bearing in certain instances, notably in the determination of the critical points of tool steels, the pyrometer may be said in general to be of more scientific interest. The microscope, on the other hand, has a more direct application in the industrial laboratory since with it one is able to make an examination of any desired material as it is used or as it exists, and to interpret from the structure, backed by experience, the condition of the material and its suitability for the purpose in view.

Microscopic examination of metals and alloys is passing through the same cycle that the chemical analysis of iron and steel did some years ago. We have the enthusiast, who would claim for the microscope the power to usurp the functions of other testing methods; and the skeptic, who treats it as a toy and scoffs at any suggestion of utility outside of the laboratory of the scientific investigator. The chief argument of the latter is that the field of view of the microscope is only an extremely small part of a very small sample cut from a large mass of material and it can disclose, therefore, only local conditions. Such argument is hardly tenable; it would apply with equal force to the one-gram sample, the chemical analysis of which controls the 60-ton heat of a steel furnace; or to the purchase of a car-load of coal or a boat-load of ore on determinations of heating value, composition, etc., made on equally small units; or to our methods of design of structures from material whose strength is taken as that of a small test sample. In fact, all testing methods are based on the principle of a fair average sample of the material under test.

Osmond, the noted French worker, has aptly classed the divisions in the microscopic examination of metals and alloys as anatomical, biological, and pathological. Taking up the last division first, it is needless to point out that the microscope is useful in the detection of incipient cracks and flaws, slag or foreign inclusions, porosities, and the numerous other ills that metals are heir to. Fig. 1 illustrates this point; it is a section of a piece of wrought iron taken perpendicular to the direction of rolling, and shows a slag inclusion. It needs no comment, as it must be very evident that slag particles so breaking the continuity of the metal will have a material effect on the physical properties.

In Fig. 2 is shown a section of a brass casting made in the course of an investigation for a manufacturer who was having trouble with his product. The brasses used were of a composition of about 80 per cent. copper, 10–15 per cent. zinc and 5–10 per cent. lead, the last named being the very common addition agent to brasses to facilitate machining. But brass will hold in solution after solidification only a very small percentage of lead, and any excess will therefore separate out in the free state. This is clearly indicated in the photomicrograph where the free lead is shown in its typical form of black globules. Its effect in machining becomes apparent, since it will break into short chips the otherwise long curling ones of the high copper brasses. On the other hand, it must have equal influence in lowering the strength and ductility of the product; and it is surely not a desirable addition in brasses to be subjected to high temperatures, since the lead will soften or melt at temperatures much below the fusion point of the body material.

Figs. 3 and 4 illustrate a case where the utility of the microscope was rather indirect. Two brass manufacturing concerns A and B were putting on the market a standard article for which there was a large demand. But B's proved stronger than A's and analysis of B's goods indicated the presence of 1 per cent. of iron in the brass. However, when A tried out the new composition it failed to give the strength of B's. Although the compositions are identical the structure differences are pronounced, as indicated in Fig. 3 (of A's) and Fig. 4 (of B's). The coarse structure of A's, together with its marked dirtiness and porosity as compared with the other, led to further investigation, with the final development that the 1 per cent. of iron in B's product had little direct bearing on the strength, and was only that something which was inevitably left behind on the addition of ferromanganese to deoxidize the bath, the manganese being slagged off, and the brass casting left with a clear, fine-grained structure of great strength.

The most work with the microscope has been done in the anatomical division, in the determination of the inner make-up of metals and alloys. Use is made of three facts so fundamental and so vital that they may be presented as axioms.

(1) Metals and alloys are crystalline.

(2) The structure is homogeneous or heterogeneous. Solubility relations govern. It is homogeneous in pure substances, in solid solutions, or in the metallic compounds, and heterogeneous if there is no solubility, or only partial solubility of the constituents after solidification.

(3) The individual melting points of the constituents have no bearing on the order of their crystallization from the melt. The solubility relation of the constituents is again the governing factor.

Fig. 5 is a photomicrograph of Swedish iron and shows the typical homogeneous structure and crystalline habit of a pure metal. The irregular boundaries of the grains are not due to the crystal faces, but indicate rather that crystallization has proceeded from nuclei, or centers, with varying rates of speed, and that the limit of growth has been that due to interference by an adjoining grain. Each grain is a crystalline aggregate of definite crystal system and uniform orientation.

The heterogeneous structure of certain alloys is illustrated in Figs. 6, 7 and 8, the sections being a series of lead-antimony alloys of compositions respectively of 50 Sb, 50 Pb; 13 Sb, 87 Pb; and 5 Sb, 95 Pb. This series is of the type of alloys where the solubility is *nil* after solidification, with consequent complete separation of the constituents as shown, the white being the antimony and the black the lead. In this series, the antimony freezes at 632° C. and the lead at 326° C. and we might expect, therefore, that the antimony would always crystallize out first in a matrix of still fluid lead. This is far from the facts, however, and we see in Fig. 6 the excess antimony crystallizing in a matrix of the eutectic of antimony and lead; in Fig. 8 the lead has solidified first in its typical form in the same matrix as before; while in Fig. 7 we have the eutectic, with its finely divided, intimate mixtures of lead and antimony, due to solidification together at a constant temperature of 228° C. or about 100° C. below the freezing point of the more fusible constituent.

Advantage is taken of this selective crystallization in bearing metals. While suitable bearing metals had been made long before metallography came to our aid, it has pointed out the reasons for success in the use of certain mixtures, and the line of attack necessary in looking for new ones. There are two chief desiderata for a bearing material: First, a low coefficient of friction; this is lowest with the hard metals. Second, plasticity, in order that as unequal wear occurs the pressure of the shaft will squeeze the bearing into conformity and thus avoid local heating by distributing the load equally over the entire surface; this plasticity is obtained with soft materials. Two such opposite properties, hardness and softness, are manifestly not to be obtained by the use of any single homogeneous substance. But by taking advantage of the selectiveness of freezing, we can obtain alloys in which we have a hard constituent bedded in a plastic matrix; the exact nature of the alloy will, of course, depend upon the character of service and the amount of unit stress on the bearing material. One of our common alloys, Magnolia metal, is of the lead-antimony series, carrying about 20 per cent. of antimony, and consisting therefore of antimony crystals bedded in a plastic eutectic of lead and antimony. Its microstructure would be intermediate between those shown in Figs. 6 and 7.

In Fig. 9 is shown the structure of a Babbitt metal of the copper-tin-antimony series with two hard constituents, the cubes of SbSn and the needles of $SnCu_3$ bedded in the backing of copper.

All of our bearing materials, including Babbitt metals, machinery brasses and bronzes, and cast iron, may be shown to fulfil the conditions laid down above.

In no field is greater use made of the properties resulting from selective freezing than in the ordinary carbon steels. Figs. 10–15 give the structures of several steels with carbon percentages of 0.10, 0.30, 0.60, 0.93, 1.46, and 1.80. We note, as the percentage of carbon increases, that the relative area of the black constituent, as compared to the white, becomes greater, until in Fig. 13, with 0.93 per cent. C., the entire field is occupied by the black constituent. Above this holding of carbon, the white areas increase in magnitude. Structurally, these photomicrographs mean that our slowly cooled carbon steels are heterogeneous, and composed of two constituents, iron (ferrite) and combined carbon (cementite). They are, therefore, made up of an excess substance, either ferrite or cementite, depending upon whether the total carbon is below or above 0.90 per cent., together with the eutectoid of the two constituents, and technically called the pearlite.

In the greatest proportion of commerical steels, with a carbon content below 0.90 per cent., the structure is a heterogeneous mixture of ferrite and pearlite, with the pearlite containing all of the carbon in the form of Fe_3C, the amount of the pearlite increasing as we approach the eutectoid proportion at 0.90 per cent. C. Three facts form the basis of selection of steels of varying carbon percentages for different classes of service; namely, cementite or combined carbon (Fe_3C) is hard, brittle, and of high strength; ferrite, or iron, is soft, ductile and relatively weak; and by shift of carbon composition we can manipulate the relative proportions of these constituents.

In structural steels, with comparatively steady load, we require reasonable strength and elastic limit and high ductility and softness; micrographically, therefore, we need much iron plus some combined carbon, or much ferrite plus some pearlite, which is obtained with a steel of about 0.20 per cent. carbon.

In rails, on the other hand, the load is in the form of a shock, with heavy stresses for short intervals; the requirements are high strength and high elastic limit with reasonable ductility and hardness to resist abrasion. Micrographically this means much combined carbon + some iron, or much pearlite + some ferrite. In open-hearth rails, therefore, we can use steels with carbon from 0.60–0.70 per cent.; but if, because of the irregularities occasioned in manufacture, as in the Bessemer process, we cannot utilize to the full the properties of the pearlite, we cut the carbon to 0.50 or 0.60 per cent., and reduce the risk of breakage by obtaining higher ductility at the sacrifice of hardness and elasticity.

In line with the above discussion, the microscope shows (Fig. 16) that white cast iron is in reality a very high-carbon steel, with an excess cementite occupying about half of the total field, because of the total carbon content of from $3^1/_2$–4 per cent. And we must expect this material to be very hard and brittle and exhibit the silvery fracture from which it derives its name, since the fracture is necessarily along the line of least resistance, or through the brittle cementite areas.

Chemical analysis indicates that gray cast iron differs from the white cast iron not in the quantity of total carbon carried, but because in the gray iron this carbon is largely in the form of free graphite. A simple fracture test shows this, in that a break along the line of least resistance exposes the dark graphite cleavage; hence, the name gray iron. Microscopic examination confirms this, and the distribution of this graphite is shown in Fig. 17 in its typical form as flakes or sheets disseminated throughout the mass of metal. Is it any wonder that cast iron is brittle and weak in tension, when the effective area of the metal is so reduced by the weak plates of graphite? On the other hand, the very thinness of the flakes, while having a maximum effect in lowering the resistance to tensile stress, accounts for the high resistance of cast irons to direct compression. The plates are already so thin that their interposition in the body metal does not result in any further yielding to a direct compressive load.

Except for its free graphite, gray cast iron is seen to be (Fig. 18) nothing more than a steel matrix of high, medium or low carbon, depending upon what proportion of the total carbon has been converted into free graphite because of slow cooling or the presence of silicon or analogous elements.

The microscope is of service in indicating the physical changes taking place in the conversion of hard, brittle white cast iron into the relatively soft and ductile product which we know as malleable cast iron. Due to heat alone (the annealing) the combined carbon is decomposed to iron (ferrite) plus graphite. But since the temperature of annealing is well below that of fusion, the graphite is not free to assume its normal crystalline form (the flake or sheet) and is forced by the comparative rigidity of the metal to assume that shape which will enclose the greatest volume with the minimum of surface. We find the body of the malleable casting to be composed of globules of amorphous carbon bedded in a matrix of iron (Fig. 19). Also, in the usual practice of annealing in mill scale, or its equivalent, the surface layer is decarbonized, to an amount and to a depth depending upon the time, temperature and oxidizing conditions, and appears in the photomicrograph in the typical structure of a carbon-steel. Thus the malleable casting consists of a steel shell of great strength, together with a center of iron in which is embedded graphite in such form as to minimize the detrimental effect such as accompanies its crystallization in the normal form appearing in gray cast iron.

In Fig. 20 is shown a photograph to illustrate the utility of the microscope in studying the make-up of materials outside the field of the metals and alloys proper. It is a microsection of a non-metallic base impregnated with a molten metallic compound. The value of the material and its future development depended largely on the nature of the interaction during impregnation. The result might be a single new compound, or two new compounds, or simple solution, or mere mechanical mixture. Chemical analysis proved of little service in this differentiation. But the structure is heterogeneous—this eliminates the single compound or the solid solution. Further microscopic study with selective methods of attack served to identify the constituents and class the product as one of mere mechanical impregnation.

In no field does the microscope become such a useful auxiliary as in the examination of the special or alloy steels; here its usefulness is rather of the future than of the past. It is impossible to dwell upon this phase which is beyond the scope of a paper of this character. It is of interest to note, however, the most important revelation that, in spite of the multiplicity of alloying elements and their various combinations, their influence is largely one of degree and that, after all, the underlying structural considerations are common to all.

While the greatest amount of work of a more scientific nature has been done in the anatomical or structure-composition division perhaps the greatest utility of the microscope in the works laboratory is in the biological division, or that branch correlating the structure changes with the treatment received, for the properties of metals are most vitally dependent upon their mechanical working (whether cast, forged, or rolled) and the heat treatment. Microscopic study, together with determinations with the pyrometer, have given us a rational understanding of the annealing and the tempering of steels. We recognize that the hardening of steels by quenching is due to structural influences occasioned by changes of the relations of carbon and iron; and we can apply this knowledge to advantage in the heat treatment, whereby we can manipulate the properties as desired by taking advantage of the ability to check the structure at any stage between the abnormal one of the quenched state and the normal one of the annealed steel.

One point is vital in this connection and may almost be taken as an axiom. The strength of a steel is inversely proportional to the grain size, and the growth of grain is a result of temperature and time.

Figs. 21–26 are microsections of a steel casting of 0.50 per cent. carbon, and serve to illustrate the marked variations of structure, with consequent changes of physical properties, resulting from heat treatment or mechanical working. Fig. 21 is the steel as cast, with its rather coarse grain due to normal cooling from the high casting temperature. Fig. 22 is the same material after forging, and shows the mechanical breaking down of the grain with a resultant increase of strength. But an annealing of the forged piece at the high temperature of 1100° C. has again (Fig. 23) coarsened the grain, nullifying the effects of forging and leaving the material in no better physical condition than the original casting. A moderate temperature of 800° C., however, restores the fine-grained structure (Fig. 24). Fig. 25 shows the steel heated to 1000° C. and quenched in water, and gives the typical martensitic structure of a hardened steel. Finally, reheating the material of Fig. 25 to 650° C., and again quenching, results in the sorbitic texture (Fig. 26), where the transition from the martensitic structure of the hardened steel to the pearlitic structure of the slowly cooled state has been practically completed, but without chance for segregation of the constituents as would be the case if slow annealing had been resorted to. This last figure shows the finest texture it is possible to obtain in steels, and it results, consequently, in the highest combined strength and ductility.

The considerations treated above are of great importance in the control of the annealing and tempering of steels, and have a bearing on the proper finishing temperatures in rolling and forging operations.

In Fig. 27 we have the well-known Roberts-Austen circle, illustrating the marked variations of structure resulting from different heat treatments of a piece of blister steel of 1.50 per cent. carbon, the original structure of which is given in the center.

Fig. 28 is a section of a steel axle broken by fatigue, or continued repetition of stress. The larger grained structure is of the material at fracture, and the fine grain is the result of judicious annealing of the same material. Whether or not the coarse crystallization is the result of the repetition of stress is problematical. It is likely that the original structure in the area of fracture was coarse, favoring therefore the early failure by fatigue because of the more uniform orientation of the crystal cleavages, whereas a fining of the grain by judicious treatment would have resulted in longer life because of a breaking up of the regularity of cleavage directions.

Figs. 29 and 30 are photomicrographs of a steel rail, the former of the original material, with very good grain, and the latter after heating to high temperature. Remembering our axiom regarding the correlation of grain size and strength, it is evident that the heating has resulted in a marked deterioration in quality. These illustrations point out the reasons for the wearing down at the joints of cast welded track, or the weakness of electric welded rail or any welds made without subsequent treatment. The material shown is not burnt, and the structure of Fig. 30 can be changed to one of good quality by proper treatment, either by judicious annealing or, as is the common practice in welding, by hammering or mechanical working of the material.

Fig. 31 illustrates the effect of punching a piece of structural steel. The distortion produced can be traced back from the edge of the hole by the curvature of the black pearlitic areas in the direction in which the punch was driven through the plate. The depth of distortion depends upon the thickness of the plate and the size (also the sharpness) of the punch; it can easily be measured, and it has been found that for a three-fourth inch hole in a three-quarter inch plate, about one-tenth inch increase of diameter of hole by reaming is necessary to remove all affected material.

Fig. 32 is a section of a steel casting cut by the oxyhydrogen blowpipe. Passing inward from the cut edge, we note the burnt or oxidized portion in the blurred part immediately adjacent; next the enlarged grain of the overheated but not burnt area; then through a graduation of grain size to the normal structure of the interior. This method seems at first sight to have a very detrimental effect, but is in reality slight, since measurement shows a depth of affected material of only four- or five-hundredths of an inch.

Numerous other instances might be cited of the usefulness of the microscope. It has materially assisted in the determination of the nature of the various zinc coatings for the protection of iron surfaces, and we are trying it out in the study of the progression of rusting on metal specimens.

But it will be necessary to conclude with a comment on the probabilities of the future. While the great field of application of metallographic study has naturally been to the metals and alloys, there is every reason to expect extension of its scope to allied lines, such as the examination of complex ores and slags, to ceramic materials and perhaps to coal and coke. In all of these instances we find good and poor materials of identical analysis; the probability is that the interrelations of the constituents are different. An interesting application along this line has just been pointed out in the use of microscopic examination to detect iron blast-furnace slags which are suitable, or otherwise, as a raw material for Portland cement. That vitrification which is essential in the proper slags is brought out very neatly.

Finally we may look to improvement in the microscope itself. We are at present restricted to the study of the heterogeneous structure revealed by ordinary reflected light. The petrographer has the advantage of being able to use transparent sections and polarized light, and in consequence can determine the crystal systems of the constituents of the rock under examination. When suitable apparatus is perfected (it is now being developed) to enable us to determine the crystal forms of the constituents of an opaque specimen by reflected light, then the metallographic microscope will have a materially enlarged scope of application and utility.

NORTHERN CHEMICAL ENGINEERING LABORATORIES,
MADISON, WISCONSIN.

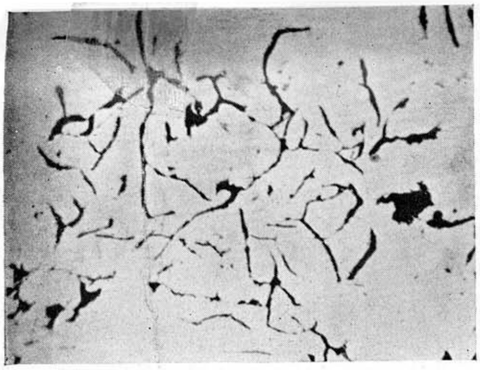
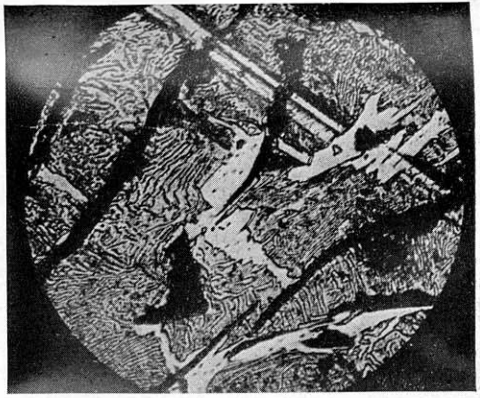


Fig. 17.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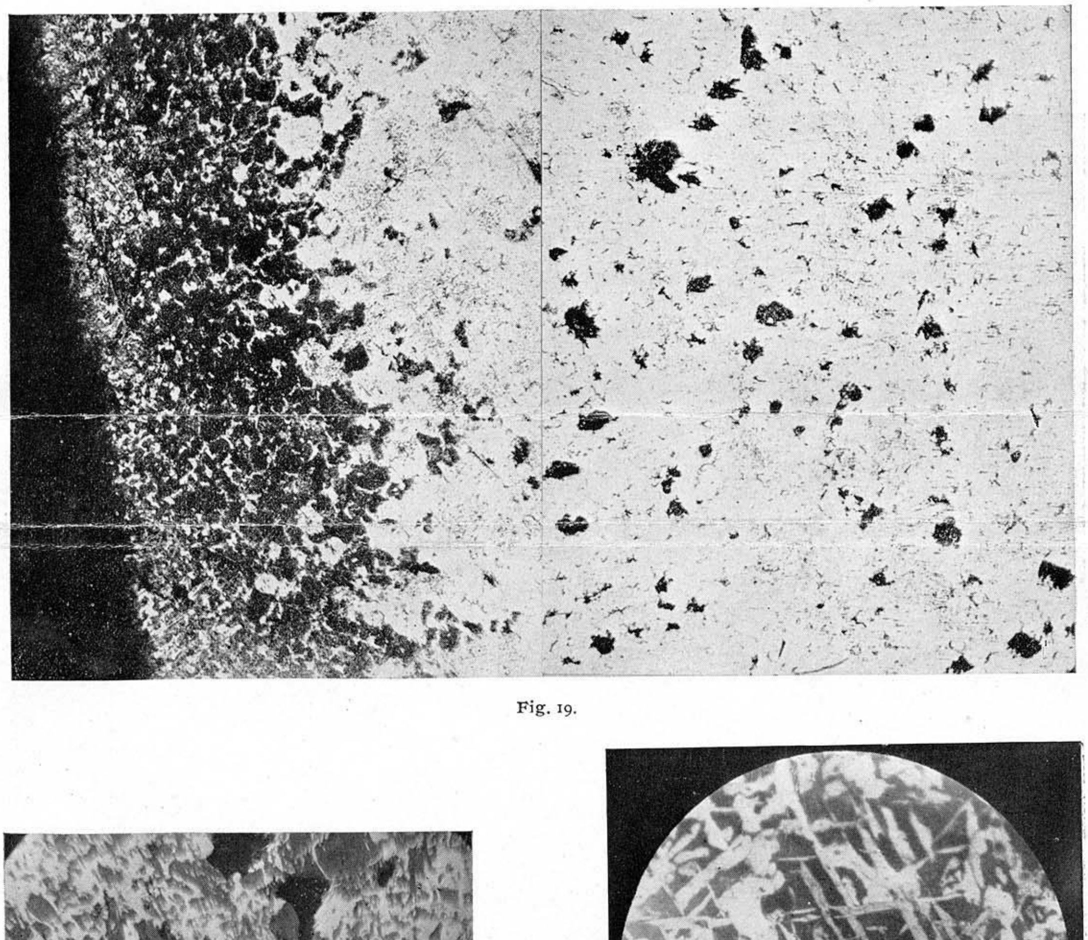
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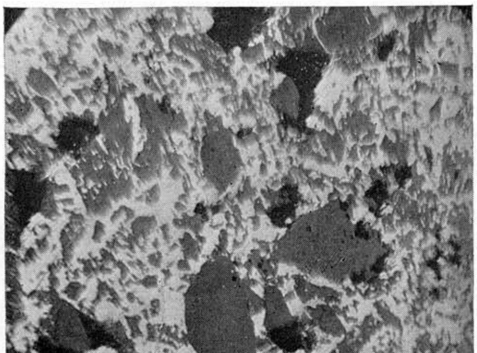
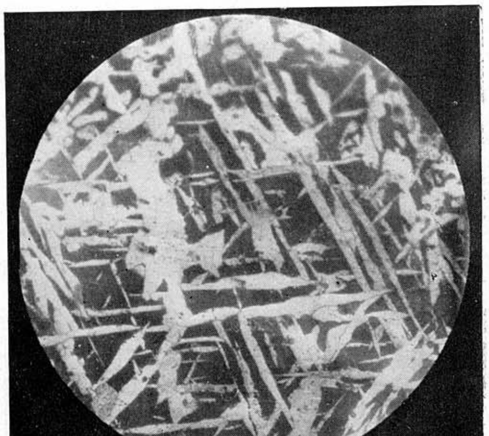


Fig. 20.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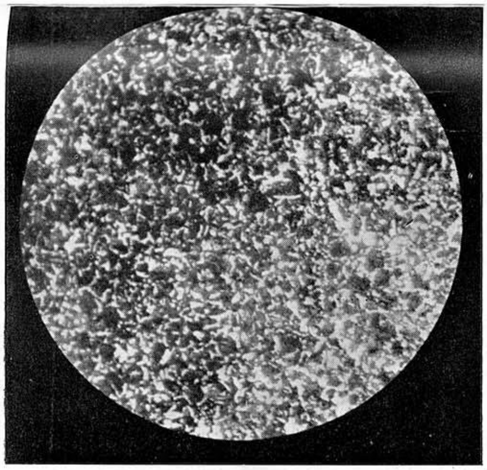

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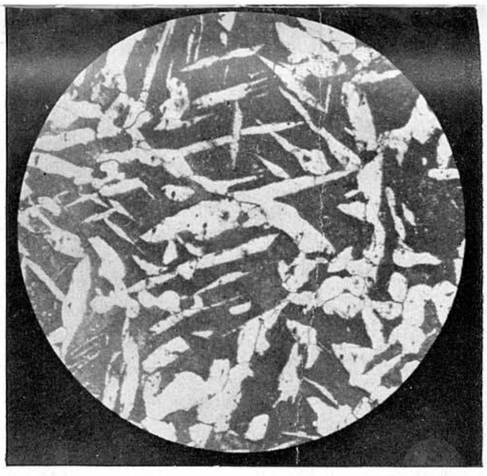

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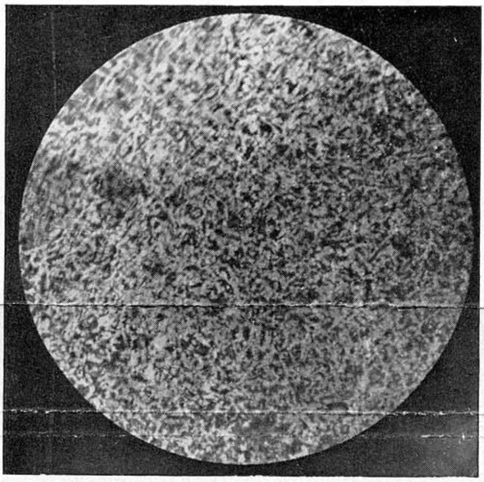

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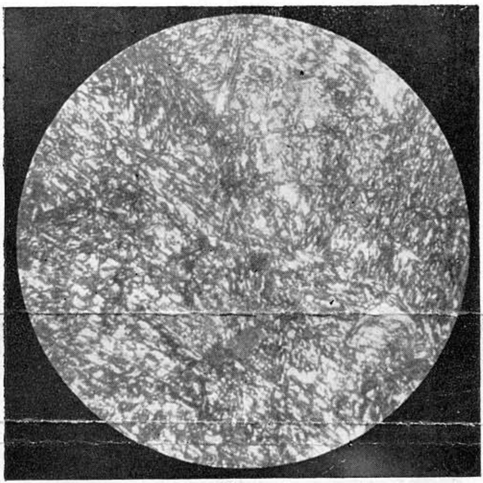

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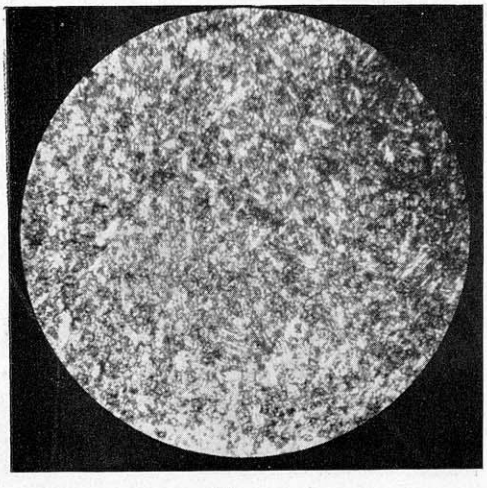

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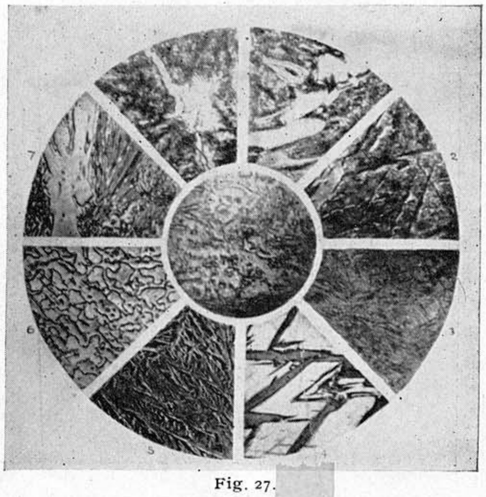

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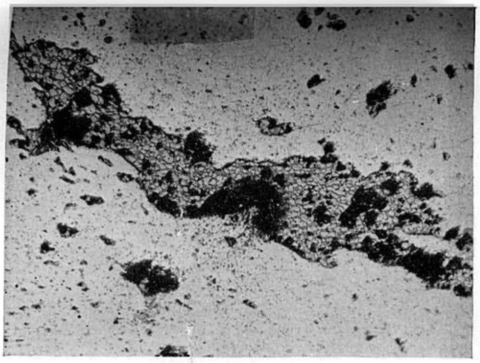

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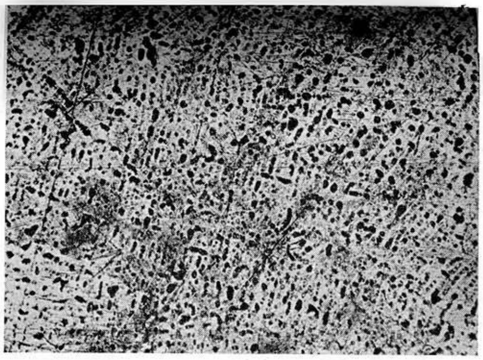

Fig. 2.

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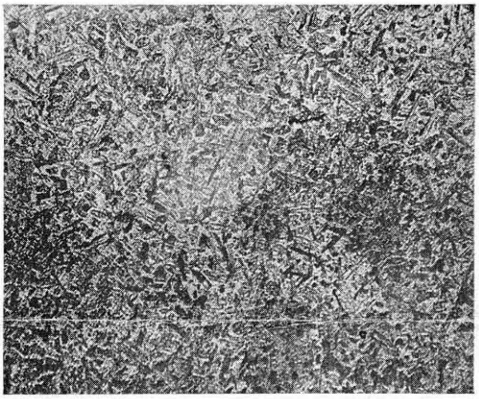

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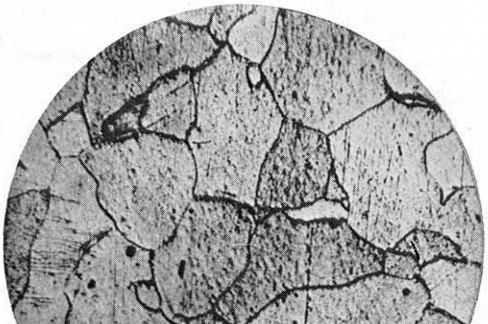

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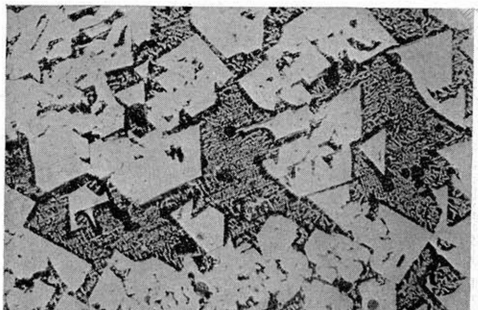

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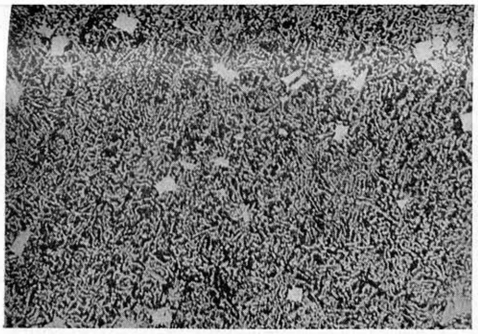

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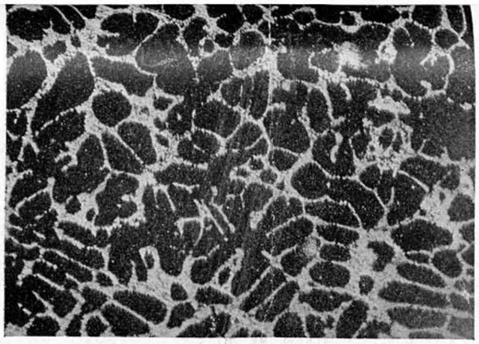

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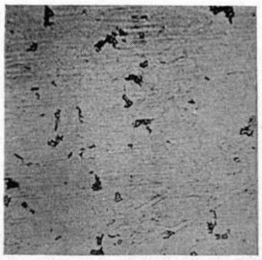

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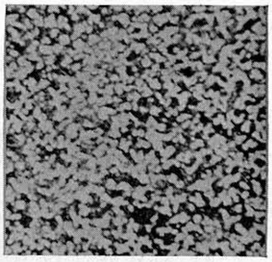

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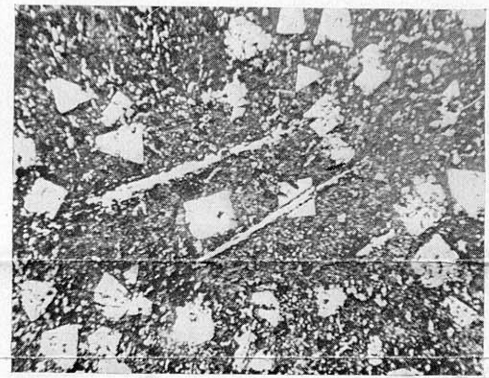

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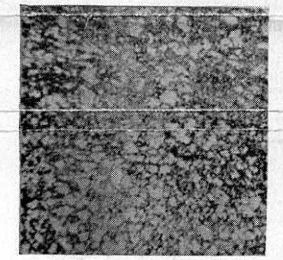

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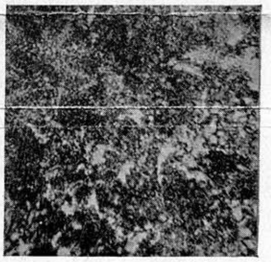

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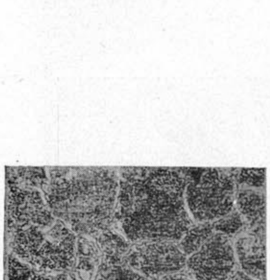

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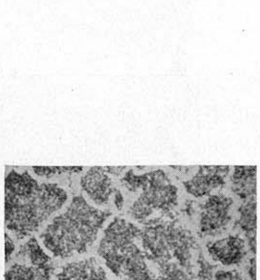

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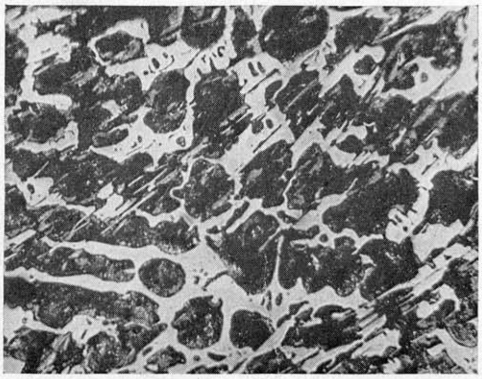

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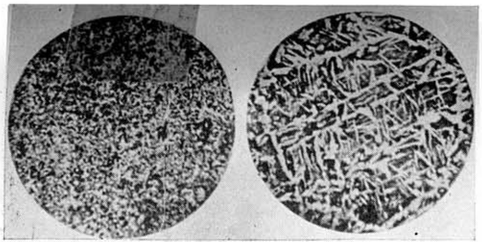

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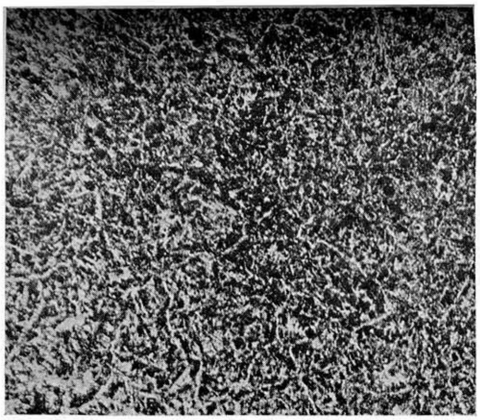

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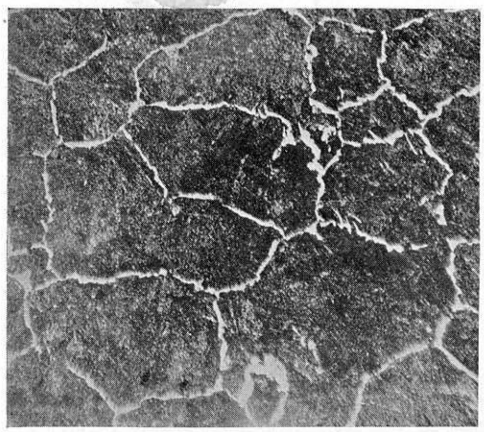

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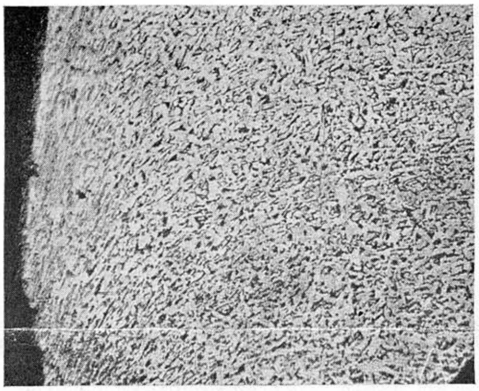

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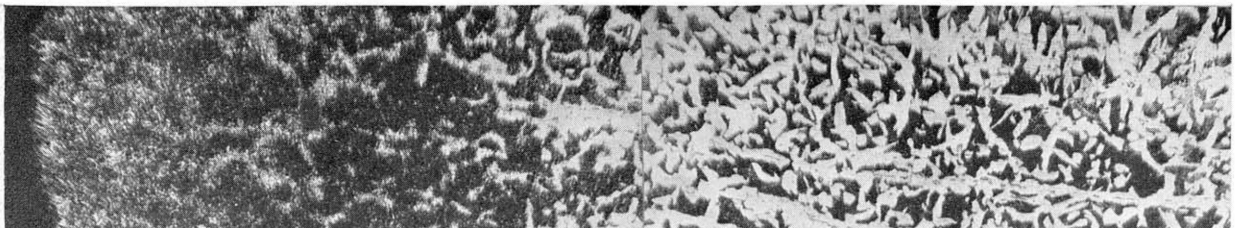

Fig. 32.

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SOME ALLOYS OF CALCIUM

BY

JAMES MILLER BRECKENRIDGE

A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
THE UNIVERSITY OF WISCONSIN

THE UNIVERSITY OF WISCONSIN
1911

CONTENTS

SOME ALLOYS OF CALCIUM

INTRODUCTION

Until recently calcium has been a metal of high cost and great rarity on account of the difficulty of separating it from its compounds. Through improvements in electrolytic reduction methods it has become of moderate price and may now be classed amoung the technically available metals. It is as yet a matter of speculation as to what uses it may serve, and it is natural, therefore, that there should be some general interest in a study of alloys containing calcium as an ingredient.

A review of the literature shows that some alloys of calcium have been made. Three general methods have been employed. First lime was heated with metal to be alloyed in the presence of metallic sodium. Second, calcium carbide and an oxide of the metal were heated together, and third, fused calcium choloride was electrolyzed, using the metal to be alloyed as cathode.

METHODS USED

In this investigation which was carried out in the chemical engineering laboratories of the University of Wisconsin, the alloys were made by adding metallic calcium to the molten metal, the calcium being added in small pieces. This slow addition tends to moderate the violence of the reaction which occurs where the two metals have reached the necessary temperature. In some cases, even when a small quantity of calcium (one or two grams) was added, the violence of the reaction forced some of the molten metal from the crucible.

Crucibles made from Acheson graphite were employed in the preparation of these alloys, an electric furnace of granular resistor type being used to furnish the necessary heat.

Preliminary experiments were made to determine some of the characteristic changes produced by the addition of calcium to pure metals. In each case there was found to be a decrease in the tensile strength accompanied by an increase in the brittleness of the alloys produced. A further increase in the calcium content in some cases produced an alloy which could be pulverized easily.

ALLOYS OF CALCIUM WITH ALUMINUM, MAGNESIUM AND SILICON

Since calcium is a strong reducing agent is was thought that a considerable number of binary and ternary alloys could be made which would be of value as reducing agents. This suggested a study of the alloys of calcium with aluminum, magnesium and silicon.

Several alloys of calcium-aluminum and calcium-aluminum-silicon were made. The metals were melted in a graphite crucible containing sufficient calcium chloride to cover the molten alloy. The metals were added in this order; aluminum, magnesium, calcium. In the case of alloys containing silicon it was found advantageous to add the silicon to the binary alloys of aluminum-calcium or of aluminum-magnesium as the solubility of this element was greater in these combinations than in the aluminum alone. In each case there was an evolution of heat when the alloy was formed, and in some cases the reaction was sufficiently violent to force a portion of the molten metal from the crucible.

The violence of the reaction was diminished to a considerable degree by inoculating the molten metal with a small quantity of metallic calicum after which larger quantities of calcium could be added without losing any portion of the charge. The resulting alloy was stirred thoroughly by means of a graphite rod and when sufficiently fluid was poured into an iron mould. This method of operation tended to keep the alloy uniform in composition.

A series of calcium-aluminum alloys was made to ascertain how much calcium at one end of the series would make aluminum brittle and how much aluminum at the other end of the series would make calcium brittle. It was noticed that the point of brittleness sufficient to enable the alloys to be pulverised in a disc grinder lay between 20 and 25 per cent calcium. The alloy containing 20 per cent calcium was somewhat malleable and could not be pulverized in a disc grinder. An alloy containing 80 per cent calcium could be pulverised without difficulty.

Several alloys of calcium-aluminum-silicon and calcium-magnesium-silicon were made. All of these alloys containing 25 per cent calcium, or its equivalent of calcium and magnesium, or of magnesium alone could be pulverized in a disc grinder.

The binary alloys of calcium and aluminum containing the lower percentages of calcium were made without any special precaution being taken to prevent oxidation. As the percentage of calcium increased the tendency to oxidize increased to such an extent, that even with a protective layer of calcium chloride, it seemed impossible to prepare in an open crucible an alloy containing more than 85 per cent calcium. The alloys containing the higher percentages of calcium and magnesium were difficult to prepare on account of the low specific gravity of the resulting product. This rendered calcium-chloride too heavy to be used as a protective covering. No suitable protective material was secured for these lighter alloys.

CHEMICAL PROPERTIES

All of these alloys containing more than 5 per cent calcium decomposed water. The quantity of hydrogen increased with the increase in the calcium content of the alloy. In dilute hydrochloric acid the evolution of hydrogen was more rapid, and with alloys containing silicon, a spontaneously inflammable silicon hydride, gas was liberated.

The stability of some of these alloys in air was noteworthy. Pieces of various alloys weighing about 5 grams were placed on an exposure board and subjected to the atmosphere of the laboratory. At the end of four weeks it was observed that the alloys which contained the highest percentages of calcium and silicon, were disintegrating, while those alloys of the lower percentages of calcium had become coated with a layer of oxide which prevented further oxidation.

The time required to melt and pour a charge of about one pound of the alloys varied from five to twenty minutes, depending upon whether the furnace was hot or cold when the charge was put in, and also upon the calcium added as the heat generated was such as to assist materially in securing the necessary temperature. From two to five kilowatt hours were used for heating purposes.

USE IN GOLDSCHMIDT PROCESS

Since so many of the alloys of calcium, aluminum, magnesium and silicon could be pulverized to any degree of fineness, and since several of these alloys could be stored for considerable time without serious deterioration, it was thought that these might be used as a substitute for the aluminum used in the Goldschmidt process. This consists in the reduction of a metallic oxide by pulverized aluminum. An excess of this oxide to be reduced is mixed with powdered aluminum to prevent the formation of an alloy composed of the reduced metal and the reducing agent. The charge is placed in a suitable container and ignited by a magnesium ribbon fuse.

The success of the Goldschmidt reaction depends upon the heat liberated during the formation of alumina. The total heat liberated depends upon the differences of the heats of formation of the metallic oxides which are to be reduced and of the alumina formed in the reaction. From this it is evident that it is impossible to reduce by the Goldschmidt process those oxides which have a heat of formation greater than alumina, unless heat is supplied from an exterior source.

The values given by the various experimenters for the heat of formation of alumina, lime and magnesia differ considerably, as shown by the date gathered from various sources.

I. $2\,Al + 3\,O = Al_2O_3 + 386988$ calories. Strauss: Minet, Production of Aluminum, page 209.
$2\,Al + 3\,O = Al_2O_3 + 380200$ calories. Thomsen (L. & B.).
$2\,Al + 3\,O = Al_2O_3 + 392610$ calories. Richards (E. & M. I. 6–8).

II. $Mg + O = MgO + 148000$ calories. Strauss; Minet, Production of Aluminum, page 209.
$Mg + O = MgO + 143300$ calories. Beketoff.
$Mg + O = MgO + 143400$ calories. E. & M. I. 6–8.

III. $Ca + O = CaO + 151900$ calories. Guntz and Besset. C. R. 1905, Vol. 140, pages 863, 864.
$Ca + O = CaO + 131500$ calories. Thomsen (L. & B.).
$Ca + O = CaO + 145000$ calories. Moissan.
$Ca + O = CaO + 131648$ calories. Strauss; Production of Aluminum, page 209.
$Ca + O = CaO + 130900$ calories. Thomsen (L. & B.).

Guntz used pure calcium and formed pure compounds from which he determined the heats of solution. This necessitated several corrections. Forcrand made pure CaO from $Ca(OH)_2$ and used this product in his determination. His value agrees with that of Guntz. (C. R. 1908, Vol. 146, pages 217 and 220). Moissan's value was determined from the heat of combustion of metallic calcium and is therefore less liable to error than the values determined by indirect methods.

From the above table it will be seen that the average value for the heat of combustion of magnesium is 145000 calories, of calcium 137000 calories and of aluminum 129000 calories; hence from the theory of the greatest heat evolution, magnesium should reduce lime and alumina, and calcium should reduce alumina, but not magnesia. Aluminum should reduce neither lime nor magnesia. However, Goldschmidt has succeeded in reducing lime by aluminum (Minet, Production of Aluminum, page 209), and Perkin has reduced alumina by calcium. Weston and Ellis (Trans. Faraday Society, 1908) have shown that aluminum powder will reduce lime at high temperatures and that the reaction

$$2\,Al + 3\,CaO \rightleftharpoons 3\,Ca + Al_2O_3$$ [1]

is reversible. This leaves the question of the relative reducing powers of calcium and aluminum in doubt. It has been shown conclusively, however, that magnesium[2] will reduce alumina and lime vigorously at ordinary temperatures.

In view of the relative reducing powers of these three metals the preparation of binary and ternary alloys of calcium, magne-

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[1] Trans. Faraday Society, 1908.

[2] Trans. Faraday Society, 1908.

sium and aluminum was undertaken with the hope of obtaining reducing agents which would have a higher heat of oxidation per unit of oxygen than has aluminum, and whose mixed oxides would form a slag more fusible than alumina. It was also thought that there would be a decided advantage, so far as the fluidity of the slag was concerned, in having the particles of the different oxides produced in intimate contact. This would be the case to a much greater degree when the metals are alloyed, than when the oxides are formed from isolated particles of each metal in a mechanical mixture.

Twenty-three alloys of calcium with one, two or all three elements, aluminum, magnesium and silicon, were prepared. Their composition is shown in the following table.

No. of Alloy.	Formula.	Aluminum.	Calcium.	Magnesium.	Silicon.
1	....	75.	25.	....	....
3	....	74.5	25.5	....	....
4	....	45.	55.	....	....
5	....	....	30.	70.	....
6	....	60.	....	40.	....
7	$CaMg_2$	....	45.5	54.5	....
8	....	50.	30.	20.	....
9	AlCaSi	28.4	42.	....	29.5
11	AlCaMg	29.7	43.9	26.3	....
12	$AlCaMg_2$	23.5	34.8	41.7	....
14	$Al_4CaMgSi_3$	41.4	15.8	9.4	33.8
15	$AlCa_2Mg_2$	17.4	51.6	31.	....
16	....	93.8	6.4	....	....
17	....	90.	10.	....	....
18	....	84.	10.	6.	....
19	....	67.1	12.9	....	....
20	....	80.	20.	....	....
21	....	80.	12.5	7.5	....
22	....	27.2	72.8	....	....
25	....	60.	....	40.	....
31	....	65.	....	....	35.
32	....	45.	....	20.	35.
33	....	60.	40.	....	....
34	40% Al + 60 $CaSi_2$	40.	25.	....	35.
35	$Al_2Ca_3Mg_2$	24.3	54.1	21.6	....

The percentage composition given in the above table was calculated from the amounts of the constituents originally weighed out, and is subject to errors of from 2 to 3 per cent, as the balance used was for rough weighing only, and as there was a variable amount of calcium chloride adhering to the sticks of calcium. Determinations of calcium in two alloys containing a high percentage of this metal showed the errors to be within the limits mentioned.

Attempts were made to reduce the compounds MoO_3, MoS_2, WO_3, SiO_2, Fe_3O_4, Mn_3O_4, TiO_2 and mixtures of SiO_2 with MnO_2, of TiO_2 with MnO_2 and of TiO_2 with Fe_3O_4. The alloys employed in these reductions were Nos. 8, 11, 14 and 15.

The first experiment was an attempt to reduce MoO_3 by alloy No. 8. The oxide was the usual fine powder of commerce and the alloy a mixture of all sizes that would pass a twenty-mesh sieve. The reaction was very rapid, and was accompanied by the projection of melted material, flame and much smoke. At the end of the reaction the crucible was nearly empty, and contained no metal. Thinking that the sudden expansion of air contained between the particles of the charge might be responsible for much of the loss of material, the experiment was repeated in a vacuum cylinder constructed from a piece of eight-inch steam pipe. Less material was projected than before, but the loss was still great. Forty grams of well-fused molybdenum were obtained.

Several other experiments were tried in vacuo. SiO_2 was only partially reduced, yielding a brown product resembling silicon monoxide in appearance. A mixture of MnO_2 and SiO_2, reduced by alloy No. 11 (AlCaMg) gave an excellent ingot of silicon-manganese, well separated from the slag. The yield was only 22 per cent. of the theoretical, probably due to the large amount of material projected from the crucible. In order to reduce the velocity of reaction, pulverized fluor spar and lime were added to several charges, with a slight improvement in the yield of metal. After eight trials in the vacuum cylinder, experiments under atmospheric pressure were resumed.

Reduction of a mixture of MnO_2 and TiO_2 by No. 15 ($AlGa_2Mg_2$), in pieces one-fourth to one-eighth of an inch in length, was violent, with much flame and smoke, and the projection of some slag. Only a few globules of metal were obtained. Other reactions were tried with quite similar results. The only alloy that gave quiet reactions was No. 14 ($Al_4CaMgSi_3$). This acted much like aluminum itself.

To control the violence of the reaction the charges were fired in a closed steel cylinder designed to withstand a pressure of 10,000 pounds per square inch. A lining of magnesia was placed within the cylinder and the remaining space was completely filled with the charge which was ignited by means of an aluminum fuse wire. With this apparatus several difficult reductions were carried out. Mixtures of the alloys with molybdenite in theoretical proportions failed to react, but on adding a large excess of the alloy and enough calcium peroxide to oxidize it, an ingot of well fused metal was obtained.

The most difficult reduction carried out in the closed steel cylinder was that of rutile. By means of the calcium peroxide method[3] mentioned above, a single button weighing fifteen grams and several smaller globules of metal were secured. The metal obtained was hard but not sufficiently so to scratch glass. It was not in the least malleable and was broken by severe pounding with a hammer. In appearance it resembled freshly broken Goldschmidt manganese.

Several attempts to produce fused tungsten by the reduction of WO_3 with different alloys failed. Since the heat of reaction was not sufficient to produce this result, an attempt was made to pre-heat the charge in order to secure the desired temperature. For this purpose the charge containing WO_3 and the alloy in the necessary proportions was placed in a magnesia crucible four inches in diameter and six inches in depth. This crucible containing the charge was imbedded in a layer of thermit ($2\,Al + Fe_2O_3$) three inches in thickness which in turn was surrounded by a layer of magnesia one inch in thickness. The magnesia and the Fe_2O_3 were dried at 400°C in order to remove moisture. The thermit was ignited by a magnesium ribbon, and when the heat produced by this reaction was sufficiently great it ignited the charge in the magnesia crucible. The resulting temperature within the magnesia crucible was much higher, but was not sufficiently high to produce fused metal. An attempt to increase

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[3] Bull. of Univ. of Wisconsin, No. 145, page 313.

the temperature produced in this reaction by pre-heating the thermit failed to produce the desired temperature.

The following table gives a list of the more difficult reductions carried out by means of these alloys:

Compound.	Reducer.	Result.	Yield.
MnO_3	15	58 grams fused metal............	46.7
MnO_3	15	58 grams fused metal............	47.2
MoS_2	15	31 grams fused metal............	32.0
WO_3	11	Finely divided metal	....
SiO_2	11	Amorphous silicon	....
Mn_2O_3	14	59 grams fused metal............	47.2
Mn_2O_3	36	31 grams fused metal............	21.
Fe_3O_4......	36	143 grams fused metal...........	78.1
Fe_3O_4......	36	143 grams fused metal...........	77.
TiO_2........	32	50 grams fused metal............	....

The cause of the violent nature of the reactions with these alloys, whether carried out in vacuo or in air, whether the reducing agents were coarsely or finely pulverized, was puzzling. The following explanation is offered: When all the products of a reaction are non-volatile, and when no gases are present, it would seem that mere rapidity of reaction would not account for the ejection of one-half the charge from the crucible. If the cause does not lie in the volatile nature of the products formed it must be sought in the original charge. This excessive violence is due to the presence of metallic calcium. This metal boils between 1290°–1300° [4] and the expulsion of the material is no doubt due to this particular physical characteristic of the metal in question.

An attempt was made to avoid the vaporization of calcium. Since calcium silicide is a product formed at high temperatures it should be stable at the temperatures reached in these reductions. Therefore, it should follow that if the calcium and silicon are added in the proportion to form calcium silicide, none of the calcium should be volatilized until the silicide is decomposed through the agency of oxidation. When the silicide is thus decomposed it is evident that the calcium would be oxidized to lime without vaporization.

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[4] Trans. A. E. S., Vol. XIII, p. 149.

Two alloys containing calcium and silicon in the proportions to form calcium silicide were made to test this theory. When Fe_3O_4 is reduced with either of these alloys the reaction is gentle. No material is projected from the crucible. The presence of the silicon in these alloys, whether combined or free, would greatly reduce the temperature obtained. It is possible, however, that the decrease in violence is due to a reduction of temperature, yet the fact that the temperature is high enough to make the iron sufficiently fluid shows that there is little, if any, reduction of temperature.

Conclusions.

(1) The alloys of this series containing up to seventy-five per cent calcium can be prepared without much difficulty.
(2) Alloys containing twenty-five per cent or more of calcium or magnesium can be pulverized.
(3) Violence of reaction is due to the calcium content of these alloys.

CALCIUM–ZINC ALLOYS

A study of the alloys of calcium and zinc was next undertaken. A review of the literature shows that several members of this series have been made. The general method employed was that used by Caron[5] and Tarugi.[6] This consisted in heating calcium chloride with metallic sodium in the presence of metallic zinc. Donski[7] has succeeded in making several of the alloys of this series by heating the two metals together in evacuated tubes or in neutral gases.

The alloys of this investigation were made by adding the metallic calcium to a bath of molten zinc, which has been heated in a graphite crucible. Several attempts to add metallic calcium to the molten zinc resulted in the loss of a considerable portion of the charge, owing to the violence of the resulting reaction. This loss of material was avoided by adding the calcium to the zinc as soon as the latter was melted. With this method of work the

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[5] Liebig's Ann. Vol. 115, 355.

[6] Bull. Soc. Chimie. Vol. 24, 250.

[7] Zeit. f. Anorg. Chem. Vol. 57, 186.

two metals were heated in contact so that the alloy could be formed at a lower temperature and thus the violence of the reaction could be greatly reduced.

PROPERTIES

The hardness of this series of alloys increased up to 6 per cent calcium. Beyond this percentage the alloys increased in brittleness to such an extent that several fell to pieces before they were removed from the mould. Several attempts to form solid bars of alloys containing 12 per cent to 14 per cent failed. Beyond this point, although the alloys were brittle, they could be formed into bars without much trouble.

Several of this series of alloys were stable in air. Those alloys which contained less than 10 per cent calcium did not oxidize to any appreciable extent upon being exposed to the atmosphere of the laboratory for two weeks. Beyond this point the rate of oxidation increased to such an extent that the alloy containing 22 per cent calcium disintegrated in a few days. Between 22 and 35 per cent calcium the stability of the alloys increased so that those containing from 28 to 35 per cent were equally stable with those containing from 12 to 14. Beyond 40 per cent the disintegration was quite rapid.

The color and fracture of the alloys belonging to this series changed gradually from those characteristic of zinc to those characteristic of calcium. The combinations containing the smaller percentages of calcium lost the characteristic crystalline structure of zinc and assumed a very smooth even structure instead. No trace of the typical zinc crystallization was in evidence. A change of color accompanied this change in crystalline formation. The alloys containing from 3 to 8 per cent calcium were silver-white metals which did not tarnish even after six months' exposure to the atmosphere of the laboratory. Beyond 8 per cent the alloys slowly assumed a yellowish tinge which changed into black as the higher percentages of calcium were reached.

USE IN GALVANIZING PROCESS

Since the alloys containing the lower percentages of calcium possessed a silver-white color which is not modified on exposure to air it was thought that these might be used in the galvanizing process.

A series of tests was made using alloys containing 0.5, 1.0, 1.25, 1.5, 2.0, 3.4, 5.0 percentages of calcium. The method employed was as follows: Pieces of sheet iron were cleaned and dipped in a bath of molten zinc, protected from the air by a mixture of zinc chloride and ammonium chloride. These pieces were immersed for different periods and the physical characteristic of the coating noted. These were used as standards.

Each of the above series of alloys was used in place of the zinc. A difficulty arose from the fact that the calcium of the alloy gradually replaced the zinc of the zinc chloride forming calcium chloride which was pasty at the temperature of the bath. This interfered with the mechanical part of the process to such an extent that the covering had to be dispensed with. No suitable covering was found.

Results

The coatings made by the alloys may be characterized as follows:—

(1) No traces of zinc crystallization appeared.

(2) The alloys produced a white silvery surface which remained unchanged upon exposure to air for several months.

(3) The coatings produced by the alloys were not so smooth and uniform as those produced by zinc alone.

(4) The coatings were equally adhesive with those of zinc when the deposit is in a very thin layer. When the coating is heavy the alloy becomes brittle and is easily removed by bending the plate.

(5) The brittleness of the coating is dependent upon the calcium content of the alloy.

Constitution of Alloys

Since both the calcium-aluminum and the calcium-zinc series of alloys presented marked variations in the physical and chemical behavior of its individual members, it was deemed advisable to investigate the constitution of the alloys composing these series.

Modern research has shown that combinations of metals may take the form of simple mixtures, solid solutions or chemical compounds. In case of the two former it must be expected that the physical properties of the alloy in question must result from a blending of the properties of the original metals. With the compounds, on the other hand, the union of these metals in atomic proportions may result in a substance with properties entirely at variance with those of the original constituents.

The marked variations, above mentioned, in the calcium-aluminum and the calcium-zinc series must be due, therefore, to the formation of combinations of definite proportions.

Several methods are adapted to the study of the nature and constitution of alloys. Roberts-Austen [8] has classified them under the two following heads:—

(1) The chemical grouping of the metals in a solid alloy.
(2 The separation of the constituents during solidification.

The first group includes the following special methods:—

(a) The specific gravity of alloys.
(b) The electrical resistance of alloys.
(c) The diffusion of metals in alloys.
(d) Electrolytic conduction.
(e) The heat of combination of metals to form alloys.
(f) The electromotive force of alloys.
(g) Microscopic examination of alloys.

The second group deals with those methods involving a study of the separation of the constituents of an alloy on solidification and includes:—

(a) Measurement of the fall of temperature during solidification by means of a pyrometer.
(b) Mechanical separation of constituents of an alloy by heating to definite temperatures and pressing out liquid portion.

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[8] Alloys. Law. Page 39.

METHODS OF INVESTIGATION

In this particular investigation an attempt was made to locate the compounds formed by the following methods:—

(1) Measurements of single potentials in non-aqueous solutions.

(2) Measurement of electrical conductivity.

(3) Microscopic examination.

The measurement of single potential was introduced by Laurie[9] and has given valuable results. Puschin[10] has employed this method with a number of alloys and finds that the compounds located in this way agree exactly with the compounds located by means of cooling curves. Laurie and Puschin have found that a sharp depression in a single potential curve indicates the presence of a compound at that point.

These conclusions are in agreement with Toutourine[11] whose work goes to prove that:—

(a) The single potential is a function of the composition of an alloy.

(b) Depressions in curve indicate compounds.

(c) The initial and terminal point of each line is determined by the single potential of the phases forming the series.

(d) Solid solutions do not affect the series.

The study of the electrical conductivity of alloys began with the work of Matthiessen in 1860. He showed that the conductivity curve was similar to the cooling curve of the same alloy. Le Chatelier[12] and Rayleigh[13] have shown independently that the temperature factor for the conductivity of alloys is entirely independent of the temperature factor of pure metals. Kurnakow and Zemczuznyj[14] have shown that solid solutions lower the conductivity and that the curve formed by such solutions is continuous and has a minimum value. Guertler[15] has shown that

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[9] Chem. Soc. Journal. Vol. 53 (1888) 105.
[10] Zeit. f. Anorg. Chem. Vol. 56, 1.
[11] Soc. Chimique France. 1908.
[12] Compt. Rendu. Vol. III, 454. Vol. 119-126, 1709.
[13] Nature, Vol. 54-154.
[14] Ber. St. Petersb. Polyt. Inst. Vol. 6-559.
[15] Zeit. f. Anorg. Chem. Vol. 52-413.

it is possible to establish the exact relationship between the conductivity curve and the compounds formed in a series of alloys. He shows that Liebenow's[16] conclusion concerning the locations of compounds by means of sharp upward projections in the conductivity curve is not entirely true, for in many cases a compound occurs when there is but a slight elevation or perhaps a slight depression. Guertler concludes that the absence of an elevation does not necessarily indicate the absence of a compound but the presence of such an elevation is absolute evidence of the presence of a compound.

The evidence afforded by the microscope in the study of the composition of metals and alloys has been of much value. The systematic study of metals as revealed by the microscope was first undertaken by Dr. Sorby[17] of Sheffield, who was studying the structure of meteoric irons. In 1865 his paper entitled *On the Microscopic Structure of Meteorites and Meteoric Iron* was published by the Royal Society. Nothing further appears to have been done until Professor Martens[18] published in 1878 the results of the researches which he carried on independently. The importance of the study of the micro-structure of metals and alloys was soon recognized, and the work of Dr. Sorby and Professor Martens has been taken up and greatly extended in recent years.

The preparation of the alloys for single potential and conductivity measurement in this investigation was as follows: The calcium was added to the fused metal with which it was to be alloyed as soon as the latter was liquid. This allowed the two metals to be heated in contact so that the resulting alloy formed at the lowest possible temperature. After the required amount of calcium had been added the molten metal was stirred vigorously so as to render the product as uniform as possible. The molten metal was poured as quickly as possible into an iron mould which had been heated to a temperature just below the freezing point of the alloy. This produced a chilling effect sufficiently great to prevent the segregation of the metals forming the alloy.

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[16] Zeit. f. Anorg. Chemie. Vol. 60-209.
[17] Br. Assoc. Reports. Part II, 1864-189.
[18] Engineering, Vol. 28-88.

The amount of metal poured in each case was sufficient to fill the entire mould as well as the entrance chamber above the mould. This enabled the alloy to pass from the temperature of the molten metal to a point considerably below its solidification temperature in the absence of air.

During the progress of these experiments it was found advantageous to hold the temperature of the alloy constant for some time after pouring. The mould was then cooled slowly.

Fused calcium chloride was used as a covering for these alloys during the process of melting.

SINGLE POTENTIAL MEASUREMENT

Several difficulties were encountered in the attempt to measure the single potential of these combinations. It was necessary to use a non-aqueous electrolyte on account of the calcium content of these alloys. After considerable experimental work with various non-aqueous electrolytes a solution of calcium chloride in ethyl alcohol was selected for this work.

The ethyl alcohol was allowed to stand over freshly ignited lime for five days. This mixture was shaken from time to time. The alcohol was distilled from the lime in a moisture free apparatus, after which it was treated with a fresh supply of lime and allowed to stand for some time. This process was repeated twice. The alcohol was then treated with anhydrous copper sulphate and allowed to stand for five days, during which time the mixture was shaken from time to time. The alcohol was distilled off, using the same precautions as before. After two treatments with anhydrous copper sulphate the material showed no evidence of the presence of water when placed upon the anhydrous sulphate, even after an interval of ten days.

In each distillation the first twenty-five cubic centimeters of the distillate were rejected.

A twelfth-normal solution of calcium chloride was prepared. Kahlbaum's anhydrous calcium chloride was used. This had been heated for eighteen hours at 120°C. A fine white precipitate remained in suspension in this solution. This stock solution was kept in a glass-stoppered bottle.

Considerable difficulty was encountered in an attempt to prevent the diffusion of the aqueous solution of the normal calomel electrode and the non-aqueous solution in which the single potential of the alloy was to be measured. The ordinary connection of the normal calomel electrode was worthless. A modification of this worked very well.

Pieces of glass tubing were heated and pulled so as to form a narrow constriction in the tube. These were packed on either side with finely macerated filter paper moistened with water. The constriction served to hold the plugs in place. These tubes were dried in an oven and the macerated filter paper was pressed firmly together. The filter paper plugs were three-quarters of an inch in length. These glass tubes containing the plugs were sealed to the tubes leading to the normal calomel electrode and to the half cells in which the single potentials of the alloys were to be measured. These tubes served as the connections with the intermediate vessel. That the diffusion was reduced to a minimum is shown by the fact that when the electrolyte was placed in the half cell and the alloy placed in contact with the solution, it was necessary to add more electrolyte in order to make a reading only after the lapse of several hours.

The half cells were dried for several hours at 115°C and allowed to cool in a desiccator containing sticks of sodium hydroxide. The electrolyte was poured in and the alloy placed in contact with the solution. The half cell was stoppered with a rubber stopper. Rubber stoppers were used in all cases. The half cells were kept in desiccators when not being actually measured.

The alloy whose single potential was to be measured, was thoroughly cleaned and its surface polished so as to remove the scratches visible to the naked eye. Electrical contact with the alloy was made by means of a fine copper wire. The junction of the wire and the alloy and that portion of the wire within the half cell was covered with a heavy layer of wax to prevent the formation of a couple in case the electrolyte should come in contact with the wire and the alloy.

The intermediate vessel was closed with a two-hole rubber stopper so that the arms from the normal calomel electrode and the half cell could be inserted without loss of time when a single potential measurement was to be made. When not in use, this vessel was kept closely stoppered so as to prevent the entrance of moisture. An alcoholic solution of calcium chloride was used as the intermediate solution between the calomel electrode and the half cell. After each measurement the contents of the intermediate vessel were thrown away and a new supply used for the next measurement. This arrangement reduced the amount of moisture present to a minimum.

The single potentials were measured by means of a direct reading Leeds and Northrup potentiometer. This enabled individual readings to be made in less than one minute. A D'Arsonval galvanometer was used as a zero instrument.

The electromotive force varied considerably at first. Measurements were repeated every thirty minutes at the beginning of the work. As the amount of variation decreased the interval between the readings was increased. In some cases forty-eight hours were required to obtain constant readings.

Measurements were made at room temperatures.

A series of zinc-calcium and aluminum-calcium alloys were made. These were analyzed and the single potential curve plotted on the basis of analyzed percentages. Table *I* contains data for the calcium-zinc series and Table *II* for the calcium-aluminum series.

TABLE I.

E. M. F.	Time in Hours.	% Calcium.	Single Potential.
.9502	10	.7	.3972
.9421	10	1.3	.3821
.8930	10	1.7	.3330
.9000	9	2.0	.3400
.9060	9	2.8	.3460
.8580	8	5.6	.2980
.9650	6	6.0	.4050
.9730	3	8.2	.4150
.9675	9	9.6	.4075
.9641	7	11.9	.4041
1.0350	4	14.1	.4750
1.0430	9	15.3	.4830
1.0530	8	16.1	.4930
1.0580	10	18.2	.4980
1.0640	10	24.2	.5040
1.0510	10	26.2	.4910
1.0580	10	27.3	.4980
1.1608	19	28.9	.6008
1.1840	4	31.5	.6240
1.0580	14	32.0	.4980
1.2820	40	32.3	.7220
1.2720	29	33.2	.7120
1.2940	24	40.3	.7340
1.3480	14	56.3	.7880
1.3700	24	66.5	.8100
1.3790	12	70.6	.8190
1.5050	15	73.2	.9450

TABLE II.

E. M. F.	Time in Hours.	% Calcium	Single Potential.
.6550	24	Al.	.0950
.7203	36	3.07	.1603
.7300	48	6.0	.1700
.9108	24	11.5	.3508
.9300	28	12.7	.3700
.9480	22	19.4	.3880
.0)	4	23.9	.4690
1. 50	8	25.0	.4650
1 320	4	26.9	.4720
1.0450	9	27.0	.4850
1.0270	8	28.5	.4670
1.0400	7	31.2	.4800
1.0410	4	32.8	.4810
1.4720	10	34.3	.9120
1.4700	12	37.7	.9100
1.4810	16	50.3	.9210
1.5280	20	60.0	.9280
1.5220	21	70.5	.9620
1.5410	12	75.0	.9810
1 5400	21	78.8	.9800
.6240	15	80.2	1.0640

CONDUCTIVITY MEASUREMENTS

The method employed in making the conductivity measurements was as follows: Each bar of the individual members of the series was supported upon two knife edges which were connected to a direct reading Leeds and Northrup potentiometer. In this way the same length of bar was measured in each case. Several measurements of the diameter of each bar were made and the average was used in the computations. As there was some variation in the final conductivity values of the bars of each of the different percentages the average value was taken. A direct current of from ten to fifty amperes was passed through the bars. The ammeter and potentiometer readings were taken simultaneously. Contact with the bars was made by means of two heavy brass springs which held the bars firmly upon the knife edges.

Measurements were made at room temperatures.

Table *III* gives the data obtained in the measurement of the conductivity of the alloys of the calcium-aluminum series.

TABLE III.

% Calcium.	Diameter in Cm.	Amperes.	Milli-volts.	Microhms per Cm^3.	Specific conductivity.
3.07	.819	37.50	.8	15.8	63291
6.00	.822	32.75	.9	20.2	49505
....	.812	34.75	1.25	27.1	36900
12.5	.822	28.75	1.50	38.4	26042
19.4	.829	29.25	2.0	49.5	20202
23.9	.835	32.25	4.5	99.5	10050
25.0	.836	28.25	4.5	113.4	8848
28.5	.842	10.75	1.8	117.0	8547
31.3	.855	11.50	2.0	118.0	8474
32.8	.887	26.00	4.6	112.0	8928
37.7	.860	19.00	3.1	110.0	9091
50.0	.862	20.0	4.2	141.0	7093
60.0	.847	28.50	7.0	171.0	5848
75.0	.850	6.25	1.7	189.0	5298
78.8	.837	9.5	1.5	112.0	8928

The length of bar measured in each case was 2.56 centimeters.

Five breaks occur in the single potential curve for the calcium-zinc series. These appear at the following percentages of calcium: 5.6 per cent, between 11.9 and 14 per cent, 29 per cent, between 32.5 and 33.5 per cent, and at 71 per cent. These breaks would correspond to combinations of the following formulae: $CaZn_{10}$, $CaZn_4$, Ca_2Zn_3, Ca_2Znx and Ca_4Zn.

A peculiarity of this series was observed during the measurements of single potentials of the alloys containing between 29 and 34 per cent calcium. Several combinations corresponding in composition to these alloys were made. Their single potentials varied, some having a value of 0.49 volts, while others had a value of 0.61 volts. The calicum content of these alloys differed in some cases by less than 0.5 per cent. This would tend to show that there were two combinations present. Tamman and Donski[19] have located two polymorphic forms between these two limits.

In the single potential curve for the calcium-aluminum series a marked increase in value occurs between 33 and 34 per cent

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[19] Zeit. f. Anorg. Chem . Vol. 57–191.

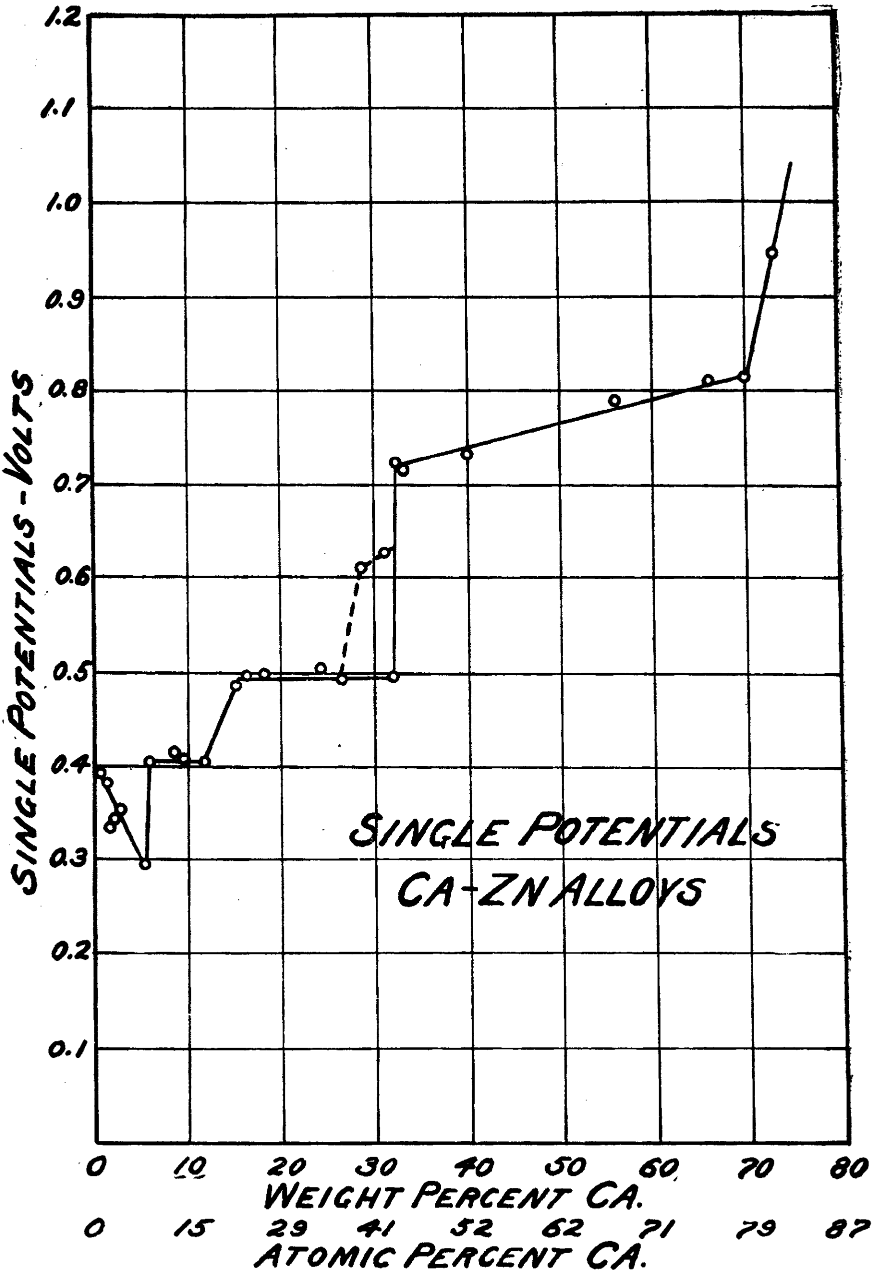
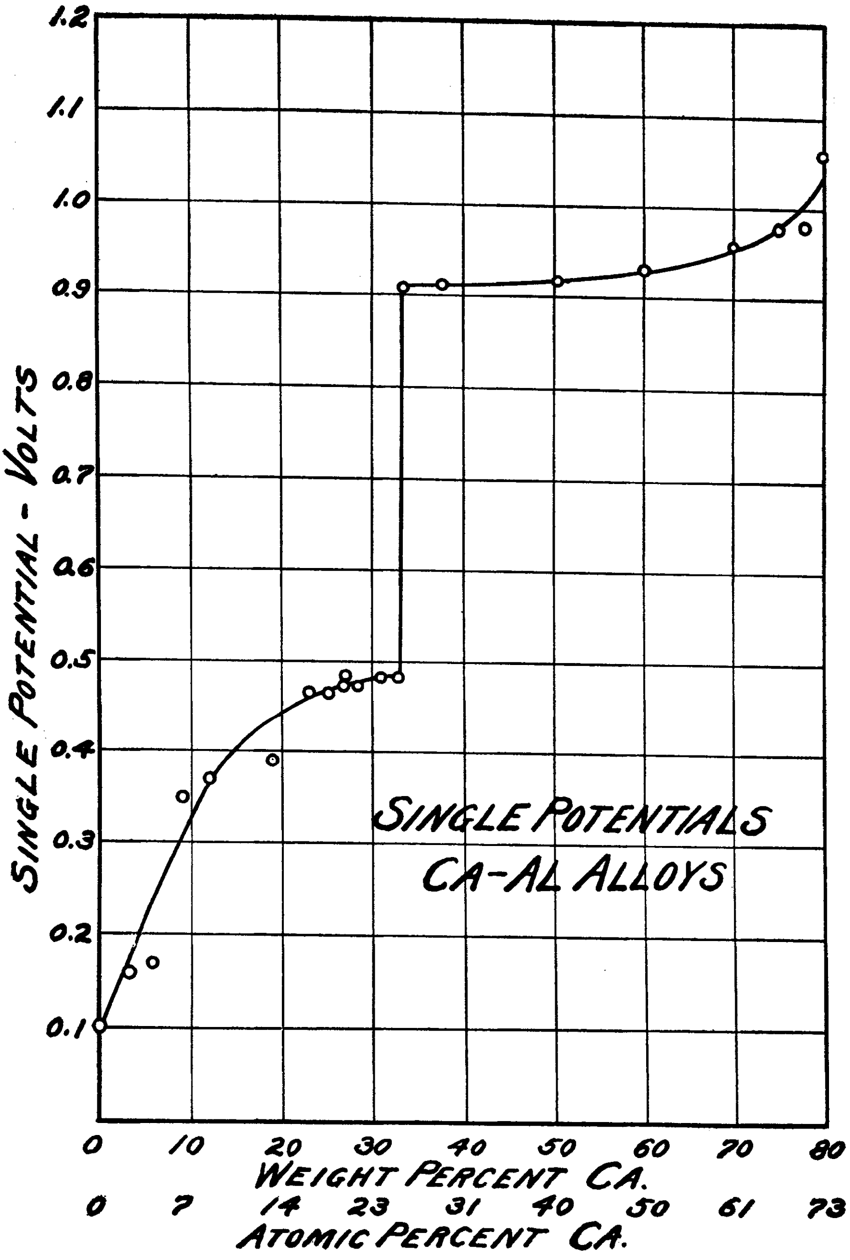

SINGLE POTENTIALS - VOLTS
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
SINGLE POTENTIALS
CA-ZN ALLOYS
0 10 20 30 40 50 60 70 80
WEIGHT PERCENT CA.
0 15 29 41 52 62 71 79 87
ATOMIC PERCENT CA.

FIG. 1.



Single Potential - Volts
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Single Potentials
Ca-Al Alloys
0
10
20
30
40
50
60
70
80
Weight Percent Ca.
0
7
14
23
31
40
50
61
73
Atomic Percent Ca.

Fig. 2.

calcium. Several unsuccessful attempts were made to get an alloy whose calcium content would lie between these limits. This would define the composition of the alloy more exactly. This particular percentage of calcium corresponds to the compound Al_3Ca, which is in agreement with the work of Donski.[20]

The conductivity curve for this series shows a maximum value between 32.8 and 37.7 per cent calcium, which indicates the presence of the compound Al_3Ca.

MICROSCOPIC STUDY

The preparation of these alloys for micrographic study gave some trouble. In the calcium-zinc series the alloys over a considerable range are soft and brittle. After some experimental work it was observed that if a small quantity of rouge moistened with paraffin was rubbed on the surface of canvas, this would serve very well for the rougher polishing. For the final preparation of the specimen, a piece of very soft cloth was used. In many cases this produced a surface which revealed the structure without etching. Whenever an etching agent was necessary very dilute hydrochloric or nitric acid was used. In some cases oxidation tinting served very well.

The microscopic study of the structure of the calcium-aluminum series furnished evidence in agreement with the facts observed in the study of the conductivity and the single potentials. Alloys containing 28.5 and 32.8 per cent calcium presented a mass of polygonal crystals interspersed with a decreasing mass of eutectic. Beyond 34.7 per cent calcium the microscope revealed the same ground mass in which a new form of eutectic appeared. All these alloys were brittle and as a result it was impossible to secure suitable micrographs.

In the study of the zinc-calcium series the microscope revealed the presence of definite compounds. Figure 4 shows the homogeneous structure of the compound $CaZn_{10}$. Figure 5 shows the ground mass of Figure 4 in which an increased amount of eutectic has crystallized. Figure 6 shows a new

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[20] Zeit. f. Anorg. Chem. Vol. 57–201.

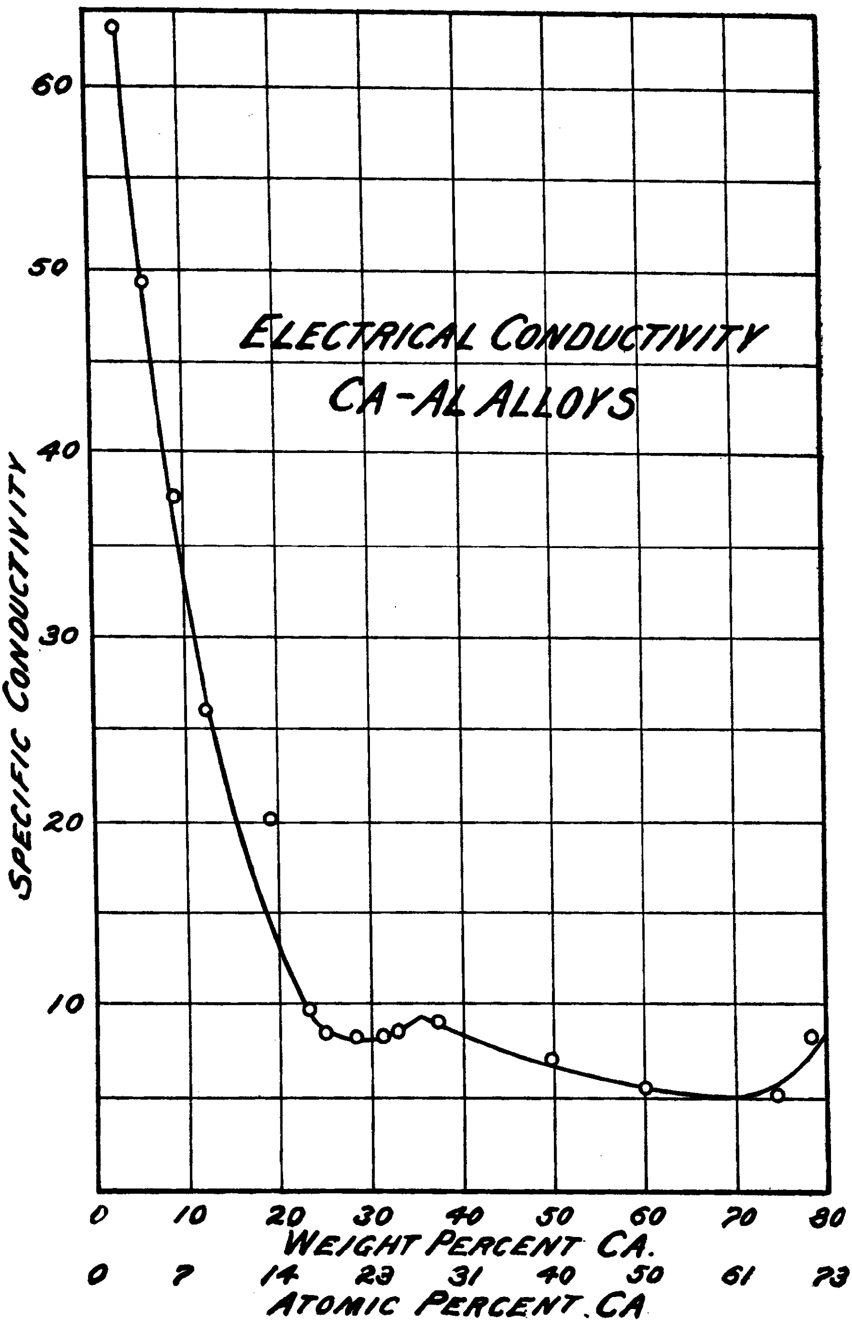
ELECTRICAL CONDUCTIVITY
CA-AL ALLOYS
SPECIFIC CONDUCTIVITY
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
WEIGHT PERCENT CA.
0
7
14
23
31
40
50
61
73
ATOMIC PERCENT. CA

FIG. 3.

crystalline structure which is distinctly different from Figure 7. Figure 8 and Figure 9 present the homogeneous structure of the alloys represented by the formulae $CaZn_3$ and Ca_2Znx.

Micrographs were made at a uniform magnification.

CONCLUSIONS

(1) The breaks in the single potential and conductivity curves for the calcium-aluminum series correspond to the composition of the compound Al_3Ca.

(2) The breaks in single potential curve for the calcium-zinc series correspond to the compounds $CaZn_{10}$, $CaZn_4$, Ca_2Zn_3, Ca_4Zn.

(3) The study of the single potentials, conductivity and microscopic structure of alloys are valuable aids in determining the nature and constitution of the series.

In conclusion, the author wishes to express his gratitude for the timely suggestions and advice received from Professor C. F. Burgess and Professor O. P. Watts during the progress of this investigation.

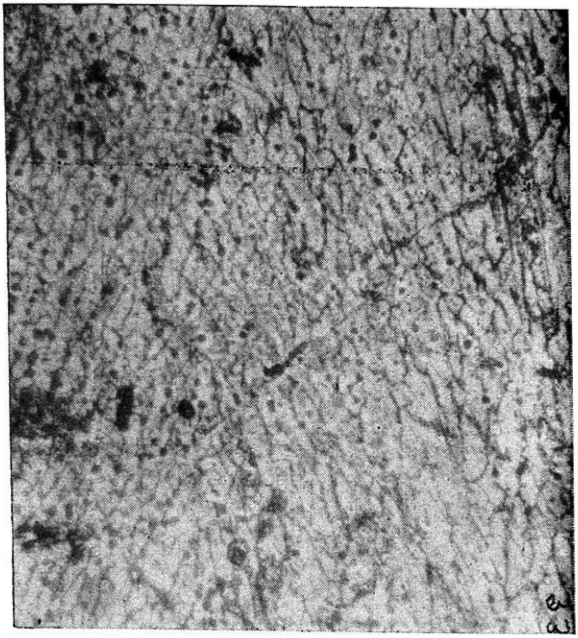

FIG. 5.

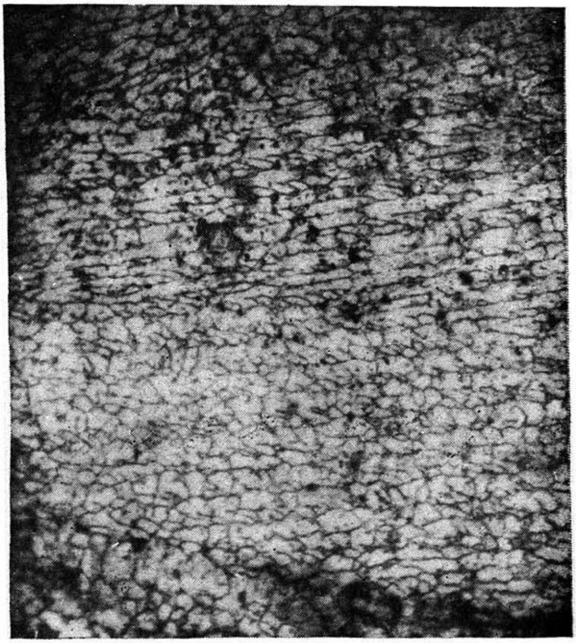

FIG. 4.

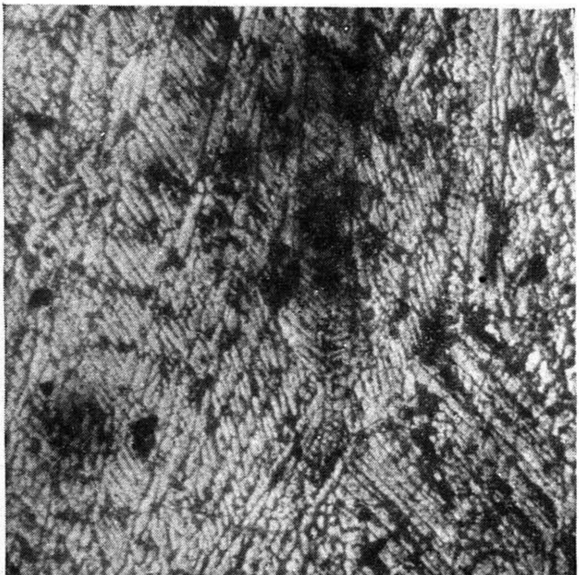

FIG. 6.

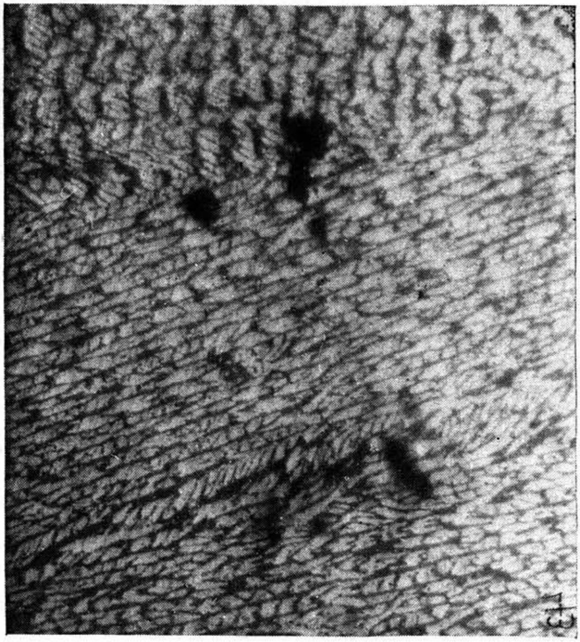

FIG. 7.

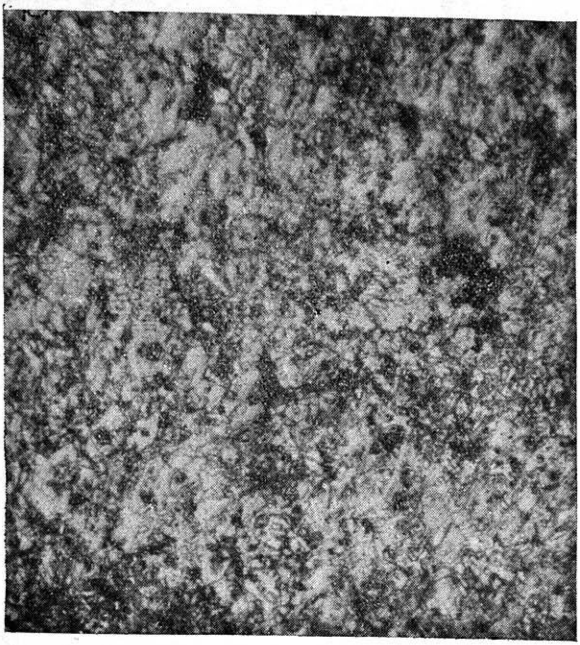

FIG. 9.

FIG. 8.

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8

MALLEABLE CAST IRON.

James Aston,

Iron owes much of its supremacy as a metallurgical product to its relatively low cost, due largely to the abundance and richness of its ores, to the low cost of mining, and to the readiness with which these ores are reduced to the metallic state. Aside from this consideration, however, it is undoubtedly true that the great commercial utility of iron is due to the activity with which it alloys with other elements, to its adaptability to various methods of working and to the susceptibility of the alloys to heat influences.

Out of an approximate annual production for the United States of thirty millions tons, of finished iron and steel products the greatest part, say sixty per cent, is formed by rolling or forging. Rolling is particularly suited to the production of large outputs of simple standard shapes, such as rails, structural sections, bars, rods, etc. Many shapes are, however, too intricate to be produced by rolling or forging, and are cast to form by pouring molten metal into a mold formed by a suitable pattern. The foundry industry is an important division of iron and steel metallurgy, producing roughly forty per cent of the iron and steel products. Castings may be of three kinds—cast iron, steel, and malleable cast iron. Each has its particular sphere of usefulness, dependent upon the nature of the service and the fitness of the material for this service, and also upon the cost of the product.

Leaving out of consideration any special alloy additions, commercial iron and steel consists of iron in association with carbon, silicon, sulphur, phosphorus and manganese. The properties of the material are dependent not alone upon the quantities of these elements present, but also upon the manner in which they are associated; an association which is manifested in the structure. Ordinary cast iron is the most impure of the three forms. The general composition is as follows:

Carbon—3½ to 4¼ per cent.
Silicon—1 to 3 per cent.
Sulphur—0.05 to 0.20 per cent.
Phosphorus—0.20 to 1 per cent.
Manganese—0.50 to 1 per cent.

By suitable regulating of chemical composition and rate of cooling, it may range in fracture from gray to white, and in hardness from a material which can be readily machined or filed, to a product which is glass hard. Being a result of simple melting of pig iron and cast scrap, without material chemical conversion, it is of comparatively low cost. Add to this the fact that its high fluidity and "life" enable it to run into thin sections or intricate forms, and we have the principal reasons for its favor. The usual requirement is for a material soft enough to be machined; strength is a secondary consideration. Cast iron has, however, an extreme resistance to compression, and is thus well adapted to machine frames, and the like; if strength in tension or resistance to shock are wanted, they are obtained by massiveness of structure.

Where high strength and ductility are required, the steel casting is most suited. The general chemical composition will be about as follows:

Carbon—0.20 to 0.80 per cent.
Silicon—about 0.20 per cent.
Sulphur—0.02 to 0.08 per cent.
Phosphorus—0.03 to 0.10 per cent.
Manganese—0.50 to 0.75 per cent.

The requisite strength is obtained by suitable chemical control, together with judicious heat treatment. Increase of carbon results in increase of strength at a sacrifice of ductility. The other elements, also, phosphorus in particular, have their influence. Steel castings may be the result of various methods of working; crucible, Bessemer or open hearth, either acid or basic. Because of high cost of raw materials, or the necessity of skillful and costly manipulation in the conversion of the impure iron into the finished steel, the product is necessarily of considerably higher cost than cast iron. Again, its low fluidity and "life," its high temperature, and high shrinkage, are in many cases serious disadvantages. Steel castings, therefore, are generally comparatively bulky in section, and find their greatest application where the added strength is enough to offset the increased cost and other disadvantages.

Malleable cast iron occupies a position between ordinary cast iron and cast steel. It has higher tensile strength than cast iron, but is not so strong as steel. Again, it is fairly ductile and malleable, and may be bent or twisted or hammered to a certain extent without danger of breaking. The great advantage, however, is that it is originally cast of white cast iron, with all of the advantages of fluidity and life to enable it to run into small thin sections and intricate shapes, and low cost of initial production. The ductility and malleability are the result of subsequent treatment.

Although it was predicted that the development in the manufacture of steel castings and the possibility of making small castings of this material, would make serious inroads upon the malleable casting industry, this prediction has been fulfilled only in special cases. The industry has experienced a growth entirely comparable with the other divisions of foundry practice, and today, perhaps a million tons annually represents the output of this country. Malleable castings are largely used in railroad equipment, agricultural implements, pipe fittings, stoves, etc.; in fact, the great outlet is in lines requiring large numbers of pieces of comparatively small size from the same pattern, and where low cost and a fair ductility are factors.

It is not the purpose of this article to go into details of the manufacture of malleable castings; its object is rather to point out the underlying reasons for the properties which this product possesses; but a few words regarding the process will not be amiss. Those who are interested in the details of practice are referred to the new books of Dr. Moldenke, perhaps the foremost authority in this country.

The pig iron used as a raw material is usually classed as malleable Bessemer; that is, it conforms to the usual requirements of a Bessemer pig, except that the phosphorus exceeds the steel making limit of 0.10 per cent. Ordinarily it is the product of a coke blast furnace, but for the highest grades of product, charcoal pig iron is used. The general analysis will be as follows:

Carbon—about 4 per cent.
Silicon—0.75 to 2.0 per cent.
Sulphur—about 0.05 per cent.
Phosphorus—not over 0.225 per cent.
Manganese—0.50 to 0.75 per cent.

With this is mixed the proper amount of steel or malleable scrap to bring the castings of an appropriate analysis of

Carbon—about 3 per cent.
Silicon—0.50 to 1.0 per cent.
Sulphur—below 0.08 per cent.
Phosphorus—below 0.225 per cent.
Manganese—0.25 to 0.50 per cent.

The amount of silicon allowable will depend upon the size of the casting, and to a certain extent uon the amounts of sulphur and manganese present; these last named elements are, however, preferably kept to a minimum. Phosphorus is held to as low an amount as possible (because of its tendency to promote brittleness), and yet have sufficient fluidity in the molten metal.

In this country the melting is usually done in a cupola furnace for the lower grades of work, or in an air furnace (reverberatory) for the greater part of the output. Recently, the open hearth furnace, similar to that used in steel making, has come into a little favor. The air furnace owes its advantages to the isolation of the solid fuel from the charge, the possibility of regulation of the chemical action of the flame, and to a consequent better control and higher quality of material produced. The furnace action should ideally be one of melting only; actually there is some chemical change, principally in an oxidation of silicon and manganese, and a slight gain in sulphur.

The castings as taken from the sand are hard, white and brittle, and entirely unsuited for their intended service. They are inspected and cleaned of all adhering sand, mainly by means of a tumbling barrel; then trimmed of sprues by chipping, and sorted, after which they are ready for annealing, the distinguishing feature in the malleable casting process. For this operation the castings are packed in annealing boxes, or pots, which are open frames, usually rectangular in shape, and of somewhat varying sizes in different plants. An average size is 30 inches by 16 inches and about 16 inches deep with an initial thickness of three-fourths to one inch. They are usually cast largely of malleable scrap. The pots are stacked three or four high on a bottom plate or stool.

Into these boxes, the castings are carefully packed in mill scale, iron ore, sand or a mixture of these substances. The two first named are oxidizing agents for the carbon, while sand, or the like, is inert. The object is usually to get an oxidizing medium not too active; a refreshing of the spent or used packing with new scale usually suffices. The essential principle in the packing is to see that all castings are well surrounded with packing material in order to prevent passage of air and have uniform action, and also to prevent settling and consequent warping of the castings when heated. The stack of pots is finally covered and luted with clay and makes, therefore, a fairly airtight container for the castings.

A number of these stacks of pots (20 to 40) are run into a large brick annealing oven, and the brick doors of the oven are closed. The ovens may be gas, oil or coal fired; usually the first or last named, since the oil flame is too localized in its action, and results in uneven heating throughout the oven. The annealing operation requires about one to two days to bring the temperature up to that required, two to three days at this temperature and a day or two for cooling down, making a total of five to six days for the complete cycle. The temperature varies somewhat with the character of the casting and the melting stock used, as well as with the kind of melting furnace, but is generally between 1300 and 1650° F. (700 to 900° C.). The pots are withdrawn from the oven and the castings are dumped after having cooled sufficiently. After a final cleaning, grinding, and sorting, the product is ready for shipment as the finished malleable casting.

The result of the annealing operation is to convert the hard, brittle casting with white fracture, to one soft, relatively ductile and malleable, and having a black fracture (black heart) except for a steely shell (case) of varying thickness, usually 1/32 to 1/16 inch. The tensile strength according to the standard specifications of the American Society for Testing Materials must be not less than 40,000 pounds per square inch, with an elongation of not less than 2½ per cent in 2 inches. The great advantage, however, is a product resilient enough to withstand the shocks and repeated stresses of severe service.

The popular idea among the uninformed is that the packing of the castings n an oxidizing substance has resulted in an abstraction of carbon from the body of the casting, producing a material which is a mean between ordinary steel and the original white cast iron, depending upon the activity of the oxidizing substance. It must be said, however, that a product essentially the same as the every day malleable would result, even though the packing material were inert or nonoxidizing in character. A thorough understanding of the mechanism of the annealing operation has come only with a knowledge of the influence of the several elements present. Chemical analysis has been a big stepping stone; the microscope, also, while not as yet having much application in the industry, has been of invaluable assistance.

Cast iron, as pointed out previously, is a complex alloy of iron and several other elements. Carbon is of primary importance, and the material owes its properties mainly to the state of the carbon. The other elements are largely secondary, having their effect on the properties mainly by influencing the state of the carbon. All cast iron may be considered as an alloy of iron with approximately four per cent of carbon. The white castings forming the initial stage of the malleable casting may be considered in this class, although there is usually a lower amount of carbon present, due to additions of steel or malleable scrap; this fact, however, is not material to the discussion of the mechanism of the annealing process.

Carbon is associated with iron in three different states; in the free or elemental state, as graphite; as a definite carbide, combined carbon or cementite, with a formula Fe_3C; and as a solid solution of carbon or combined carbon in iron. The last named is of particular importance in the consideration of the hardening and tempering of steels, and needs not be considered in connection with the problem under discussion. During the solidification and cooling to normal temperatures of a molten bath of cast iron, the carbon may finally exist entirely combined with the iron as Fe_3C, in which case the product is known as white cast iron, and is hard, brittle, and of silvery fracture because of the influence of the properties of this iron carbide; or the carbon may become separated in the free or elemental state as graphite, forming gray cast iron, with gray fracture and soft, due to the influence of the free carbon; or there may be any degree of mixture of the combined carbon and free graphite, resulting in the commercial mottled irons. Should all of the carbon exist in the combined state, as Fe_3C, carrying 6.67 per cent carbon, an ordinary iron with three and one-half per cent of carbon would consist roughly of one-half cementite and one-half free iron. On the other hand, if all of the carbon exists as free graphite, the material structurally, on the basis of specific gravities of 3 to 1 for iron and carbon, will be made up or iron plus ten per cent by volume of free graphite.

The fundamental influences affecting the state of the carbon are the rate of cooling and the effect of the secondary elements, especially silicon, and to a lesser degree sulphur and manganese. Silicon promotes the formation of graphitic carbon; sulphur and manganese tend to form combined carbon. For simplicity, we may consider the function of silicon as first, to counteract the adverse chemical influence of the sulphur and manganese, and second, to overcome any effects of cooling, and throw out carbon in the free state. As for the influence of cooling, a slow rate promotes the separation of free graphite, while rapid cooling tends to form combined carbon. Manifestly by judicious control of chemical composition and rate of cooling, it is possible to vary the character of cast iron within wide limits.

Ordinarily, in gray iron castings, softness is the desired feature. This means much free graphite in the product, and little combined carbon; or a moderate silicon contents of 1.5 to 2.0 per cent with low sulphur for bulky castings which cool slowly, and 2 to 3 per cent in lighter and thinner products which necessarily cool more quickly. In this kind of castings the graphite separates out during normal solidification, and in a still molten matrix of iron; obviously conditions are entirely favorable to crystallization of the carbon, and we find it existing in the well known form of flake graphite. Figures 1 and 2 are typical of this distribution, at a magnification of 70 diameters. In Fig. 1 the graphite is very coarse in texture, due to the slow cooling of a piece of pig iron; while Fig. 2 illustrates the finer texture in a casting of average section. With such distribution of the carbon, we can expect nothing else than a weakness in tension, and an entire absence of ductility; on the other hand, because of the very thinness of the graphite flakes, there is little weakening of the material under compressive stress.

The malleable casting is initially made of white cast iron. The silicon content is so controlled that under the existing rate of cooling, its influence is not sufficient to throw out the graphite in the free form, and it is therefore all combined as Fe_3C in the castings. These are hard, brittle, and practically worthless for service. Typical micro-sections of white cast iron are shown in Figures 3 and 4, both at a magnification of 70 diameters. The former is of white pig iron, and is coarser in its crystallization than the latter, a section of a thin casting. To the uninitiated it may be well to mention that the black areas in these photographs should not be compared with the graphite of the previous figures. These black areas show the distribution of the iron bearing constituent, which is differentiated by acid corrosion; the white areas, in contrast, show the free combined carbon. The brittleness and whiteness of fracture are due to a cleavage through these areas of combined carbon.

Although the silicon content is not sufficient to cause a separation of free carbon during the normal cooling of the casting, the combination of this silicon content, with the proper application of temperature effect and time of reheating, will effect the change, according to the reaction:

$$Fe_3\,C + \text{heat} = 3\ Fe + C$$

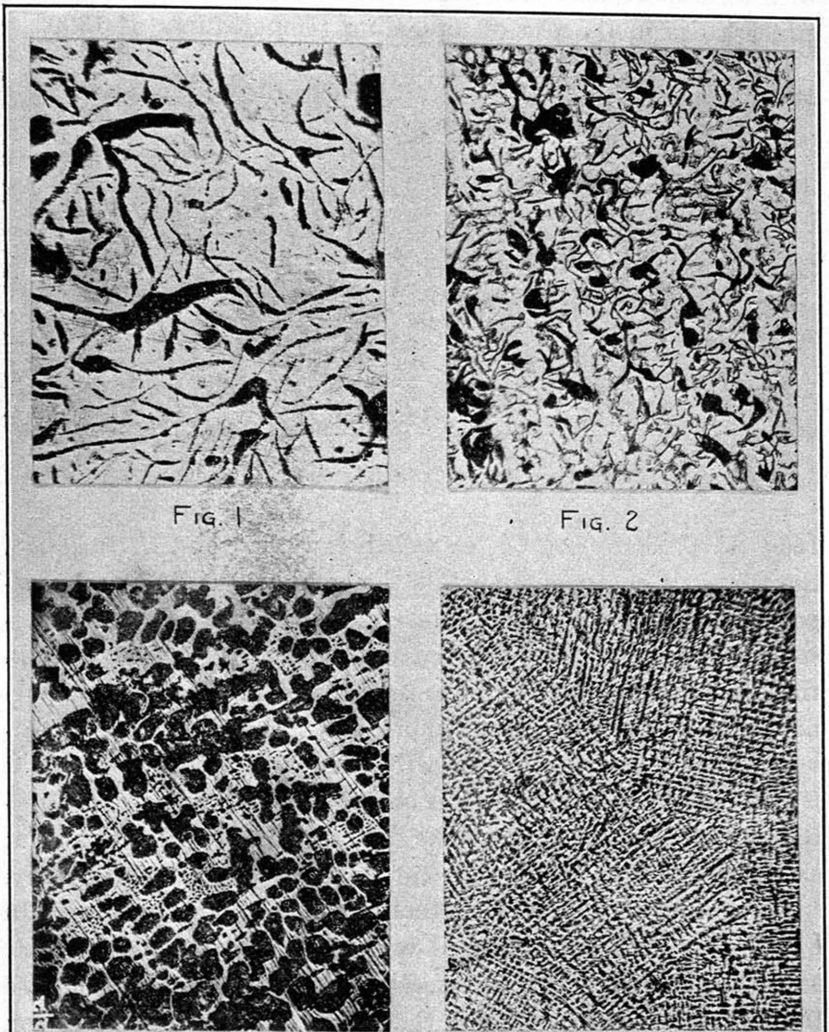
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Plate 1.—*Showing Micro-sections of Various Grades of Cast Iron.*

This is the essential feature of the annealing operation, and it is obvious that, with chemical composition, temperature, and time correctly regulated, the nature of the packing material is of little importance. The vital feature of the malleable casting process lies in the use of annealing temperatures of 1300° to 1650° F. (700 to 900° C), or well below the point of fusion of the metal. Consequently, while the combined carbon is decomposed and the carbon precipitated, the latter is not free to assume its normal crystal form as thin flakes, but must collect in the most compact state, and is thus found in the form of globules in the amorphous condition, the so called "temper" carbon. Such a distribution, as will be noted in Figures 5 and 6, is without the disastrous effect on the tensile strength and ductility characteristic of the flake distribution in gray cast iron; and the resultant product is one of fair strength and ductility.

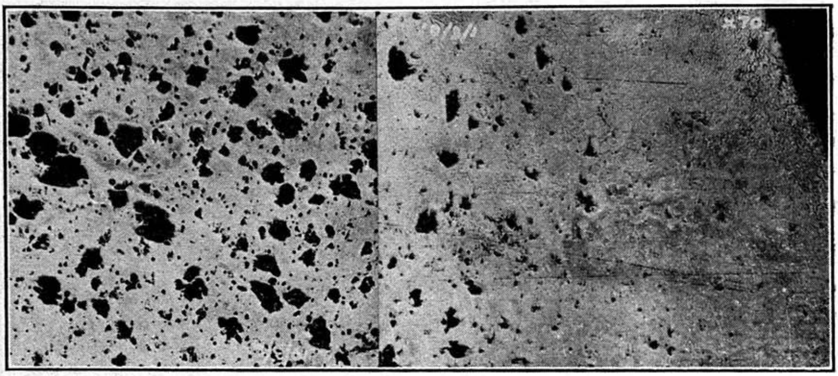

FIG. 5.— *Micro-Section Showing Effect of Oxidizing Packing.*

Figures 5 and 6 show the effect of the oxidizing packing. In Fig. 5, of a section not etched with acid, it will be noted that adjoining the edge of the annealed casting there is a zone free from graphite areas. This is the result of the decarbonization of the surface layer by the iron oxide, according to the reaction

$$Fe_3\ C + FeO = 3\ Fe + Co + Fe$$

After etching, as shown in Fig. 6, this surface zone is seen to be a shell of steel which may be of mild, medium, or high carbon, and of a depth depending upon the time and temperature of heating and the avidity of the decarbonization. This surface decarbonization, together with the use of steel or malleable scrap to lower the total carbon in the castings, are details of practice making for greater success of the process, but

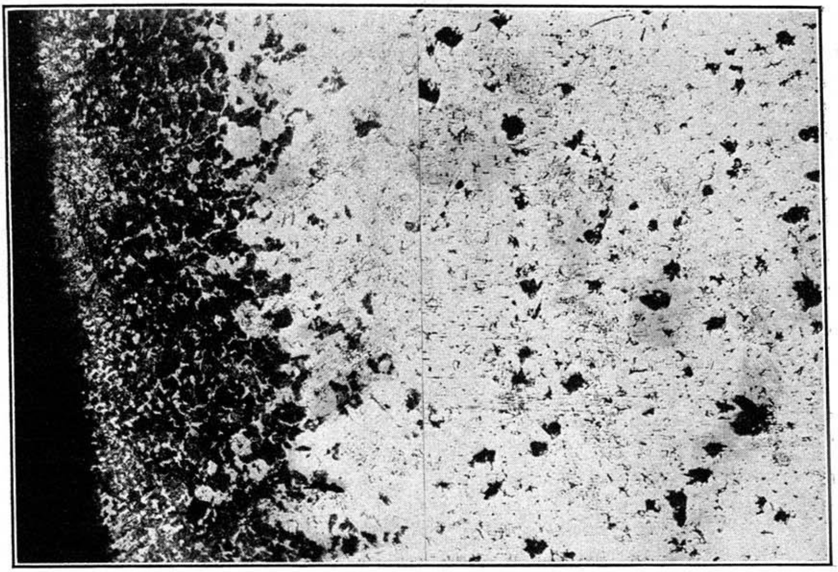

Fig. 6. — *Micro-Section Showing Effect of Oxidizing Vacking. Section Etched with Acid.*

are not the fundamental principles involved. The entire process is built upon the ability to control the state of the carbon by proper regulation of three factors: chemical composition, temperature and time.

A paper presented at the Twentieth General Meeting of the American Electrochemical Society, in Toronto, Canada, September 21, 1911, President W. R. Whitney in the Chair.

THE ELECTRICAL RESISTANCE OF IRON ALLOYS.*

By Charles F. Burgess and James Aston.

In the design of electrical machinery, the electrical resistance of the iron used for electromagnets is of an importance second only to the magnetic permeability, particularly for alternating current working. A high resistance is desired, since it will reduce to a minimum the eddy currents set up by the reversals of the magnetic flux. It is also of interest to know the conductivity of the various iron alloys, regardless of their magnetic properties, because of their possible utility in rheostats, resistance heating wires and the like.

We therefore, in connection with a series of tests on the various properties of electrolytic iron and its alloys, determined the electrical resistance of the numerous bars used in the magnetic tests. Starting with electrolytic iron as a base material, and making up the alloys with every precaution to avoid contamination, the results given represent the influence of the addition elements.

It is to be regretted that many of the compositions given are based upon the added amounts of the several elements, and have not been checked by analysis. However, the compositions noted for upwards of eighty of the binary alloys are those determined by analysis; and the elements used in the more complex series are largely those which readily alloy with iron in the added proportions. The analyzed bars can be readily recognized in the tables, since the compositions are given to the third decimal place. Again, the curves of Figs. 1 and 2 are plotted from these accurately determined compositions.

Since all of the bars were of a uniform diameter of one centimeter, a measurement of the drop of potential over a length of 7.854 cm. is equivalent to that taken over 10 cm. length of a bar

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* This investigation is being conducted in the Chemical Engineering laboratories of the University of Wisconsin largely through a grant of the Carnegie Institution of Washington.

1 cm. square. The apparatus used consisted of two knife edges, 7.854 cm. apart, upon which the test bar was laid, and pressed into firm contact by means of spring clips; the latter were outside the knife edges, and served also as conductors to lead the current into the bar. The current was measured by an ammeter, and the fall of potential by a millivoltmeter. Such values of current were used, up to a maximum of 50 amperes, as would give a large deflection on the millivoltmeter scale, a 0-20 instrument. From these two readings a simple slide-rule calculation gave the specific

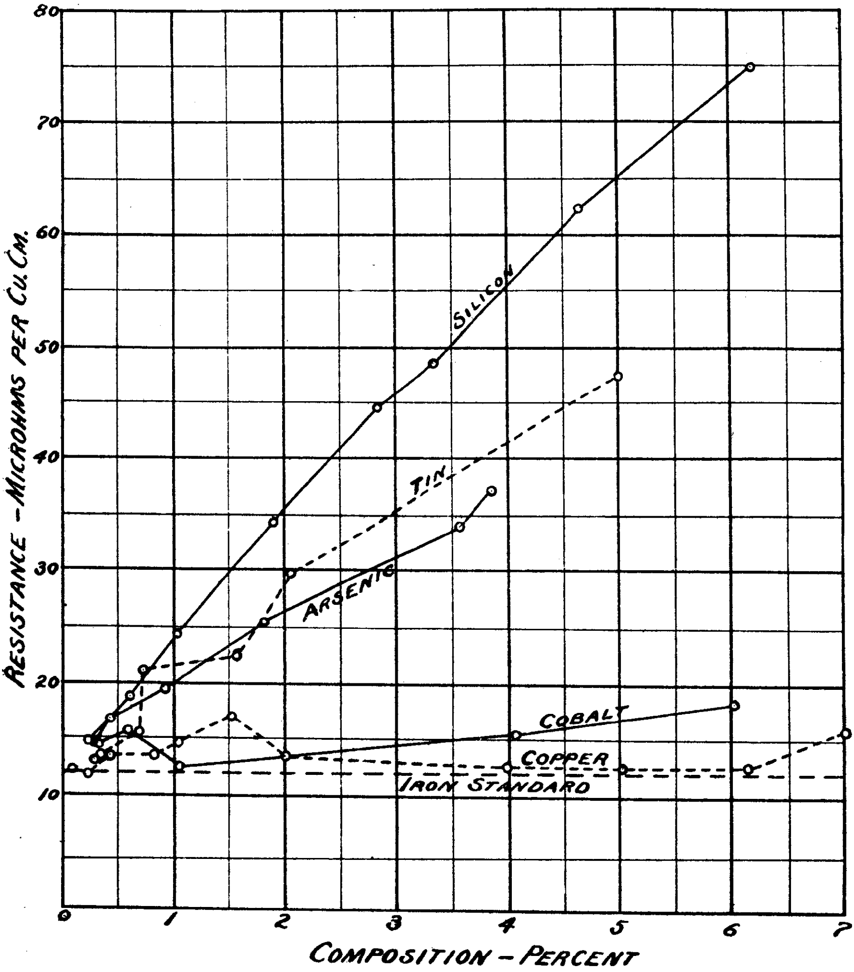

FIG. 1.

resistance in terms of Bar 117 A, of forged electrolytic iron. This bar has a resistance of 12.1 microhms per cubic centimeter in the quenched condition, a value which is not the minimum observed for electrolytic iron. But it was thought best to adhere to the same standard used for the magnetic tests data.

The results of these measurements are noted in Table I, Figs. 1 and 2. The arrangement is in groupings in alphabetical order under the headings of the alloying element, in the binary series; ternary or higher alloys appear in the group of the principal alloying element. In the final miscellaneous group appear those materials in which are more than one of the five elements—chromium, manganese, molybdenum, nickel and tungsten, which tend to produce self-hardening in steels.

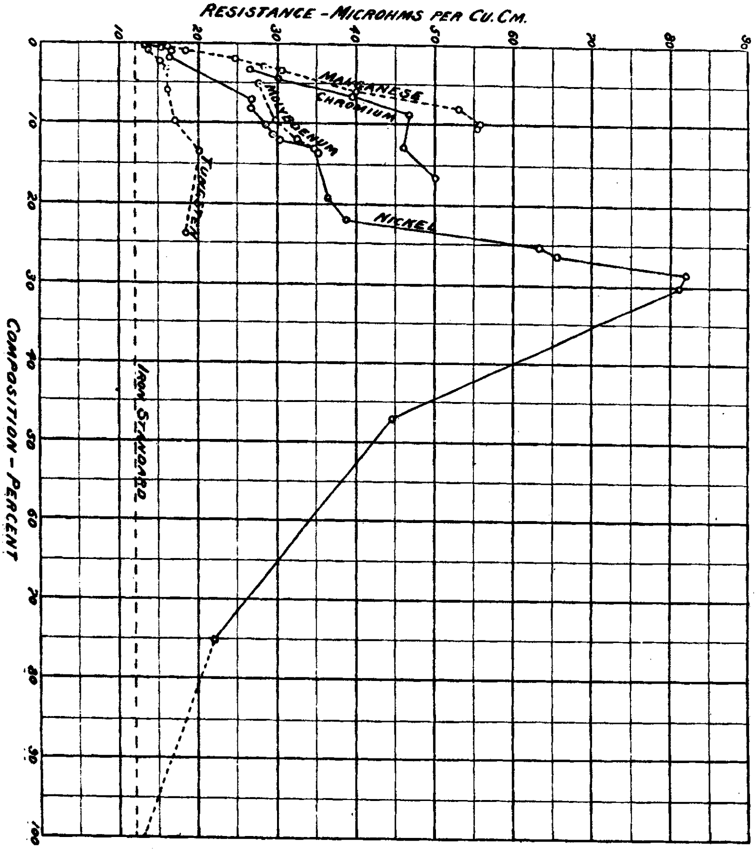

FIG. 2.

TABLE I.

Electrical Resistance.

No.	BAR	COMPOSITION	AS FORGED		AFTER TREATMENT		
			Mohs. per Cm.³	Rela. Res.	Mohs. per Cm.³	Rela. Res.	Condition
		IRON					
1	NSW	Swedish Anode			11.6	0.96	Quench 900
2	117A	Electro Forged			12.1	1.00	" "
3	AB	" "			11.1	0.92	" "
4	ELI	" "			11.1	0.92	" "
5	172A	" "	14.0	1.16			
6	117B	" "	13.1	1.08	10.6	0.88	Anneal 1000
7	117C	" "	13.4	1.11	13.4	1.11	" "
8	AC	" "	10.7	0.88	10.9	0.90	" "
9	85	" "	14.4	1.19	13.0	1.07	" "
		ALUMINUM					
10	55D	0.067 Al			23.9	1.98	Quench 900
11	76C	0.8 Al	20.6	1.70	16.1	1.33	Anneal 1000
12	109C	1.333 Al			17.4	1.44	Quench 900
		ANTIMONY					
13	172E	1.0 Sb			20.2	1.67	Anneal 1000
		ARSENIC					
14	121I	0.292 As			14.7	1.22	Quench 900
15	121H	0.430 As			16.8	1.39	" "
16	113A	0.915 As			19.5	1.62	" "
17	92A	1 As	18.1	1.50	14.3	1.18	Anneal 1000
18	113B	1.810 As			25.5	2.11	Quench 900
19	113C	3 As	25.3	2.09	26.1	2.15	Anneal 1000
20	113D	3.862 As			37.1	3.07	Quench 900
21	113H	3.563 As			34.0	3.82	" "
22	113E	5 As	26.7	2.21	20.8	7.72	Anneal 1000
23	172C	Transformer			18.7	1.55	" "
24	172D	Transformer + 5 As			30.2	2.51	" "
		BISMUTH					
25	172G	1.0 Bi			13.4	1.11	Anneal 1000
26	172H	2.0 Bi			14.5	1.20	" "
27	172J	4.0 Bi			15.3	1.27	" "
28	172K	6.0 Bi			13.0	1.08	" "
29	172L	10.0 Bi			16.6	1.38	" "
		CHROMIUM					
30	137C	3.27 Cr			26.7	2.21	Quench 900
31	133E	4 Cr 0.84 Si	41.6	3.44	46.9	3.88	Quench 1000
32	133D	5 Cr 0.84 Si	39.6	3.27	39.6	3.27	" "
33	133B	5 Cr 1.4 Si	47.7	3.94	57.0	4.72	" "
34	160J	5 Cr 0.3V	35.0	2.89	35.4	2.93	" "
35	160H	5 Cr 0.5V	34.4	2.84	34.4	2.84	" "
36	160K	5 Cr 1 V	36.1	2.98	26.8	2.22	" "
37	133L	6 Cr 0.4 Si	35.0	2.89	42.4	3.50	" "

TABLE I—*Continued.*

Electrical Resistance.

No.	Bar	Composition	As Forged		After Treatment		
			Mohs. per Cm.^{3}	Rela. Res.	Mohs. per Cm.^{3}	Rela. Res.	Condition
		CHROMIUM—Cont.					
38	133K	6 Cr 0.84 Si	42.4	3.42	49.1	4.06	Quench 1000
39	147Z	6 Cr 1.3 Si	47.4	3.92	59.5	4.92	“ “
40	133F	6.00 Cr.	52.5	4.34	64.4	5.32	“ “
41	137E	6.68 Cr			39.7	3.28	Quench 900
42	133M	8 Cr 1 Si	53.2	4.29	61.2	5.06	Quench 1000
43	78C	8.7 Cr 1 Cu 1 Al	35.6	2.94			
44	121G	8.83 Cr			46.8	3.87	Quench 900
45	111S	10 Cr 2 Si	75.0	6.20	59.8	4.94	Quench 1000
46	155K	10 Cr 2 Si 0.3 V 0.6 C	59.2	4.89	77.4	6.40	“ “
47	137L	10 Cr 2 Si 2 Ti	79.5	6.57	86.0	7.11	“ “
48	122E	10 Cr 3 Si	87.5	7.23	84.0	6.95	“ “
49	112A	10 Cr 5 Si	103.0	8.50			
50	160I	10 Cr 0.3 V	49.2	4.07	45.7	3.78	“ “
51	155L	10 Cr 0.3 V 0.65 C	49.9	4.13	55.0	4.55	“ “
52	160G	10 Cr 0.5 V	51.3	4.24			
53	163O	10 Cr 1 V	45.9	3.79	74.8	6.18	“ “
54	141C	10.3 Cr 1 V 2 Si 0.3 C	83.4	6.89	84.9	7.01	“ “
55	136G	13.01 Cr			46.0	3.80	Quench 900
56	133N	13 Cr 1.8 Si	75.8	6.26	85.6	7.08	Quench 1000
57	141E	15 Cr 2 Si	92.6	7.55			
58	137H	16.57 Cr.			50.0	4.13	Quench 900
59	136H	17 Cr 1½ Si	72.8	6.02	76.0	6.28	Quench 1000
		COBALT					
60	123A	0.32 Co			14.4	1.19	Quench 900
61	123B	0.580 Co			15.5	1.28	“ “
62	123C	1.035 Co			12.5	1.03	“ “
63	123D	2.000 Co			13.5	1.12	“ “
64	123E	3.0 Co	14.7	1.21	11.7	0.97	Quench 1000
65	123F	4.055 Co			15.4	1.27	Quench 900
66	123G	6.020 Co			18.3	1.51	“ “
		COPPER					
67	147B	0.089 Cu			12.2	1.01	Quench 900
68	158A	0.202 Cu			12.0	0.99	“ “
69	158B	0.422 Cu			13.6	1.12	“ “
70	86A	½ Cu	14.0	1.16	12.2	1.01	Anneal 1000
71	92F	½ Cu ¼ Si	17.0	1.40	13.1	1.08	“ “
72	90F	½ Cu ½ Si	22.0	1.82	21.8	1.80	“ “
73	158D	0.804 Cu			13.6	1.12	Quench 900
74	113T	1 Cu	11.4	0.93	11.8	0.96	Anneal 1000
75	50A	1 Cu	16.4	1.36	13.2	1.09	“ “
76	92C	1 Cu ½ Si	21.7	1.79	18.3	1.51	“ “
77	90E	1 Cu 1 Si	22.9	1.89	19.2	1.59	“ “
78	103G	1 Cu 1 Sn	16.7	1.40			“ “
79	111U	1 Cu ½ Al	18.8	1.55	14.5	1.20	“ “
80	147H	1.006 Cu			14.7	1.22	Quench 900

TABLE I—*Continued.*

Electrical Resistance.

No.	Bar	Composition	As Forged		After Treatment		
			Mohs. per Cm.^{3}	Rela. Res.	Mohs. per Cm.^{3}	Rela. Res.	Condition
		COPPER—Continued					
81	147J	1.510 Cu			17.0	1.41	Quench 900
82	84B	2 Cu	15.6	1.29	11.2	0.93	Anneal 1000
83	88B	2 Cu 1 Si	24.6	2.03	22.2	1.83	“ “
84	144AE	2 Cu ½ Al	22.1	1.63	19.7	1.64	“ “
85	111V	2 Cu ½ Al	18.5	1.53			
86	158G	2.005 Cu			13.4	1.11	Quench 900
87	111L	2½ Cu			9.5	0.79	Anneal 1000
88	111M	3 Cu	15.5	1.28	12.4	1.03	“ “
89	111R	3 Cu 1 As	22.1	1.83	15.1	1.25	“ “
90	94F	3 Cu ½ Si	20.2	1.67	8.1	0.67	“ “
91	88C	3 Cu 1 Si	25.3	2.09	17.8	1.47	“ “
92	111X	3 Cu 1 Al	21.8	1.80	8.0	0.66	“ “
93	113W	3½ Cu	14.7	1.22	8.6	0.71	“ “
94	158I	3.990 Cu			12.7	1.05	Quench 900
95	121L	4 Cu	13.6	1.12	12.5	1.03	Anneal 1000
96	86C	5 Cu	15.7	1.30	12.8	1.06	“ “
97	121K	5 Cu 1 As	20.5	1.69	19.6	1.62	“ “
98	83C	5 Cu 1 Si	25.3	2.09	22.6	1.87	“ “
99	88D	5 Cu 2 Si			26.5	2.19	“ “
100	144AD	5 Cu 1 Al	20.0	1.65	18.1	1.50	“ “
101	111Y	5 Cu 1 Al	19.9	1.64	17.6	1.29	“ “
102	158J	5.070 Cu			12.5	1.03	Quench 900
103	113U	6 Cu 1 Si			22.8	1.88	Anneal 1000
104	113S	6 Cu 1 Al	19.8	1.64	17.6	1.45	“ “
105	158K	6.160 Cu			12.7	1.05	Quench 900
106	88A	6.67 Cu 6.67 Si	23.4	1.93	15.7	1.30	Anneal 1000
107	147U	7.050 Cu			15.8	1.31	Quench 900
108	86E	90 Cu	5.53	0.46			
109	49A	90 Cu	5.09	0.42			
110	86F	94.340 Cu			3.92	0.24	Quench 900
111	50C	98 Cu	4.46	0.37			
		LEAD					
112	122B	0.061 Pb			13.9	1.15	Quench 900
		MANGANESE					
113	123H	0.505 Mn			16.1	1.33	Quench 900
114	170A	1 Mn			18.4	1.52	Anneal 1000
115	170B	2 Mn			24.8	2.05	“ “
116	170C	3 Mn			28.4	2.35	“ “
117	144V	3½ Mn	30.2	2.58	30.6	2.53	“ “
118	123I	4.514 Mn			30.1	2.49	Quench 900
119	170D	6 Mn	40.8	3.37	40.0	3.31	Quench 1000
120	170E	8 Mn	49.1	4.06	53.0	4.38	Anneal 1000
121	170F	10 Mn	54.8	4.53	55.8	4.61	“ “
122	123J	10.419 Mn			55.3	4.57	Quench 900

TABLE I—*Continued.*

Electrical Resistance.

No.	Bar	Composition	As Forged		After Treatment		
			Mohs. per Cm.^{3}	Rela. Res.	Mohs. per Cm.^{3}	Rela. Res.	Condition
		MOLYBDENUM					
123	160E	4 Mo 0.6 V	17.8	1.47	22.6	1.87	Quench 1000
124	163M	5 Mo 1 V	22.9	2.47	25.0	2.06	" "
125	155N	5.12 Mo			27.8	2.30	Quench 900
126	160D	8 Mo 0.5 V	25.1	2.07	25.4	2.10	Quench 1000
127	156E	8 Mo 0.3 V 0.6 C	22.6	1.87	27.8	2.30	" "
128	155M	9.84 Mo			29.9	2.47	Quench 900
129	160A	10 Mo 0.3 V	27.3	2.25	27.2	2.25	Quench 1000
130	160C	10 Mo 0.3 V 0.4 C	17.1	1.41	26.6	2.20	" "
131	160B	10 Mo 0.5 V	30.7	2.54	30.3	2.51	" "
132	163I	10 Mo 1 V	30.1	2.49	29.4	2.47	" "
133	163N	10 Mo 1 V	30.1	2.65	32.1	2.65	" "
134	163H	10 Mo 1 V 0.4 C	24.2	2.00	19.9	1.65	" "
135	141F	10 Mo 1.2 C	25.2	2.08	29.5	2.44	" "
136	146Y	12 Mo	36.6	3.02	32.6	2.70	" "
137	155O	13.69 Mo			35.1	2.90	Quench 900
		NICKEL					
138	144C	0.270 Ni			13.1	1.08	Quench 900
139	144D	0.560 Ni			15.4	1.27	" "
140	144E	1.070 Ni			16.9	1.40	" "
141	144F	1.93 Ni			16.4	1.36	" "
142	160N	5 Ni 0.3 V	22.3	1.84	24.6	2.08	Quench 1000
143	160O	5 Ni 0.6 V	24.5	2.02	25.0	2.06	" "
144	144J	7.05 Ni			26.9	2.22	Quench 900
145	157A	8.17 Ni			26.7	2.20	" "
146	160L	10 Ni 0.3 V	30.1	2.49	29.4	2.47	Quench 1000
147	160M	10 Ni 0.6 V	31.2	2.58	32.2	2.66	" "
148	146P	10 Ni 2 Si 1 C	54.5	4.50	70.3	6.03	" "
149	157D	10.20 Ni			28.6	2.36	Quench 900
150	157E	11.29 Ni			29.4	24.3	" "
151	157H	12.07 Ni			30.3	2.50	" "
152	144M	13.11 Ni			34.8	2.62	" "
153	144P	19.21 Ni			36.2	2.99	" "
154	166G	22.11 Ni			38.7	3.20	" "
155	154S	25.20 Ni			63.2	5.22	" "
156	166I	26.40 Ni			65.5	5.41	" "
157	166C	28.42 Ni			82.0	6.77	" "
158	166L	35.09 Ni			81.1	6.70	" "
159	166O	47.08 Ni			44.7	3.69	" "
160	166Q	75.06 Ni			22.1	1.83	" "
		SELENIUM					
161	121D	0.017 Se			16.2	1.34	Quench 900
162	121E	0.019 Se			14.6	1.21	" "

TABLE I—*Continued.*

Electrical Resistance.

No.	BAR	COMPOSITION	AS FORGED		AFTER TREATMENT		
			Mohs. per Cm.^{3}	Rela. Res.	Mohs. per Cm.^{3}	Rela. Res.	Condition
		SILICON					
163	96F	0.233 Si			14.7	1.22	Quench 900
164	83A	½ Si	19.5	1.61	19.8	1.64	Anneal 1000
165	96A	0.603 Si			18.7	1.55	Quench 900
166	44A	1 Si	18.6	1.54	15.9	1.31	Anneal 1000
167	96B	1.033 Si			24.3	2.01	Quench 900
168	96C	1.897 Si			34.4	2.84	“ “
169	126D	2 Si 10 V	78.9	6.51	75.5	6.24	Anneal 1000
170	109B	2½ Si	45.7	3.78	44.2	3.65	“ “
171	109A	2.826 Si			44.6	3.68	Quench 900
172	113V	3.334 Si			48.6	4.02	“ “
173	111N	4 Si	54.8	4.53			
174	44D	4 Si	48.6	4.02			
175	96H	4.655 Si			62.2	5.13	Quench 900
176	83B	5 Si	40.3	3.33	36.9	3.05	Anneal 1000
177	109D	6.2 Si	77.2	6.37	74.9	6.18	“ “
		SILVER					
178	118A	0.281 Ag			12.5	1.03	Quench 900
179	118B	0.492 Ag			13.3	1.10	“ “
180	113K	0.533 Ag			13.1	1.08	“ “
181	118L	0.691 Ag			13.8	1.14	“ “
182	113M	0.506 Ag			13.6	1.12	“ “
183	122A	0.677 Ag			13.5	1.12	“ “
184	118C	0.581 Ag			14.7	1.21	“ “
185	113N	4 Ag	12.2	1.01	7.7	0.64	Anneal 1000
		TIN					
186	111B	0.288 Sn			13.0	1.07	Quench 900
187	103C	0.342 Sn			13.3	1.10	“ “
188	103D	0.686 Sn			15.4	1.27	“ “
189	111&	0.717 Sn			21.1	1.74	“ “
190	103H	1 Sn 2 Al	18.9	1.56	1.82	1.50	Anneal 1000
191	103E	1 Sn 1 Si	28.1	2.32	19.6	1.62	“ “
192	111A	1.568 Sn			22.4	1.85	Quench 900
193	121J	2.059 Sn			29.8	2.46	“ “
194	111Q	3 Sn 0.23 P	25.6	2.12	25.6	2.12	Anneal 1000
195	113R	3½ Sn	24.1	1.99	25.0	2.06	“ “
196	111D	5 Sn			47.4	3.92	“ “
		TUNGSTEN					
197	154V	0.406 W			13.4	1.11	Quench 900
198	154W	0.93 W			13.6	1.12	“ “
199	154X	2 W	19.8	1.63	17.6	1.45	Anneal 1000
200	154Y	2.33 W			15.1	1.25	Quench 900
201	154AB	3.35 W			16.1	1.33	“ “
202	154Z	4 W	19.5	1.61	15.4	1.27	Anneal 1000

TABLE I—*Continued.*

Electrical Resistance.

No.	Bar	Composition	As Forged		After Treatment		
			Mohs. per Cm.^{3}	Rela. Res.	Mohs. per Cm.^{3}	Rela. Res.	Condition
		TUNGSTEN—Continued					
203	160P	4 W 0.4 V	18.1	1.50	20.0	1.65	Quench 1000
204	163J	4 W 0.4 V 0.5 C	23.2	1.92	38.9	3.22	" "
205	163D	4 W 0.4 V 0.6 C	23.0	1.90	35.0	2.89	" "
206	163K	4 W 0.4 V 0.8 C	24.1	1.99	43.1	3.56	" "
207	155X	5 W 0.5 C	18.5	1.53	24.5	2.02	" "
208	155A	5.98 W			16.2	1.34	Quench 900
209	154L	6 W	24.2	2.00	16.1	1.33	Anneal 1000
210	WIC	6 W + C?	22.6	1.87			
211	160Q	7 W 0.3 V	20.3	1.68	22.2	1.84	Quench 1000
212	163E	7 W 0.3 V 0.6 C	24.1	1.99	33.3	2.75	" "
213	155B	8 W	19.9	1.65	18.2	1.50	Anneal 1000
214	155C	9 W	23.0	1.90	16.5	1.36	" "
215	155D	9.85 W			17.1	1.41	Quench 900
216	155E	12 W	20.7	1.71	17.8	1.47	Anneal 1000
217	155F	13.64 W			20.2	1.67	Quench 900
218	155G	16 W	24.2	2.00	19.3	1.59	Anneal 1000
219	155H	18 W	23.4	1.93	18.7	1.54	" "
220	155I	23.87 W			18.5	1.53	Quench 900
		MISCELLANEOUS					
221	136L	20 Cr 3 Mn 1 Si	65.3	5.39	67.1	5.55	Quench 1000
222	141G	21.4 Cr 3 Mn 1 Si 1V	76.8	6.34	82.0	6.78	" "
223	150C	2 Cr 10 MO 0.5 C 0.3 V	37.0	3.06	38.9	3.22	" "
224	155S	10 Cr 5 Mo	47.9	3.96	50.0	4.13	" "
225	155R	10 Cr 10 Mo	48.1	3.98	49.4	4.08	" "
226	155U	2 Cr 10 W	28.0	2.31	28.3	2.34	" "
227	156F	3 Cr 8 W	30.0	2.48	30.5	2.52	" "
228	163A	5 Cr 2 W 0.6 C	47.4	3.92	57.8	4.78	" "
229	163G	5 Cr 5 W 0.6 C	56.8	4.70	57.8	4.78	" "
230	148A	6 Cr 18 W 0.3 V 0.69 C	50.3	4.15	48.0	3.97	" "
231	126B	7.23 Cr 9 W 3 Si	89.5	7.39	87.9	7.26	" "
232	163C	10 Cr 2W	51.4	4.25	51.5	4.26	" "
233	156K	10 Cr 2 W 2 Si	72.8	6.02			
234	156J	10 Cr 2 W 0.6 C	53.6	4.43	55.7	4.60	" "
235	156H	10 Cr 2 W 0.3 V	53.3	4.40	49.8	4.12	" "
236	156I	10 Cr 2 W 0.3 V 0.6 C	60.0	4.95	60.4	5.00	" "
237	126A	10Cr 5 W 3 Si	92.2	7.61	87.9	7.26	" "
238	155V	10 Cr 10 W	60.7	5.02	57.8	4.78	" "
239	150B						
240	150D	2Cr 10W 10Mo 0.3V 0.4C	45.8	3.78	38.3	3.16	Quench 1000
241	163B	2Cr 16W 5Mo 0.3V 0.5C	44.5	3.68	38.8	3.21	" "
242	156G	7 Cr 3 W 2 Mo	43.9	3.63	40.9	3.38	" "
243	156M	10 Cr 2 Mo 2 W	50.9	4.20	49.7	4.11	" "
244	156P	10 Cr 2 W 2 Mo 0.6 C	61.6	5.09			" "
245	136M	10Cr 2W 2Mo 2Si 0.3V	77.4	6.39	83.8	6.93	" "
246	140Q	5 Cr 3 Mn 4 Mo 1 Si	48.6	4.02	54.0	4.46	" "

TABLE I—*Continued.*

Electrical Resistance.

No.	BAR	COMPOSITION	AS FORGED		AFTER TREATMENT		
			Mohs. per Cm.^{3}	Rela. Res.	Mohs. per Cm.^{3}	Rela. Res.	Condition
		MISCELLANEOUS—Con.					
247	144Z	5Cr 6Mo 10Mn 10Ni 1C	63.8	5.27	78.0	6.45	Quench 1000
248	154E	2 Cr 10 Ni	44.9	3.71	45.8	3.78	" "
249	154F	5 Cr 10 Ni	55.7	4.60	59.4	4.91	" "
250	154A	7 Cr 10 nI	64.4	5.32	67.3	5.65	" "
251	154G	10 Cr 8 Ni	68.4	5.65	67.3	5.56	" "
252	154K	10 Cr 10NI	66.9	5.44	33.2	2.74	" "
253	154H	10 Cr 10 Ni 1 C	73.8	6.10	69.7	5.76	" "
254	154I	10 Cr 10 Ni 1 Si	74.2	6.13	70.9	5.86	" "
255	154B	10 Cr 10 Ni 2 Si	78.8	6.51	76.2	6.30	" "
256	146L	10 Cr 12 Ni	99.6	8.23	62.5	5.17	" "
257	137S	10 Cr 20 Ni 2 Si	93.0	7.68	91.8	7.59	" "
258	136V	20 Cr 10 Ni 1 Si 0.3 V	76.0	6.28	75.7	6.26	" "
259	126F	10 Ni 5 Mo	44.6	3.68	47.5	3.92	" "
260	146Q	3.3 Ni 7.7 Mo 2 Si	53.6	4.35	52.4	4.33	" "
261	146S	10 Ni 10 Mo 1 C	52.7	4.35	49.7	4.11	" "
262	154J	10 Ni 10 Mo 0.5 C	55.6	4.60	50.5	4.17	" "
263	146R	20 Ni 10 Mo	75.8	6.26	76.9	6.36	" "
264	155Z	20 Ni 10 Mo 1 C	79.6	6.57	78.7	6.5	" "
265	155Y	10 Ni 5 W	40.6	3.36	40.7	3.36	" "
266	155AB	10 Ni 5 W	25.4	2.10	22.4	1.85	" "
267	156A	15 Ni 5 W	45.8	3.78	44.9	3.71	" "
268	155P	1 Mn 2 Mo	22.3	1.84	20.6	1.70	" "
269	156C	1 Mn 10 Mo 0.5 C	32.4	2.68	30.4	2.52	" "
270	156N	2 Mn 5 Mo 0.6 C	35.6	2.94	44.0	3.64	" "
271	136X	10 Ni 2 Mn 2 Mo 0.5 C	64.2	5.30	63.5	5.25	" "
		2 Ni 12 Mn 6 Mo 0.8 Si	68.5	5.66	67.1	5.55	" "

Iron.

There is considerable variation in the relative conductivities of the nine iron bars tested, varying from 0.88 to 1.19, as compared with the standard 117A, which is taken as 1.0. Even the Swedish anode bar (NSW) has a higher conductivity than the standard, while some of the electrolytic forged bars are of somewhat higher relative resistance. The standard is, therefore, a good average bar.

Annealing in general causes a decrease of resistance, but the decrease is slight. Likewise, because of the fact that the average resistance of the quenched bar is no higher than the annealed, quenching appears to have little effect.

Aluminum.

But three bars containing this element were available for testing. In all cases, although the percentage of aluminum is small, there is a considerable increase of resistance. It is not possible from this small amount of data to draw any deductions in regard to the effect of varying percentages of aluminum. In the case of the one bar tested under two conditions of heat treatment, there is a decrease of resistance after annealing.

Antimony.

Because of difficulty in forging, it was possible to secure but one bar of the antimony series, with an added content of 1 percent of this element. Analysis has not been made to confirm this percentage, but it is evident that some antimony is present in the bar, because of the increase of its resistance over that of the standard, amounting to 67 percent.

Arsenic.

Referring to the six bars in this series for which analyses have given the arsenic content (121I, 121H, 113A, 113B, 113D and 113H), it will be seen that there is an increase of resistance due to the presence of arsenic. The resistance is a function of the arsenic content, and for the larger percentages of 3.86 and 3.56 in Bars 113D and 113H, it has become respectively 3.07 and 3.82 times the resistance of the electrolytic iron standard.

For Bars 92A, 113C and 113E no analyses have been made to determine the arsenic content; the increase of resistance, however, enables one to predict that there is some arsenic present, but probably not in the quantities added, particularly in Bar 113E, since its relative resistance has only increased to 1.72.

Likewise it is evident that some (but not all) of the 5 percent of arsenic remained in the transformer iron to which it was added, since comparison of Bars 172C and 172D shows an increase of electrical resistance from 18.7 to 30.2 microhms per cubic centimeter, a rise of 62 percent.

This high electrical resistance in those materials of high arsenic content is a most desirable accompaniment of the high permeabilities noted in the discussion of the magnetic tests.

Bismuth.

There is but little increase of resistance in the five bars of this group, and an irregularity of this resistance according to the added bismuth content. Since analyses have not been made, it is not possible to draw any conclusions regarding the effect of bismuth. The high conductivities of all of the samples, differing but little from the standard, points to the fact that but very little bismuth has remained in the bars tested.

Chromium.

In this group of alloys the resistance of all bars is fairly high, and in many instances it is very high, with the relative resistance exceeding five times that of electrolytic iron. Among those bars with chromium alone alloyed with iron, the relative resistance increases from 2.21 for Bar 137C (3.27 percent CR) to 4.13 for Bar 137H (16.57 percent Cr).

The highest resistances are reached in those bars having silicon present in addition to chromium; also the resistance is highest in those bars with highest silicon content. The maximum relative value of 8.50 is reached in Bar 112A, with 10 percent Cr, 5 percent Si.

The effect of vanadium is not very pronounced; there is a slight tendency towards increase of resistance with increase of vanadium. Also there is but little change in the chrome-vanadium alloys after quenching; to the contrary, the magnetic coercive force was greatly increased, as was noted in a preceding discussion of permanent magnets. This lack of alteration of the resistance is at variance with the general effect, which may be verified by comparison of the tables for electrical resistance (Table I) and for permanent magnets,[1] that the resistance changes follow the changes in coercive force and physical hardness due to annealing or quenching.

Cobalt.

In the seven bars of this group, varying in cobalt content from 0.32 percent to 6.02 percent, there is but little increase of resistance over that of the standard, and no regularity of increase or decrease due to variations of the cobalt present.

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[1] These Transactions **18**, 264 (1910).

Copper.

Among the binary alloys of copper and iron there is but little change in the conductivity up to a content of copper of 7 percent, the limit of forgeability; and in general the resistance is slightly higher than for iron alone. At the other end of the series, those alloys having 90 percent or upwards of copper have resistance somewhat less than half that of iron; thus the presence of small amounts of iron to the copper decreases the conductivity very markedly.

The further addition of silicon, aluminum, tin or arsenic to the copper-iron alloys increases the resistance, and, particularly in the case of silicon, the increase varies with the increase of added element.

Annealing has resulted in a considerable betterment of the conductivity.

Lead.

But one alloy of lead and iron was tested, and analysis indicated only a small content of lead (0.061 percent). The resistance of this bar is slightly higher than the standard by 15 percent.

Manganese.

In this group are listed only binary alloys of manganese and iron, with a content of added element varying from 0.50 to 10.42 percent. It will be noted that there is a successive increase of resistance with increase of manganese, from the relatively low value of 1.33 for Bar 123H to the relatively high value of 4.57 for Bar 123J. Plotting the relative resistance as a function of the manganese percentage gives a resultant curve which is practically a straight line.

In the few cases for which tests have been made under varying heat treatment, but little change has resulted from annealing or quenching.

Molybdenum.

The alloys of this group have a higher resistance than pure iron, but the increase is not very great. Also, the conductivity is but little lowered by the greater quantities of molybdenum, as is evidenced by the relative values of 2.30, 2.47 and 2.90 for Bars 155N (5.12 percent Mo), 155M (9.84 percent Mo) and 155 O (13.69 percent Mo).

Additions of vanadium and carbon have but little influence on the conductivity, and there is no change upon quenching, except for those bars containing carbon, where the electrical resistance increases in conformity with the increase of physical hardness.

Nickel.

A most interesting study is that of the electrical resistance of the binary series of nickel-iron alloys. The data from Table I are plotted in Fig. 1. There is a gradual increase of resistance with increase of nickel, from a relative value of 1.08 in Bar 144C (0.27 percent Ni) to 3.20 in Bar 166G (22.11 percent Ni). Here there is a sudden rise in the curve at compositions corresponding to those of the non-magnetic alloys. The maximum values are reached at 28.42 percent Ni (Bar 166C) and 35.09 percent Ni (Bar 166L). At these two points the resistances are respectively 82.0 and 81.1 microhms per cu. cm., or 6.77 and 6.70 times the resistance of the standard. The three non-magnetic bars, 154S, 166I and 166C, have the high relative resistance of 5.22, 5.41 and 6.77.

Above 35 percent of nickel the two determinations made indicate a fall of resistance with increase of nickel in a curve very similar to that on the other side of the maximum range. The relative resistances are 3.69 for 47.08 percent Ni (Bar 166 O) and 1.83 for 75.06 percent Ni (Bar 166Q). The final point of the curve at a nickel content of 100 percent is taken from a standard hand book.

Might not the maximum point in the curve of resistance be at 34 percent nickel, corresponding to the compound Fe_2Ni? Measurements of other kinds, such as dilatation, indicate a change of properties at this composition and tend to support the above view.

Vanadium appears to have but little influence on the conductivity, and there is no change due to quenching. However, in the one bar (144P) containing silicon, the resistance has reached the fairly high value of 4.50 in the forged condition, and has increased to the very high figure of 6.03 after quenching, due, no doubt, to the hardening effect of the 1 percent of carbon present.

Selenium.

The selenium content of the two bars tested is very small (0.017 percent and 0.019 percent), and no conclusions can be drawn from the data at hand. The resistance is higher, however, than the standard, the increase being 34 percent and 21 percent for the two samples.

Silicon.

The effect of additions of silicon to iron is a most marked increase of electrical resistance, an increase which is a function of the silicon content. Bars 96H (4.65 percent Si) and 109D (6.2 percent Si) have the high relative values of 5.13 and 6.18 after annealing. Since these silicon percentages are about those desired in the high permeability steels so much used in electrical machinery, we have in this alloy the additional valuable property of high electrical resistance.

Annealing of the several samples has resulted in a decrease of the resistance.

Silver.

Of the eight iron-silver alloys listed in this group, analyses of seven show so little silver present, and this amount so nearly constant in all bars, that no conclusions can be drawn from the data. The relative resistances differ but slightly from those of the standard electrolytic sample.

Tin.

In the five analyzed iron-tin alloys listed in this group, we note the increase of resistance with increase of tin. Bar 121J, with 2.06 percent Sn, has the relative value of 2.46. The highest value reached is 3.92, in Bar 110D, with an added tin content of 5 percent. Although this sample has not been analyzed, the high relative resistance indicates a high tin content; and the magnetic tests data previously discussed confirm this deduction.

In this series, therefore, we again have the desirable accompaniment of a high electrical resistance with high magnetic permeability.

Tungsten.

There is a slight increase of electrical resistance due to the addition of tungsten to iron; however, the effect is not very marked, and the relative resistance has been increased to only about 1½ times that of iron with an addition of about 24 percent of tungsten.

Also, the further addition of vanadium and carbon has but little effect. Annealing results in a slight increase of conductivity, but quenching causes very little change, except in those bars containing carbon, in which case there is a marked increase of resistance as the accompaniment of physical hardening.

Miscellaneous.

In this group appear a large number of alloys containing various combinations of chromium, manganese, molybdenum, nickel and tungsten, which promote self-hardening in steels. In a previous discussion of materials for permanent magnets, this group furnished a large part of the suitable materials.

Examination of the table shows that almost all the materials are of comparatively high resistance; and a comparison of this table of electrical resistance with Table III[2] of data for permanent magnets indicates an intimate correlation between these properties. In general those samples having physical hardness and high coercive force have high electrical resistance. Likewise, quenching has again had a varied effect, causing a decrease of resistance, or little change, or an increase; if the change has been marked, it is in general an increase of resistance. This is in confirmation of the results of the tests for permanent magnets.

As to the effect of the various combinations, the highest general resistance is attained with the nickel-chrome alloys, either alone, or with silicon, carbon or vanadium present. Nickel-molybdenum and nickel-tungsten alloys do not reach such high resistances except where the nickel content becomes so high that its presence alone results in high resistance. Also, chromium together with tungsten or molybdenum has not a very high resistance except where silicon is present; and the chrome-silicon alloys have high resistances without the added tungsten or molybdenum.

[2] These Transactions 18, 264 (1910).

Conclusions.

Summarizing, it appears as a result of these tests that all three of the elements of arsenic, silicon and tin, which are beneficial to

TABLE II.

High Electrical Resistance.
Relative Above 5.

No.	Bar	Composition	Microhms per Cm.^{3}	Relative Resistance	Condition
1	112A	10 Cr 5 Si	103.0	8.50	Forged
2	154B	10 Cr 12 Ni	99.6	8.23	"
3	146L	10 Cr 20 Ni 2 Si	93.0	7.68	"
4	126A	10 Cr 5 W 2 Si	92.2	7.61	"
5	141E	15 Cr 2 Si	92.6	7.55	"
6	126B	7.23 Cr 9 W 3 Si	89.5	7.39	"
7	122E	10 Cr 3 Si	87.5	7.23	"
8	137L	10 Cr 2 Si 2 Ti	86.0	7.11	Quenched
9	133N	13 Cr 1.8 Si	85.6	7.08	"
10	141C	10.3 Cr 1 V 2 Si 0.3 C	84.9	7.01	"
11	156P	10Cr 2W 2Mo 2Si 0.3V	83.8	6.93	"
12	141G	21.4 Cr 3 Mn 1 Si 1 V	82.0	6.77	"
13	166G	28.42 Ni	82.0	6.77	"
14	166L	35.09 Ni	81.1	6.70	"
15	146R	20 Ni 10 Mo 1 C	79.6	6.57	Forged
16	154I	10 Cr 10 Ni 2 Si	78.8	6.51	"
17	126D	2 Si 10 V	78.9	6.51	"
18	140Q	5Cr 6Mo 10Mn 10Ni 1C	78.0	6.45	Quenched
19	155K	10 Cr 2 Si 0.3 V 0.6 C	77.4	6.40	"
20	109O	6.2 Si	77.2	6.37	Forged
21	154J	20 Ni 10 Mo	76.9	6.36	Quenched
22	136H	17 Cr 1½ Si	76.0	6.28	"
23	137S	20 Cr 10 Ni 1 Si 0.3 V	76.0	6.28	Forged
24	111S	10 Cr 2 Si	75.0	6.20	"
25	163O	10 Cr 1 V	74.8	6.18	Quenched
26	154H	10 Cr 10 Ni 1 Si	74.2	6.13	Forged
27	154K	10 Cr 10 Ni 1 C	73.8	6.10	"
28	156K	10 Cr 2 W 2 Si	72.8	6.02	Quenched
29	146P	10 Ni 2 Si 1 C	70.3	5.81	Forged
30	136X	2 Ni 12 Mn 6 Mo 0.8 Si	68.5	5.66	"
31	154F	7 Cr 10 Ni	67.3	5.65	Quenched
32	154A	10 Cr 8 Ni	68.4	5.65	Forged
33	136L	20 Cr 3 Mn 1 Si	67.1	5.55	Quenched
34	154G	10 Cr 10 Ni	66.9	5.44	Forged
35	166I	26.40 Ni	65.5	5.41	Quenched
36	133F	6 Cr 1.68 Si	64.4	5.32	"
37	154S	25.20 Ni	64.2	5.30	Forged
38	154S	25.20 Ni	63.2	5.22	Quenched
39	96H	4.65 Si	62.2	5.13	"
40	156M	10 Cr 2 W 2 Mo 0.6 C	61.6	5.09	Forged
41	133M	8 Cr 1 Si	61.2	5.06	Quenched
42	155V	10 Cr 10 W	60.7	5.02	Forged
43	156I	10 Cr 2 W 0.3 V 0.6 C	60.4	5.00	Quenched

the magnetic properties of iron, have the desirable accompaniment of high electrical resistance.

Among the materials adapted for high resistances, various combinations of iron with nickel, chromium and silicon are most suitable.

The change of resistance due to heat treatment in general follows the changes of physical hardness due to the treatment. Annealing usually results in a decrease of resistance. Quenching is uncertain in its effect; usually there is an increase of resistance with physical hardening of the bar.

High Resistance Materials.

There are grouped in Table II, in the order of their relative resistances, all those iron alloys tested which showed a relative value as compared with the electrolytic iron *of five or upwards.* The highest resistance recorded is 8.50, reached by Bar 112A, with 10 percent Cr, 5 percent Si. Examination of the table shows 43 bars listed, all of which contain chromium, nickel or silicon, either alone or in various combinations.

Chemical Engineering Laboratories,
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DISCUSSION.

Mr. C. A. Hansen: The following specific resistance on the high nickel end of the nickel-iron series may be of interest as supplementing the results given in this paper. These measurements were made on drawn wire by the Standardizing Laboratory of the General Electric Company:

	Percent Fe	Percent C	Percent Si	Microhms per Cm.^{3} at 20° C	(20°–90° C)
Nickel...........	...	.071	.170	16.3	.00259
“	...	.110	.640	19.7	.00222
“ iron........	3.70	.120	.350	20.0	.00265
“ “	7.14	.110	.260	19.6	.00242
“ “	10.34	.110	.094	21.4	.00273
“ “	18.75	.190	.014	24.1	.00325

Dr. E. F. Northrup: Were these resistance measurements made at room temperatures?

Dr. O. P. Watts: All were made at room temperatures of the laboratory, which would be about 23° to 24° C.

Mr. Carl Hering: Do you know how he made the arsenic alloys, as arsenic volatilizes so readily?

Dr. Watts: The material was weighed out into these crucibles, put inside the graphite crucible, then a graphite cover placed over it, and the crucible placed in a granular resistor furnace, in which it was allowed to cool, after the metal was melted.

Mr. Hansen: I think I have seen that arsenic series before, where he has put 10 percent arsenic in the alloy and given an analysis of 3½ percent. In this series he seems not to have given any analysis, but gave the added percentage. Another thing we are particularly interested in is that all those bars were forged.

Dr. Watts: All bars were forged.

President Whitney: That means you can forge a bar of 10 percent chromium and 5 percent silicon?

Dr. Watts: Yes, all these bars were forged. I have seen a hundred other bars smashed before my own eyes.

Mr. Hansen: I think the list of the hundred alloys that were smashed, if we could have a little amplifying detail, might be as valuable as the list of materials forged would be to the people who are interested in making electrical resistance alloys.

Dr. Watts: Those must be placed in the series of which the President spoke this morning, of unsuccessful experiments. We have not published them as yet.

Mr. James Aston (*Communicated*): Referring to the discussion of the results given in the paper, it must be confessed that they are open to criticism from the standpoint of exact physical measurement, in that no endeavor was made to correct for slight temperature changes; also that the method does not approach the accuracy of Wheatstone bridge or potentiometer measurements. No apology is necessary, however, since the data was obtained and put forth not as being the last word on the subject, but to give the general effect of the various alloying elements on the conductivity of the pure iron base.

We regret that two errors crept into the paper as presented, one of which has been corrected in this final publication. In the description of the method employed, there was the following paragraph: "The apparatus used consisted of two knife edges, 7.854 cm. apart, upon which the test bar was laid, and pressed into firm contact by means of spring clips; these also served as conductors to lead the current into the bar." Interpreting this to mean that the knife edges served as the current conductors, and in view of the fact that large currents (50 amperes) were often used, it is evident that there would be marked errors when these same knife edges were also the contacts for the millivoltmeter connections. However, this was not the case, since the spring clips which pressed the bar firmly into contact with the knife edges were the current conductors, and the knife edges which were between or inside the spring clips carried only the small current taken by the millivoltmeter. This ambiguity has been eliminated by making the paragraph read as follows: "and pressed into firm contact by means of spring clips; the latter were outside of the knife edges, and served also as conductors to lead the current into the bar."

The uncorrected error is in plotting the curve for the nickel series, in that the point at 81 microhms per cubic centimeter, applying in the tables to the alloy with 35 percent Ni, was plotted as 30.5 Ni.

In regard to the iron-arsenic alloys, they were made by a simple melting of the two materials in a magnesia crucible, as explained by Dr. Watts. Although arsenic volatilizes long before the melting point of iron is reached, the analyses of the alloys agreed very closely with the added proportions up to 4 percent As. This seems to be the saturation point under the conditions of melting, and although added amounts up to 10 percent were tried, the highest percentage on analysis was 4.14 percent.

All bars for which results are given were forged and turned into shape. In many cases added percentages only are given as the composition of the bars; but, as mentioned in the paper, the plotted data is all from analyzed bars, and most of the others are alloys of iron with such elements as are taken up in practically the added proportions.

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A paper presented at the Twentieth General Meeting of the American Electrochemical Society, in Toronto, Canada, September 22, 1911, President W. R. Whitney in the Chair.

THE PREPARATION AND PROPERTIES OF METALLIC CERIUM.*

By Alcan Hirsch.

INTRODUCTION.

In view of the amount of research[1] on the rare-earths, it is remarkable that little has been done on the metals themselves. This is easily understood, however, when one considers the scarcity of pure material to work with and the difficulty of reducing these very electropositive elements from their compounds. What metal has been obtained has been, in most cases at least, small in amount and very impure, usually contaminated with the other members of the group. On account of the rarity of the materials to work with, little has been done in a study of the physical and chemical properties of these rare-earth metals, and the field of alloys has been almost untouched.

In the present research, cerium, the leading member of the cerium group, was chosen as the rare-earth element to be studied. The investigation was undertaken with a two-fold purpose. First, starting from as pure cerium salts as it was possible to obtain, it was desired to prepare the metal in quantities sufficiently large that its physical and chemical properties could be studied and a large number of alloys could be made. Second, by preparing metal from the unpurified rare-earth residues from monazite sand, obtained as a by-product in the incandescent gas-mantle industry, it was hoped that alloys of commercial value could be obtained. In other words, whereas the application of these residues as oxalates or oxides is very limited to-day, their value might possibly be increased materially if a useful metallic or alloyed product be prepared from them.

The writer gratefully acknowledges his indebtedness to Pro-

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* Presented as a thesis for the doctor's degree at the University of Wisconsin, June, 1911.

fessors Burgess and Lenher, of the University of Wisconsin, for the facilities of their laboratories and their helpful advice and encouragement during the progress of this research. The electrolytic work was done in the laboratories of Applied Electrochemistry, while the analyses and the chemical preparations were made in the Department of Inorganic Chemistry.

This research was begun in December, 1907, and concluded June, 1911. The actual time devoted to this study covered a period of over three years.

HISTORICAL.

In 1751 Cronstedt[2] discovered the mineral cerite in a mine of Bastnaës. In 1784 Bergmann and d'Elhyar[3] confused the rare-earths with lime, and published an incorrect analysis of this mineral cerite. In 1794 Gadolin[4] discovered the rare-earths in a heavy black mineral, afterwards called gadolinite.

In 1804 cerium was discovered simultaneously by Klaproth[5] in Germany and by Berzelius and Hisinger[6] in Sweden. The first investigator named the oxide ochre earth because of its color, but Berzelius and Hisinger called the new element cerium, after the planet Ceres. About the same time Vauquelin[7] confirmed the discovery of a new earth by analysing cerite, and then undertook the study of the salts of cerium.[8] In 1814 Berzelius and Galin[9] separated the oxides of cerium and yttrium. Between this period and that of the famous researches of Mosander, numerous articles were published on cerium and the minerals in which it was found, but the material used was necessarily very impure, and what was called at that time cerium oxide was in reality the mixed oxides of the cerium group.

In 1839 Mosander 10[10-11] announced that cerium oxide was a mixture of two oxides, those of cerium and lanthanum. In 1841 he stated that cerium oxide contained still another oxide, that of didymium. In 1868 Wolf[12] determined the equivalence of cerium and announced that the so-called cerium compounds were mixtures of two or more rare-earth elements. In 1879 Lecoq de Boisbandran,[13] while examining the didymia obtained from the mineral samarskite, isolated a new element which he called samarium. In 1885 Auer von Welsbach[14] showed that didymia was a mixture of the oxides of two new rare-earth elements, neodymium and praseodymium.

At the present time there are about 15 well identified elements which, for chemical reasons, among other properties that of the insolubility of their oxalates in slightly acid solution, are classified as rare-earths. These rare-earths are usually subdivided into three groups in the order of their basicity—the cerium group, the gadolinium goup and the yttrium group. There is no absolute differentiation of one group from another, but rather a gradual transition. Usually only the five elements,—cerium, lanthanum, neodymium, praseodyium and samarium,—are included in the cerium group.

The present research is concerned with the cerium group, and principally with cerium itself. But in the rare-earths' relations between members of the same group are much closer than among other kindred elements, as the platinum metals. For example, the atomic weights of lanthanum, cerium and praseodymium are, respectively, 139, 140.25 and 140.6; therefore the chemistry of one element concerns that of the other members of the group,—to a certain degree at least.

Previous Work on the Rare-earth Metals.

Two general methods of preparation have been used for the production of the rare-earth metals:

(1) Reduction of the oxide or chloride by one of the very electropositive metals.

(2) Electrolysis of a fused salt.

Mosander and Marignac[15] appear to have been the first to produce metallic cerium by a thermal reduction using the alkali metals. Wöhler[16] describes the difficulty of the reduction using sodium metal and cerium chloride, and states that 12 grams of sodium yielded only 50-60 milligrams of cerium metal. Winckler[17] used metallic magnesium and cerium dioxide and obtained a pyrophoric mixture. Recently some attempts have been made to produce the metals by improved methods of thermal reduction. Matignon[18] used metallic aluminum and magnesium, and Schiffer,[19] in Muthmann's laboratory, experimented with the reduction of the oxides by aluminum. From the writer's own experiences in the attempted thermal reduction of these oxides, which is described further on in this article, it appears that the reduction yields either a lower oxide, an impure mixture of partially reduced metal and oxide, or an alloy of the reduced metal and rare metal, such as an aluminum-cerium alloy.

In 1874 Frey[20] published a notice of the preparation of the rare-earth metals in the laboratory of Dr. Schuchardt, in Gorlitz, using the electrolytic method of Bunsen. The following year Hillebrand and Norton[21] published an account of their work on the electrolytic preparation of cerium. They succeeded in producing about six grams of cerium at a single operation, and obtained in all thirty grams of the metal. In 1895 Pettersson[22] attempted to electrolyze the oxides, but produced only the carbides. In 1902 Muthmann[23] and his associates published the first of a very comprehensive series of articles[24] on the metals of the cerium group. Besides preparing the metals of the cerium group, they devised a new type of electrolytic vessel which they found useful in their method of electrolysis. They have also prepared an alloy which they call "mischmetall," which is an alloy of the cerium-yttrium group metals. Borchers and Stockem[25] have devised a method in which they use the double cerium-calcium chlorides, and have patented this process (German Patent 172,529). The above-mentioned electrolytic methods will be referred to again further on in this article.

PREPARATION OF MATERIAL.

The general scheme followed in this research was to use the mixed rare-earth oxides for experimenting on the exact conditions required for the preparation of the desired salt, and after the proper conditions of the process had been determined, to prepare the pure cerium salt. Oxalates of the rare-earths, a by-product of the commercial extraction of thorium and cerium from monazite sand, were employed for these experiments. The oxides, prepared by calcining the oxalates at a temperature of 750-800° C. in a gas muffle furnace, analyzed 97.8 percent rare-earth oxides, of which approximately 49 percent was cerium dioxide. They dissolved completely in nitric acid, and also in hot concentrated hydrochloric acid on digestion, which is usually taken as a check that the cerium content is less than 50 percent.[26]

Preparation of Anhydrous Chlorides.

The first salts required were the anhydrous chlorides (composition RCl_3). There are several hydrated chlorides of cerium known, of the compositions: $2CeCl_3.15H_2O$; $CeCl_3.7H_2O$; $CeCl_3.6H_2O$; $CeCl_3.H_2O$. Cerium chloride is similar to magnesium chloride in that when its solution is evaporated to dryness and calcined, HCl is evolved with partial decomposition of the chloride to oxychloride and oxide.

A good many methods have been proposed for the preparation of anhydrous or dehydrated chlorides of cerium, among which may be mentioned the following: Heat the hydrated chlorides with NH_4Cl until the latter salt is completely volatilized.[27] Behringer[28] heated the hydrated chlorides with NH_4Cl in a glass tube in a current of chlorine. Robinson[29] heated the oxalates to a temperature of about 130° in dry HCl gas until all of the oxalic acid had sublimed, then gradually raised the temperature to a red heat. Didier[30] heated CeO_2 in a current of CO_2 and chlorine. Muthmann and Stutzel[31] passed H_2S over anhydrous sulphate heated to a high temperature, and then a mixture of CO_2 and dry hydrochloric acid gas. Mosander[32] burned cerium in chlorine. Moissan[33] attacked the carbide by hydrochloric acid gas at 650° or chlorine at 250°. Meyer[34] converted the oxides to chlorides by vapors of CCl_4.

A number of methods for the preparation of the anhydrous chlorides were tried before a suitable one was found. The large quantity of chloride which was required (several kilograms) necessitated that the preparation should be done in as simple and rapid a manner as was possible. Both aqueous and non-aqueous methods were tried, and below are given the different processes experimented with and their relative advantages and disadvantages.

One of the best methods for the preparation of this type of chlorides (those that decompose on evaporation and calcination from aqueous solution) is to heat the hydrated chloride with NH_4Cl. In the case of cerium chloride, Muthmann[35] describes in some detail this method, and mentions the tediousness and care required. To prepare a kilogram or so may require several days' work to effect the dehydration. The use of a platinum finger crucible is recommended, and not more than 50 grams of the hydrated cerium-ammonium chloride should be heated at a time. The heating must be done very cautionsly or the product will be contaminated with oxychloride or oxide. The writer has tested thoroughly this method, and finds it very poor in this case for large scale operations. One set of experiments which was tried will illustrate the difficulties encountered. Two kilograms of the mixed oxides were dissolved in 4 liters HCl (22° Bé.) and about 4½ kilograms NH_4Cl were added. Evaporation was carried to dryness in large (35 cm.) porcelain evaporating dishes. About a kilogram of the chlorides was introduced into a large Dixon crucible, which was heated in a gas crucible furnace at a low temperature until the white fumes of NH_4Cl came off copiously. The fumes were conducted out of the window by a suitable flue, and the atmosphere within the furnace was at all times a reducing one. The heating was continued until the contents of the crucible were molten and white fumes ceased to come off. A strong odor of HCl gas and chlorine was noticed toward the end of the operation. The product did not melt to a clear liquid as the properly prepared anhydrous chloride does, but fused to a slimy mass. Analysis showed that the chloride was highly contaminated with oxide, and although 1,100 grams were obtained, the product was unsuitable for electrolysis.

Borchers and Stockem[36] state that many of the difficulties encountered in the dehydration of hydrated cerium chloride can be avoided by the preparation of the double calcium-cerium chloride, and that this salt can be prepared in the anhydrous state without decomposition by simple calcination. These results could not be duplicated by the writer. Forty-seven grams of the hydrated chloride of cerium were dissolved to a clear solution in water slightly acidified with HCl, and 15 grams of $CaCl_2$ were added. The solution was evaporated to dryness and calcined. The salt which was obtained did not melt to a clear solution, and was unsuited for electrolysis.

Dennis and Magee[37] have prepared the hydrated chloride $CeCl_3.7H_2O$, which loses water in a vacuum or over dehydrating agents, whereas the hydrate $2CeCl_3.15H_2O$ does not effloresce when placed over sulphuric acid.[38] It was thought that perhaps the anhydrous chloride could be prepared from the hydrated salt $CeCl_3.7H_2O$. The concentrated solution of the chlorides, prepared by the action of concentrated HCl on the mixed oxides, was cooled to 0° C. by ice, and dry HCl gas was passed into the solution. After a time crystals began to separate out. They were filtered, dried in the air, and the chlorine content determined by titration with standard $AgNO_3$. The percent of chlorine was found to be 26.6 percent, whereas that in $CeCl_3.7H_2O$ is 28.6 percent. The presence of rare-earths other than cerium probably caused the difference in composition. When this salt was heated in a partial vacuum (water-pump) at 100° for two hours, the loss in weight was 4.4 percent. When dried over P_2O_5 in a vacuum desiccator for several days, the loss in weight was about 8 percent. The salt $CeCl_3.7H_2O$ was then dehydrated in dry HCl gas. Small quantities of the salt were placed in several porcelain boats in a porcelain tube furnace through which dry HCl gas was passed. The maximum temperature in the tube was 210°, and the average temperature was 195°. The product in the boat placed in the center of the tube lost 35 percent in weight, and analysis showed a chlorine content of 39.3 percent. The chlorine content of the anhydrous chloride $CeCl_3$ is 43.2 percent. The chloride so prepared melts to a clear liquid. Attempts were then made to prepare the anhydrous chloride on a larger scale by this method; 1,500 grams of the mixed oxides were converted into chlorides, and then the hydrate $CeCl_3.7H_2O$ was prepared by the method of Dennis and Magee, described above. The yield of salt was very small, and the operation is a difficult one to perform on a large scale, due to the fact that a low temperature is necessary and the absorption of HCl gas in water is accompanied by a considerable evolution of heat. Moreover, a simple method was found for preparing the monohydrate, and as the dehydration of the septa-hydrate passes through the stage of the monohydrate, this method was abandoned.

As the dehydration of the chlorides appeared to be the principal difficulty in the preparation of the anhydrous chlorides, it was thought that a suitable process might be developed by the use of non-aqueous solvents. As the action of non-aqueous solvents was found to be somewhat slower than the action of aqueous ones on cerium compounds, it was desirable that a readily decomposable substance be used as the starting material, and the rare-earth carbides were chosen for this reason.

The carbide[*] RC_2 was prepared by heating the mixed oxides with powdered graphite in an arc furnace. Several kilograms of this material were prepared according to the method of Moissan.[39] The proper mixture to be heated was found to be 500 parts mixed oxides and 132 parts finest graphite powder. When a graphite crucible was used as one terminal and a graphite rod (about 1 inch diameter) as the other, the carbide was easily prepared on a large scale by using a 25 kw. arc (AC or DC). Care should be taken to protect the eyes properly, as the rays emitted from the hot mass are especially harmful as they contain a certain amount of ultra-violet rays.

Alcoholic HCl,[†] made by passing dry HCl gas into cooled absolute alcohol, acts readily on the carbides. The solution of the chlorides prepared by this method always contains more or less graphite, and is very difficult to filter because of its viscosity. By evaporation to dryness, the anhydrous chlorides are obtained, but care must be taken to prevent absorption of moisture, as the syrupy liquid is extremely hygroscopic. Several minor difficulties are encountered in this method, the principal ones being the solubility of acetylene in absolute alcohol (6 times as soluble as in water) and the lesser solubility of the chlorides in absolute alcohol (one-third as soluble as in water). Because of the above disadvantages, and the expense involved in the use of absolute alcohol and its subsequent loss on evaporation, this method was not suitable to large scale operations. The action of HCl gas and chlorine on the carbides gives chlorides which are highly contaminated with carbon and are therefore useless for electrolytic purposes, as carbon in a finely divided state with the chlorides will form carbides on electrolysis.

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[*] Moissan (C. R. **124**, 1233) states that pure CeO_2 (free from iron and other earths) may be prepared from cerium carbide by fractional treatment of the carbides with dilute HNO_3. A modification of this method for the preparation of cerium dioxide free from the other rare-earths was made as follows. 100 grams of the mixed rare-earth carbides were ground to a fine powder and were treated with a small amount of dilute HNO_3. After the second treatment iron could not be detected in the residue by the sulphocyanide test. A larger amount of dilute HNO_3 was added and the solution after filtration was treated by Mosander's method. (Chlorine passed into the solution which had been made alkaline with KOH.) The precipitate after washing showed only a very faint absorption spectrum. For rapid preparation of cerium dioxide this method appears to be very good. The oxide prepared by this means is yellow when calcined at 100°, but turns darker when heated to 1000°.

[†] Meyer and Kess (Ber. **35**, 2622) have used alcoholic HCl for the preparation of cerium salts. They found that this solvent has no action on the oxides but reacts readily with the carbonates. They did not use the carbide.

In view of the fact that the non-aqueous methods were not suitable for the problem at hand, resort was again made to dehydration methods. It was found that, by treating the mixed oxides with concentrated HCl, evaporating to dryness, adding more HCl and repeating the process a number of times, a product was obtained corresponding to one of the lower hydrates of the chlorides. This white solid was very hygroscopic, and dissolved in water with avidity and evolution of considerable heat; when broken into lumps and calcined at a low temperature (not exceeding 125°) on an asbestos-covered hot plate further dehydration occurs without decomposition. The heating should be continued for a long time (about 12 hours), and the temperature must be kept low. If these directions are followed, a product corresponding approximately to the monohydrate is obtained. The great difficulty is to get rid of the last molecule of water, which is the most tightly bound of all, without decomposing the chlorides.

Matignon[40] and Bourion[41] have done a great deal of work on the preparation of anhydrous chlorides. They have found that certain chlorides of the metalloids, especially those of phosphorus and sulphur, act as catalysers in the dehydration of hydrated chlorides, and that in the presence of dry HCl gas, chlorine and sulphur monochlorides (S_2Cl_2) the chlorides of silicon, aluminum, thorium, neodymium, praseodymium, samarium and vanadium can be prepared in the anhydrous condition.

For the problem at hand this method had apparently many advantages and few disadvantages, chief of which was the very disagreeable nature of sulphur monochloride. It was resolved, therefore, to try out this method on the preparation of the anhydrous mixed chlorides. About 400 grams of the hydrated chlorides were placed in a porcelain tube furnace through which was passed a mixture of chlorine, S_2Cl_2, and HCl gases. The maximum temperature was about 300°, and the heating was continued for two and one-half hours. The product in the center of the tube was fritted together, and a sample for analysis was taken from this portion; 1.4 percent was insoluble, and the chlorine content of the soluble part was 42.4 percent—the percent of chlorine in $CeCl_3$ is 43.2 percent. The product melted satisfactorily, and the method seemed suitable, so that a plan was devised for its application on a larger scale.

A terra-cotta drain pipe, four inches (10 cm.) in diameter and four feet (1.2 m.) in length, was fitted at both ends with graphite caps, thru which passed short pieces of glass tubing, two at one end and one at the other. The furnace used was a circular-flame tube furnace in which the pipe could be heated gradually and uniformly, and the temperature was under positive control. The monohydrated chlorides, prepared by the method previously described, were dehydrated, about a kilogram at a time. The salt was spread evenly in the pipe, in a layer about ¾ inch (2 cm.) thick. The caps were then inserted and the ends heavily luted with a mixture of magnesia, asbestos fiber, cement, fire-clay and water, and allowed to dry, when a joint practically gas-tight was obtained. Dry HCl gas was passed over the chlorides, and as soon as the air was displaced the heating was commenced with a small smoky flame. After the tube was warm, chlorine and S_2Cl_2 vapors, as well as dry HCl, were passed thru the tube and the temperature was gradually raised to just below 400°. The dehydration is completed in about three hours if the temperature is correctly adjusted, but may take longer. The anhydrous chlorides are placed, while still warm, in dry bottles, and the corks paraffined in. Care must be taken to prevent the sewer-pipe from cracking when being heated, and this tendency forms one of the principal weaknesses of the process. A metallic container can not be used in the dehydration on account of the highly corrosive action of the vapors.

The sulphur monochloride seems to catalyse the dehydration process, and has the further function, together with the chlorine gas, of reconverting to chloride any oxide or oxychloride which may form. If the temperature is too high, oxide or oxychloride may form even in the presence of chlorine and sulphur monochloride. The dehydration may be carried out by HCl gas alone, and a scheme was devised for preparing pure anhydrous cerium chloride using this method. Since the process was the outcome of much work and of experience in the handling of the chlorides, it is described here in some detail.

The double cerium ammonium nitrate from the fractionating vats, where it has been purified and separated from the other rare-earths by fractional crystallization, was used. The absorption spectrum of a concentrated solution of the nitrates showed only the faintest traces of the neodymium and praseodymium bands. The contents of a large bottle containing five kilograms of the double nitrates was divided into four portions and placed in fourteen-inch (35 cm.) porcelain evaporating dishes. The dishes were filled with concentrated HCl and placed on steam-heated sand-baths. Each dish was suitably protected from drippings from the hood by wooden covers raised a few inches above the tops of the dishes and supported on silica bricks. Fresh acid was added daily as required and the evaporation continued for about three weeks, at the end of which time the nitrates had been completely converted to chlorides and all the ammonium salts had been expelled. The white solid was broken into lumps and heated on an asbestos-covered hot plate to convert it to the monohydrated chloride. The final dehydration was carried out as follows (see Fig. 1): About 400-500 grams were placed in a ten-inch porcelain evaporating dish. A short-stem funnel about nine inches in diameter was inverted and placed over the salt. A layer of asbestos fiber was packed tightly around the outside edge of the funnel and plaster of paris set over this. A glass tube passing thru the stem of the funnel and reaching to just above the layer of chloride conducted in the dry HCl gas, which was passed at a rapid rate over the heated chloride. The salt

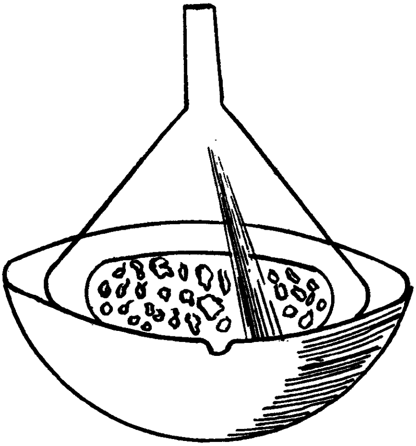

FIG. 1.

was stirred around from time to time by means of a long, thick glass rod. The heating was done gradually, and the progress of the dehydration could be watched thru the glass funnel and its completion checked nicely. The anhydrous chloride was placed, while still warm, in dry glass vessels, and the corks paraffined in to exclude moisture from the extremely hygroscopic product.

The chloride prepared by this method melts to a clear, limpid liquid, and is suitable for electrolysis. The process meets practically all the requirements,—it gives a suitable product, it is rapid, inexpensive and simple, the progress and completion of the dehydration can be watched, overheating may be avoided, and large amounts of chloride prepared in the minimum amount of time. Chlorine and sulphur monochloride may be used in addition to the dry HCl gas, but this was not found necessary, as the water was driven off rapidly and completely without their presence.

It was observed that the anhydrous rare-earth chlorides may be partially converted into oxides or oxychlorides if they were carelessly heated in the presence of air. For this reason experiments were conducted on melting the chlorides in a non-oxidizing atmosphere in a Rose crucible. In the presence of carbon dioxide some oxychloride was formed, and in an atmosphere of carbon monoxide a crust of brownish oxide appeared.

The best method of melting the anhydrous chlorides without decomposition was found to be by heating a small portion in a covered crucible until a clear melt was obtained, and then introducing successive small portions of the chlorides to the melted portion. In this manner circulation of air is avoided, as the crucible is kept covered. A good way is to first melt sodium or potassium chlorides, or a mixture of these, and then to add small amounts of the rare-earth chlorides, keeping the crucible covered as much as possible. A small amount of oxide or oxychloride will "gum up" the entire melt, and for electrolysis this condition must be carefully guarded against.

Preparation of Anhydrous Fluorides.

Another salt required in large amounts was the anhydrous mixed fluorides, RF_3. This preparation involves some of the difficulties encountered in the preparation of the anhydrous chlorides. The fluorides are more stable and less hygroscopic than the chlorides, but they are more corrosive in their action on apparatus. Porcelain vessels can not be used, and one is almost entirely limited to lead vessels in the preparation of these fluorides. However, lead linings are easily placed in evaporating dishes, especially in the large enameled iron ones, and five-gallon jars made of lead containing 10 percent antimony were found very convenient in this work.

A few methods are found in the literature for the preparation of anhydrous cerium fluoride, CeF_3, but not many. The fluorides of cerium, especially the hydrated ones, are insoluble in water and are gelatinous precipitates usually obtained by double decomposition.

The tetrafluoride $CeF_4.H_2O$ is found in nature as fluocerite, and when this mineral is heated it decomposes, forming the impure anhydrous fluoride CeF_3.[42] By precipitating cerous nitrate with hydrofluoric acid Jolin[43] obtained a gelatinous precipitate, which after drying over sulphuric acid corresponded to the formula $2CeF_3.H_2O$. When this substance was heated it decomposed, leaving a residue of oxide.

In the preparation of the anhydrous rare-earth fluorides both dry and wet methods were tried. Hydrofluoric acid gas was passed over a small amount of the pulverized carbides placed in an iron tube and heated to a temperature of about 200°. The hydrofluoric acid gas was prepared by heating CaF_2 with concentrated H_2SO_4 in a copper retort. Some fluoride was formed, but was contaminated with carbon and undecomposed carbide, and the method was regarded as unsuccessful.

The action of concentrated HF on the oxides was tried. A small amount of the mixed oxides was heated in a platinum dish with successive portions of concentrated HF. The action was vigorous at first, but soon stopped, and the residue was a mixture of oxide and fluoride.

As the anhydrous fluorides were required, a process in which no water was used obviated the subsequent removal of that water, and seemed to be at least worthy of trial. The chlorides were boiled with absolute alcohol until a concentrated solution was obtained, which was transferred to a lead tub placed in hot brine, so that the precipitation might be done from a hot solution, and HF gas passed into the hot chlorides. The objections to this method are that the fluorides so prepared are contaminated with some chloride. Furthermore, the saturation of the hot alcohol with HF gas is a very slow process, and the fluorides are extremely difficult to filter on account of their gelatinous nature. If the precipitation is done in the cold, the fluorides come down in a slimy condition almost impossible to handle, hence the reason for precipitating from hot solution. While the precipitation may be done by the action of a concentrated solution of hydrofluoric acid on the aqueous solution of the chlorides, the fluorides settle far less readily in water than in alcohol. Consequently, on account of the above reasons, the next modification in the process was to dissolve the mixed oxides in concentrated HCl, concentrate the solution and add the requisite amount of concentrated HF to the hot solution. After allowing the precipitate to settle, the supernatant liquid was syphoned off, alcohol was added, the whole was stirred thoroughly, the precipitate allowed to settle, the liquid syphoned off and the treatment with successive portions of alcohol repeated several times. The fluorides were dried at a low temperature, and were pink in color. They melted at a fairly high temperature (about 900-1000°) to a clear liquid, and the process was satisfactory except for the time required for the precipitates to settle.

In order to flocculate the fluorides so that they could be more easily filtered, the precipitate of the fluorides was placed in a round-bottom Jena flask about half full of absolute alcohol, and heated in an autoclave at a temperature of 130° and a pressure of 90 pounds per square inch. The product so treated seemed to settle somewhat more rapidly, but filtered very slowly indeed.

After many trials, the most satisfactory preparation of the anhydrous fluorides was found to be best effected by the following method: About a kilogram of the mixed oxides was placed in a large porcelain evaporating dish and digested in a steam closet with concentrated HCl until a clear concentrated solution of the chlorides was obtained. The hot solution, containing only a slight excess of hydrochloric acid, was transferred to a five-gallon lead jar and concentrated HF added to complete precipitation. The fluorides were allowed to settle somewhat, as much of liquid syphoned off as was possible, and washed twice with hot water and several times with 95 percent alcohol. Only a few minutes' time was allowed after each washing for the precipitate to settle. The fluorides were then placed in a lead-lined cage-centrifuge, and most of the remaining alcohol removed in this manner. Absolute alcohol was added and the solution evaporated to dryness without decanting. The absolute alcohol dehydrates the centrifuged fluorides very well. They were then dried at 100°, and the temperature raised to 200° at the end. About six kilograms of the fluorides were prepared in this manner. The process is a fairly satisfactory one, and as no filtering is done, the method is fairly rapid.

PREPARATION OF METALLIC CERIUM AND MISCHMETALL.

Thermal Reductions.

Thermal reductions were tried in the hope of producing rare-earth metal by this simple means. Previous work of this nature has already been referred to.[15-19] Magnesium and calcium shavings and aluminum powder were used as reducing agents on the mixed oxides. These experiments were conducted in electrically-baked magnesia linings placed in graphite containers. Carbon and silicon were also used to reduce the oxides, but external heat was applied to give the high temperature required. No metal was formed in these last instances but the carbides and silicides respectively. The carbide RC_2 is pyrophoric, but the silicide RSi_2 is not. Reductions using magnesium and calcium in excess gave alloys, many of which were pyrophoric.

Several trials to reduce the oxides with aluminum are here recorded:

$3R_3O_5 + 10Al = 5Al_2O_3 + 9R$

150 grams mixed oxides require 27 grams aluminum.

$3BaO_2 + 2Al = Al_2O_3 + 3BaO$

507 grams barium peroxide require 54 grams aluminum.

The following charge was weighed out, intimately mixed and fired by means of magnesium wire and thermit igniter.

Mixed oxides	150	grams
Aluminum powder	40	"
Barium peroxide	120	"

The reaction was vigorous, but not yiolent. A five-gram lump of metal and many small globules were obtained. The specific gravity of the metal was greater than that of aluminum.

In another experiment the following charge was used:

Mixed oxides	200	grams
Aluminum powder	61	“
Barium peroxide	200	“
Black thermit mixture	50	“

The black thermit was used to produce a higher temperature and also for the reason that the affinity of cerium for iron was thought to be greater than that of cerium for aluminum; 35 grams of hard-brittle alloy were obtained, but the content of rare-earth metals was low.

In the case of these thermal reductions, either an alloy, a compound or a lower oxide of the rare-earths was obtained. Owing to the high heat of formation of these oxides, the failure of alumino-thermics in the production of metal was only to be expected. The writer believes that a study of the equilibrium conditions of these reactions would form an interesting and valuable research and might result in the discovery of lower rare-earth oxides.

Earlier Work on the Electrolysis of the Anhydrous Chlorides.

The previous work on the electrolytic preparation of cerium has already been referred to. The method of Bunsen,[44] which the earlier investigators used, was first tried by the writer as follows: In a porcelain crucible, in which the mixed chlorides of sodium and potassium has been melted, small amounts of anhydrous cerium chloride were introduced by means of a small porcelain spatula. An annular piece of iron was used as anode, and the cathode consisted of a platinum wire, protected by a short piece of clay pipe stem. The temperature of the fused bath was lowered until a thin crust formed on the surface of the bath, when the electrolysis was commenced. Globules of cerium rose to the surface and burned with explosive force. The platinum cathode was badly attacked; in fact, part of it melted off, due to formation of an alloy with cerium. No metal was collected.

For a survey of Muthmann's work on the rare-earth metals the reader is referred to the original references.[23-24] The type of vessel used in the electrolysis of the chloride is shown in Fig. 2, and is now gnerally known as the Muthmann cell. It is a semi-water-jacketed vessel, constructed of copper, and may be used with or without the heating circuit. The principal objection which the writer has to the cell is its complicated nature.

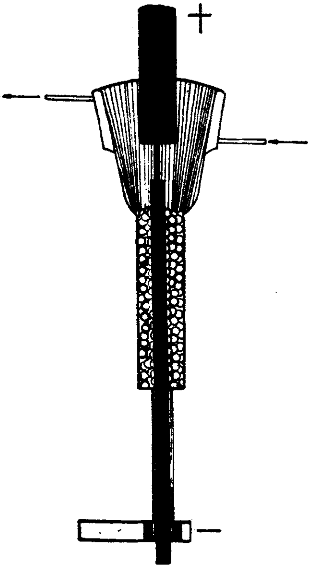

FIG. 2.

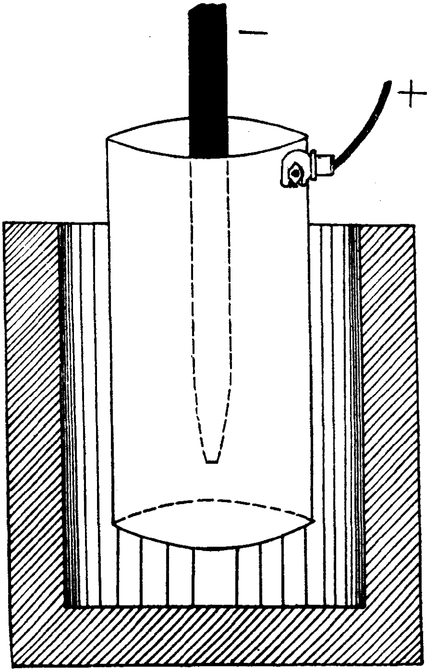

FIG. 3.

The cathode should be insulated carefully, and this is difficult, as the asbestos packing is attacked by cerium metal, and during the course of the electrolysis the insulation is apt to be destroyed and the walls of the vessel may act as cathode, with the subsequent contamination of cerium with copper. This is especially liable to occur if the temperature of the bath is too high. The heating circuit must also be insulated from the walls, and the carbon heating rods are liable to crack and break. Unless the contents of the cell are poured or tapped at the completion of the electrolysis, the entire cell has to be dismantled after each run. When worked on a small scale, the manipulation of this electrolytic cell is a troublesome and difficult operation.

In the present research, numerous runs were made before more than traces of metal were obtained. It is believed by the writer that an account of failures is often fully as important as that of successes, as it is only by correction of faults that successful results are obtained. Therefore a brief account of the earlier unsuccessful attempts to produce rare-earth metal are here given. It was only by a complete understanding of the reasons for failure that a successful solution of the problem was accomplished.

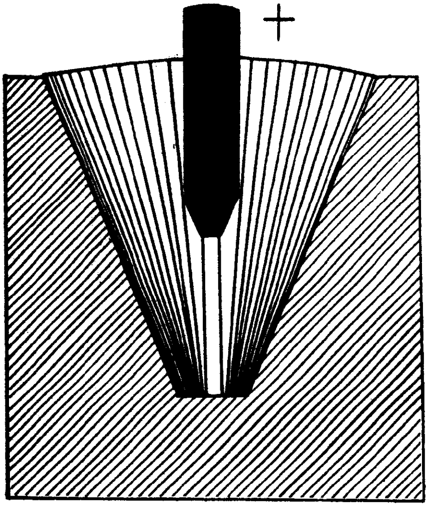

Fig. 4.

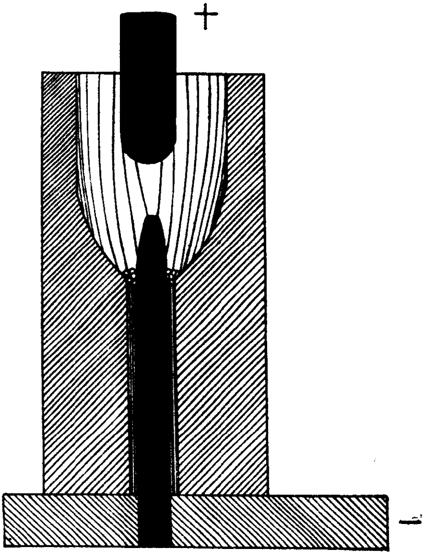

Fig. 5.

The different types of cells used where anhydrous mixed chlorides were employed as the electrolyte are shown in Figs. 3 to 5.* They were all constructed of the same material, graphite. The anodes were of graphite, but in the case of the insulated cathodes these were sometimes of graphite and sometimes of

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* The crucible shown in Fig. 4 was split longitudinally into two sections, which were cemented together by graphite-molasses paste and clamped firmly together. This makes a very convenient form of electrolytic cell, as it can be easily dismantled, and also very quickly reassembled.

iron. In many cases where a graphite crucible was used as both containing vessel and cathode, the melting was done in a resistor furnace, and then the electrolysis was begun. In some instances the heating was done by alternating current, and could be maintained and regulated during the course of the electrolysis. The melting of the electrolyte was sometimes done by a small, thin carbon heating rod placed between electrodes, as shown in Fig. 2. An arc could not be used to melt the chlorides, as they are decomposed at that temperature.

The principal difficulties encountered in these experiments were the following:

1. The salt would not melt to a clear liquid.
2. The electrolyte would remain liquid for a time, but would eventually solidify.
3. The IR drop across the cell and the amperage would vary.
4. The anode would not functionate properly.
5. On completion of the electrolysis, no regulus of metal was obtained.
6. Minor difficulties, such as short-circuiting of insulated cathodes, leakages, fracture of electrodes, etc., liable to happen in any fused electrolysis, were encountered.

The reasons for the above difficulties were found by experience to be explained as follows:

1. If the chlorides did not melt to a clear liquid, then either the chlorides were not anhydrous or they were decomposed in the process of fusion. The proper manner of melting the chlorides has already been discussed in sufficient detail.

2. The "gumming-up" was caused either by the formation of a higher melting salt, as the oxide or carbide, or the temperature of the bath was too low. (See 4, below.)

3. As the generator voltage and the external resistance were constant, changes in the voltage across the cell and the amperage were caused by a variation of the internal resistance of the cell. This variation was caused by the following factors: Change in temperature of the bath; depletion in the electrolyte, or segregation, such as double layers, etc.; formation of intermediate products of varying resistance, such as sub-chlorides; differences in thermal conductivity of the electrolyte at different stages of the electrolysis; etc. It was found that the potential difference and the amperage of any one cell can vary only between certain limits for successful electrolysis. The heating value of the current (C_2R) in cases where no external heat is applied must be such as to keep the temperature of the bath at a certain value. If the temperature of the electrolyte is too high, it is impossible to successfully electrolyse in the case of cerium chloride.

4. The function of the anode was (1) to cause the separation of chlorine and (2) to supply most of the heat necessary to keep the bath fused.

(1) In all these experiments the amperage was such that, if the cell was working properly, there was a copious evolution of chlorine gas. In many cases the voltage across the bath and the amperage would be approximately the proper values, and yet very little chlorine would be evolved. This may occur under several very different conditions. If the temperature of the bath is low, the semi-fused chloride is a very good conductor, and the entire bath may behave as a conductor of the first class. In this case practically no chlorine will be evolved. Again, if the temperature of the bath is too high, little chlorine is given off. This is due to the fact that at the cathode the chloride is partially reduced to subchloride, which diffuses to the anode and is there oxidized by the chlorine to chloride. There is a narrow limit of temperature where true electrolysis occurs, that is, where anhydrous $CeCl_3$ is decomposed by the current to metal and chlorine.

(2) In cases where the containing vessel acted as the cathode, anodic current density was much greater than the cathodic, consequently most of the heat was supplied to the cell by the anode. In the preliminary experiments the anodes were of graphite, but with the same diameter anode and the same current the heating is greater with a carbon than with a graphite anode. In some of the later runs carbon was used as the anode material for the reasons mentioned above. If the diameter of the anode is too great, a larger current is required to keep the bath molten. Besides, the anode is brought nearer the walls and most of the current may pass thru the upper part of the cell. This should be avoided, as the path of least resistance for the current should be from the anode to the bottom of the cell, as this insures good

circulation of the electrolyte and the deposition of the metal in a united form. If metal is deposited on the upper walls, some is apt to become oxidized by contact with the air, and this may result in the bath becoming viscous.

5. Many of the reasons for failure to obtain a regulus of metal have been given above. The metal may be deposited in a finely-divided, unfused condition, and may be disseminated throughout the body of the electrolyte. It may be totally or partially soluble in the electrolyte (for instance, Li in LiCl.), or the metal may react with the products at the anode (as chlorine) or the material of the cell (with copper forming an alloy, or with graphite forming a carbide).

Electrolysis of the Anhydrous Fluorides.

When it was found that the electrolysis of the chlorides was such a difficult process, it was thought that the electrolysis of some other salt might be more easily effected. Muthmann[24(c)] has used the solution of the oxides in the fused fluorides, similar to the process for the production of aluminum.

The anhydrous mixed fluorides melt at a temperature of a little over 900°, and dissolve the mixed oxides with avidity. The electrical conductivity of the molten fluorides is low, but increases rapidly with addition of oxides. The solution containing about 20 percent of oxides conducts very well.

The first cell tried with the fluorides contained a graphite cathode insulated from the graphite vessel by a porcelain ring. During the electrolysis the porcelain was badly attacked by the fused fluorides. Even a Dixon crucible was badly eroded, as the fluorides attacked the silicate binder. It was found that graphite was one of the few substances that would withstand the high temperature and the action of the fused fluorides. A vessel made of graphite plates, luted on the edges with graphite-molasses paste, clamped together with iron bands and previously baked, leaked during the electrolysis. Altho the vessel was imbedded in magnesia flour to prevent oxidation, the high temperature of the bath (well over 1000°) caused the luting to break down.

A summary of the results of the runs using fluoride-oxide electrolyte are here given.

1. 2,500 grams anhydrous mixed fluorides were melted in a

resistor furnace. The fused fluorides readily dissolved 450 grams of mixed oxides. The molten bath was electrolysed, using 450 amperes at a pressure of 14 volts. 10-15 grams of impure metal were obtained. The electrolysis was unsatisfactory, as the anode was not properly "wet" by the electrolyte. The active surface of the anode should have been much greater. A layer of carbide was found on the bottom and sides of the crucible.

2. A graphite box, inside dimensions 4½ x 5 x 6 inches (11 x 12 x 15 cm.), which was chiseled from a solid graphite block, was used as the electrolytic vessel. The anode was made as follows: A graphite block about 16 in. (40 cm.) long, 3 in. (8 cm.) wide and 2 in. (5 cm.) thick was cut at one end so as to present three blades, each ½ in. (1 cm.) thick and 3 in. (8 cm.) wide. This increased the active surface of the anode and resulted in its functioning properly. The fluorides were melted by a carbon heater placed between the electrodes. As soon as a small amount of the fluorides was melted, the heater was removed, the anode lowered and alternating current turned on. 1,000 amperes at 24 volts for about 25 minutes were required to melt 4,300 grams mixed fluorides. Mixed oxides were added gradually, and then direct current switched on. 650-750 amperes at a pressure of 10 volts were used. Oxide was added gradually during the course of the run, which was continued for about an hour, at the end of which time the solution solidified. 4,300 grams fluoride and 1,600 grams oxide were used in all. Small amounts of metal were scattered throughout the mass, but no regulus was obtained. At the bottom of the vessel was found a black layer of carbide. The melting point of the fluoride-oxide mixture was about 1400°.

The principal difficulties encountered in the electrolysis of the oxides dissolved in the fused fluorides were:

1. Oxides must be added to the fluoride to make a sufficiently conductive solution, and the melting-point of the bath is very high.

2. At the high temperature of the bath, rare-earth metal and graphite combine to form carbide.

Attempts were made to electrolyse a solution of the oxides dissolved in a mixture of fused potassium fluoride and rare-earth fluorides. Violent explosions ejected a large portion of the electrolyte during the run, due perhaps to the deposition of alkali metal, which was immediately vaporized at the temperature of the bath.

One of the principal difficulties in all the previous electrolyses had been the formation of carbides, which made the bath viscous and unfit for electrolysis. It was thought that if a non-carbon cell was used, the formation of carbide would be less likely to occur, as the only carbon in the cell would be the anode. On account of their corrosive action and high melting point the fluorides could not well be used in other than carbon vessels. It was therefore decided to try the electrolysis of the mixed chlorides in a wrought-iron vessel.

Later Work on the Electrolysis of the Anhydrous Chlorides.

1. The electrolytic vessel was a thin-walled wrought-iron crucible about 3 in. (8 cm.) high and 2 in. (5 cm.) average diameter. The anhydrous mixed chlorides were fused by means of a thin carbon rod, heated electrically to incandescence, and electrolysed with a current of about 50 amperes for several hours. The electrolyte remained fluid during the entire course of the electrolysis. About 30 grams of semi-fused metal was obtained.

The iron crucible was not attacked. The success of this run led to experiments on the best conditions for electrolysis on a larger scale.

2. The electrolytic vessel was a large iron crucible 5½ in. (14 cm.) maximum inside diameter and 7 in. (18 cm.) high. The anode was a carbon rod 1½ in. (4 cm.) in diameter. A small amount of sodium chloride was fused, and the mixed chlorides were added in small amounts until a fused bath was obtained. The electrolysis was maintained with a current of 130 amperes for four hours at a pressure of 12-18 volts. Small amounts of anhydrous potassium fluoride (about 10 grams at a time) were added occasionally to dissolve what little oxide was formed and so keep the bath perfectly fluid. The amount of additional salts used (KF plus NaCl) in all was about 10 percent by weight of the rare-earth chlorides. A lump of partially fused metal was obtained, which when re-melted under NaCl weighed 120 grams. The number of ampere hours used was 520, and the

ampere efficiency was 13½ percent. The crucible was not attacked.

3. The object of this run was to try the value of an insulated cathode. Previous experience had taught that if the insulated cathode was iron and a fairly large current used (about 200 amperes) the iron cathode would become so hot that an alloy would be produced. Consequently iron was not used as the cathode in this electrolysis. The electrolytic vessel consisted of a 6-in. (15 cm.) length of a 3-in (8 cm.) iron pipe screwed into a reducing-cap carrying a short piece of 2-in. (5 cm.) pipe. The cathode consisted of a long rod of 1½-in. (4 cm.) graphite

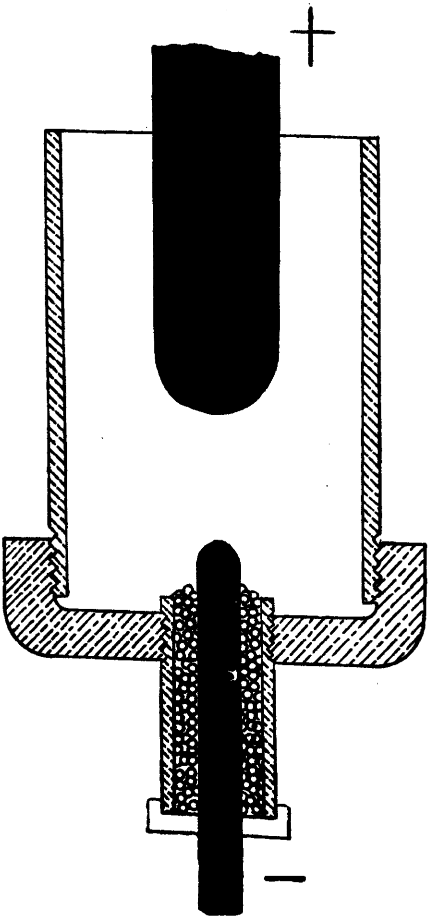

Fig. 6.

insulated from the sides of the 2-in. (5 cm.) pipe by asbestos fibre and encased at the bottom in plaster of paris. A sketch of this cell is shown in Fig. 6. The anode was a graphite rod 1½ in. (4 cm.) in diameter. A current varying from 180 to 200 amperes at a pressure of 20 volts was used for nearly four hours. A regulus of metal weighing 135 grams was found at the bottom of the vessel. Below the metal was a black layer of carbide. The number of ampere hours was 712, and the ampere efficiency was 11 percent. The electrolyte consisted of the mixed chlorides, to which were added, during the course of the run, small amounts of anhydrous potassium fluoride, sodium chloride and barium chloride. The object of the last-named salt was to increase the resistance of the bath so that the electrolyte was kept well fused and metallic conduction of the bath prevented. It must be remembered that where a graphite anode was used, a higher voltage was required to keep the bath fused.

The results of the above three experiments showed: (1) That rare-earth metal could be produced by electrolysis of the chlorides in iron vessels; (2) that the use of an insulated cathode of graphite gave a lower current efficiency and resulted in some of the metal being converted to carbide; (3) that it was necessary to regulate the temperature of the bath so as to have the electrolyte well fused and yet well below the alloying temperature of iron and rare-earth metal; and (4) that control of the electrolysis could be maintained by judicious addition of small amounts of potassium fluoride, sodium chloride and barium chloride.

The above experiments in which the anhydrous mixed chlorides were used were so successful that the method of electrolysis was applied to pure anhydrous cerous chloride, and the runs are here described.

1. The electrolytic vessel was a thin-walled wrought-iron crucible, maximum diameter about 4 inches. The anode was a round graphite electrode 1 inch in diameter, and the iron crucible was made the cathode. A small amount of sodium-potassium chloride was first melted, and then cerous chloride added. During the course of the electrolysis, rather large amounts of the alkali chlorides were used. A current of 110 amperes was employed for two hours, at the end of which time the electrolyte solidified. Forty grams of fairly-well-fused metal was obtained.

The number of ampere hours was 220, and the ampere efficiency was 11 percent. Too much alkali chlorides was added during the electrolysis, and this fact, together with the high temperature of the bath,* accounts for the low efficiency.

2. A crucible similar to the one described in the above experiment was used both as the containing vessel and cathode. A corrugated graphite anode ⅝ in. (1.6 cm.) in diameter was used. 250-300 grams of anhydrous cerium chloride and about 10 percent sodium chloride were used. The electrolysis was continued for 1½ hours, using 75 amperes at 15 volts. The bath was kept near its melting-point, so that there was no danger of a cerium-iron alloy forming. 65 grams of cerium metal was obtained. The number of ampere-hours was 112, and the ampere efficiency was 33 percent.

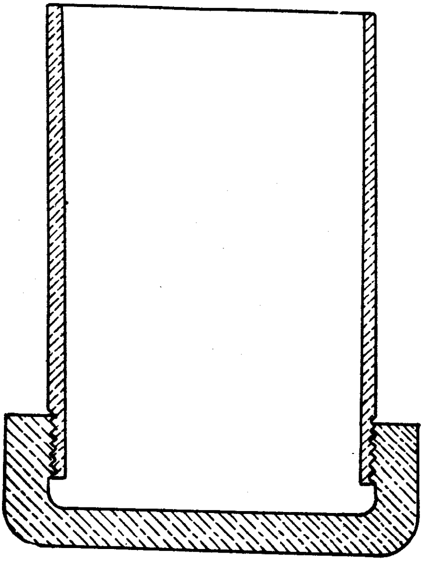

FIG. 7.

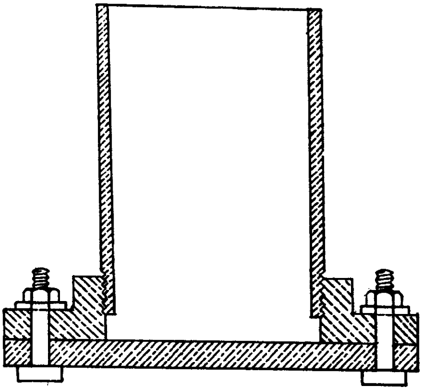

FIG. 8.

3. It was decided to try the electrolysis on a larger scale. When the mixed rare-earth chlorides were electrolysed in a large iron crucible, it was difficult to remove the solidified salt after

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*In many electrolyses a high ampere efficiency is obtained only if the bath is kept near its melting point. As the temperature is raised the efficiency decreases. This is especially true in the case of fused lead chloride and fused caustic soda, where, if the temperature of the bath is high, no metal at all is obtained.

See these transactions, 19, 167-168, 1911 (Discussion).

the run was completed. The chlorides, after cooling, form a hard, vitreous mass, upon which even a cold-chisel has little effect. The removal of slag and metal was always accomplished with difficulty and loss of some material. To obviate this difficulty a 7-in. (18 cm.) length of a 3-in. (8 cm.) iron pipe, screwed into a cap for a bottom, was used as the electrolysing vessel. (See Fig. 7.) Sodium chloride was melted first, and cerous chloride added until the fused mixture conducted well, when the carbon electrode, 1¼ in. (3 cm.) in diameter, was lowered until it was within an inch or so of the bottom; the voltage then sank to the proper value, 12 volts, and electrolysis began. The volume of the bath, of course, constantly decreases during the electrolysis, and fresh cerous chloride must be added from time to time, About every forty minutes the anode was raised until it just dipped below the surface of the bath. This increased the voltage across the bath and caused a rapid heating of the electrolyte. After a few minutes the anode was lowered until the voltage was properly adjusted, when electrolysis recommenced. The voltage varied from 12 to 14 volts, and the average current used was 200 amperes, for four hours. The electrolyte became slightly viscous toward the end of the run, but the electrolysis proceeded satisfactorily, as was indicated by the appearance of the bath, the voltage across the cell and the evolution of chlorine. Over a kilogram of cerous chloride was used. A well fused ingot of metal weighing 580 grams was obtained. The number of ampere hours was 800, and the ampere efficiency was 41½ percent. The cap could not be removed at the completion of the electrolysis, but the crucible was unattacked by the cerium. The small amount of iron introduced was caused by oxidation of the heated vessel near the top, the solution of this iron oxide in the electrolyte and its immediate reduction to metal when in contact with cerium.

4. In order to facilitate the removal of electrolyte and metal at the end of a run, the following vessel was devised: It consisted of a 3-in. (8 cm.) iron pipe screwed tightly into a 5-in. (13 cm.) iron flange, to which a bottom plate was attached by means of four large bolts and nuts. (See Fig. 8.) The electrolyte was cerous chloride containing a small percentage of sodium chloride, to which very small amounts of potassium fluoride and potassium

fluoride-barium chloride mixture were added when required (about every half hour or so). The function of these additional salts has already been explained in detail. The voltage was kept at its proper value, which should not be greater than 15 volts. The average current used was 200 amperes, for three hours. The electrolysis required attention about every twenty minutes; that is, the anode needed slight adjusting or the temperature had to be corrected. An ingot weighing 380 grams was obtained. The number of ampere hours was 600, and the ampere efficiency 36.5 percent.

The electrolyte remained liquid during the entire course of the electrolysis. About 1½ kilograms of cerous chloride was used. The cell held perfectly, and at the end of the run the electrolyte and metal were easily removed. This type of electrolytic vessel is highly recommended for similar work. Care should be taken that the flange and bottom plate are well faced and that the lap is wide enough (at least 1½ in. (4 cm.)).

ANALYSIS OF CERIUM AND "MISCHMETALL."

Two methods of analysis were used in this research for the determination of cerium.

1. *Gravimetric.* The cerium group was separated from all the other metals by precipitation of the oxalates in faintly acid chloride or nitrate solution, by means of boiling oxalic acid. Calcination of the oxalates at blast lamp temperature gave the oxides (in the case of cerium the dioxide CeO_2) which were weighed.

2. *Volumetric.* A modification of Browning's[45] method was used. It depended upon the oxidation of cerous salt to ceric, in alkaline solution, by means of potassium ferricyanide. Browning determined the excess of ferricyanide.

The modification was as follows. A slight excess of a dilute solution of potassium ferricyanide was added to the solution of cerous salt, and KOH added. This precipitation was usually done in a bottle, which was afterwards centrifuged. The supernatant liquid was decanted thru a small Gooch filter to guard against any loss of precipitate. The ceric hydroxide was washed two or three times with hot concentrated KOH to remove the ferro- and ferricyanides centrifuging after each washing. The ceric hydroxide was then treated with potassium iodide solution, whereby the cerium is reduced to the cerous state and free iodine liberated, which latter is determined by titration with thiosulphate. By this method cerium may be determined in the presence of thorium and the other members of the cerium group. This method is accurate to one-half percent.

Grams cerium present	Grams cerium found	Error Grams	Error percent
0.22648	0.22697	0.00049	+0.2
0.22648	0.22657	0.00009	+0.04
0.22648	0.22697	0.00049	+0.2
0.22648	0.22752	0.00104	+0.5
0.22648 Ce 0.4 $Th(NO_3)_4$	0.22737	0.00089	+0.4
0.11328 Ce 0.10 $La_2(SO_4)_3$	0.11388	0.00060	+0.5

Analysis of a sample of "mischmetall" by the volumetric method showed a cerium content of 70.5 percent.

Analysis of metallic cerium prepared in Run 1, above, showed the following composition:

Percent Cerium	Percent Iron
97.5	1.2
97.8	
97.8	

The determination of cerium by the gravimetric method in the cerium metal prepared in Run 4, above, showed 97.8 percent cerium.

Analysis of cerium cast into rods in an iron mold was as follows:

Percent cerium	93.6
" iron	4.5
" insol residue (oxide)	0.53
" magnesia (from MgO lining)	0.4
" carbon	0.88
" chlorine	0.07
	99.98

PURIFICATION OF METALLIC CERIUM.

The chief impurities of cerium (amounting in the aggregate to about two percent) obtained by the method previously described consisted of iron, cerium oxide and cerium carbide, of which over one percent was iron.

Owing to the fact that metallic cerium is but slowly attacked by concentrated sulphuric acid, filings of the metal were boiled with this acid. All of the iron was not dissolved, and the method is worthless for purification purposes.

The magnesium alloys of cerium, containing from 50 to 85 percent cerium, are brittle and may easily be pulverized to a fine powder. When digested with strong sulphuric acid for a few hours, the residue contains cerium, magnesium and iron. This method is also worthless.

The best method of purification consists in preparing the cerium amalgams. The amalgams are prepared by boiling mercury with cerium in a long iron pipe arranged with a condensing tube at the top. Solid amalgams are easily obtained by this method. The iron and impurities float to the top and may be skimmed off. The amalgams carefully prepared give only a very slight test for iron. The cerium and mercury may be separated by distilling the latter, but this must be done in a high vacuum to prevent oxidation of the cerium. A high temperature is required to drive off all the mercury. The amalgam should be placed in a magnesia vessel, and this in turn heated in an evacuated quartz vessel. The high temperature required would cause the collapse of an evacuated glass vessel.

PHYSICAL PROPERTIES OF METALLIC CERIUM.*

In the determinations of the physical properties, metal of approximately 98 percent of cerium was used, unless otherwise specified.

1. Atomic Weight. The atomic weight of cerium, determined from pure salts, is 140.25.

2. Specific Gravity. The specific gravity determinations were made in a 50 c.c. pyknometer of cylindrical form, with thermometer ground in central neck and with fused-in capillary tube at side. The liquids used were pure benzene and toluene, which have no chemical action on cerium. Several different specimens of metal were used for these determinations. The weight of metal taken varied from 3.4 to 11.2 grams. The average of determinations gave 6.92, at 25° C. Muthmann[56] found the specific gravity at 20° equal to 7.0424, and Hillebrand[57] gives a value of 6.728 for his remelted cerium.

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*Some of the physical and chemical properties of cerium have been determined by Hillebrand, 21 and 55, and by Muthmann and his associates, 23-24.

3. *Molecular State of Aggregation.* No reference was found in the literature as to the crystallographic properties of cerium. Attempts were made by the writer to obtain crystals, but without success. The interior of many ingots of cerium were highly crystalline, especially in the center of blow holes. The best condition for crystal growth is slow cooling from the molten condition. In order to aid the formation of crystals, a small quantity of cerium was melted under lithium chloride. The crucible was kept just hot enough to prevent the lithium chloride from solidifying, and was maintained at this temperature for several hours. The melting point of lithium chloride (about 550°) is somewhat below the melting point of cerium, and under these conditions the formation and growth of crystals would be expected. However, no definite crystals of cerium were obtained.

FIG. 9. × 70

In order to examine the inner structure of cerium, photomicrographs of different specimens were made. The specimens were prepared by dry-polishing, and were etched with alcoholic HCl. An examination of these photomicrographs (see Fig. 9) shows homogeneity of structure.

4. *Hardness.* For the determination of hardness the scleroscope was used. The hardness of cerium varies, depending upon whether the surface of the metal is rolled, freshly cut, or old. The average value of the hardness for rolled surface was 25.9. The average for freshly cut surface was 9.5. (The reading 100 is the hardness of the standard steel test plate.)

5. *Tenacity.* Cerium is malleable and highly ductile. A strip of cerium was rolled to a thin sheet of a thickness of 0.015 mm. Cerium metal can easily be cut with a knife or scissors, and can be machined fairly well, although there is some tendency for the metal to buckle, as does lead.

6. *Electrical Conductivity.* In order to make these measurements, a test bar was necessary. A good method of obtaining a known length and cross-section of metal is to take a short piece of capillary tubing, apply suction at one end, insert the other in the molten metal and so fill the tube. On account of the corrosive action of cerium on glass and silica, it was impossible to use this method.

It was difficult to cast cerium into solid rods, owing to its rapid oxidation in air. The following mold was prepared, which was so designed that molten cerium could be quickly poured into it from the melting crucible and oxidation prevented: A wrought-iron pipe, ¼ in. (0.65 cm.) inside diameter and about 5 in. (13 cm.) long, was screwed into an iron base. A piece of cast iron was turned on the lathe to the shape of a small funnel, and was screwed into the wrought-iron pipe. The cerium was melted in a magnesia-lined graphite crucible under a covering of fused salt. The mold was heated to a dull redness, and the entire contents of the crucible poured suddenly into the mold. Very little oxidation or burning of the metal occurred. A rod of cerium 3 in. (7.5 cm.) long was obtained. This metal contained 93.6 percent cerium and 4.5 percent iron. Altho the inside of the pipe had been carefully cleaned, it was impossible to prevent contamination of the cast cerium with iron. As it was necessary to pre-heat the mold, a small amount of iron oxide necessarily formed, and, on contact with cerium, was reduced to metal and entered the rod as an impurity. The rod was turned down to size on the grinder.

The electrical conductivity measurements were made by the voltmeter-ammeter method. The potential drop was taken over one inch of test bar, and all measurements were made at room temperature. The current was varied from 6 to 18 amperes. The specific resistance of the sample was found to be 71.6 microhms per centimeter cube.

7. *Magnetic Properties.* Stefan Meyer[46] has measured the magnetic susceptibility of many metals, among them that of cerium. He gives the atomic magnetic susceptibility of cerium ($K \times .10^{-6}$) equal to 34. He does not state the purity of the cerium used. The writer made no attempt to measure the magnetic susceptibility of cerium, but simply to determine if cerium is dia- or para-magnetic.

A small piece of cerium was suspended by a silk thread in a magnetic field of intensity about 5,000 lines per cubic centimeter. The metal so tested was paramagnetic, but not strongly so.

Cerium amalgam practically free from iron was sealed in a small glass tube and was tested in a magnetic field. It was weakly but definitely paramagnetic. From these determinations it was concluded that pure cerium is paramagnetic.

8. *Melting Point.* It was impossible to use the ordinary thermocouple method to determine the melting point, as no suitable protecting mantle could be found. Silica and porcelain are both attacked by cerium at its melting point. Magnesia, which is unattacked, is too porous a material for this purpose.

An attempt was made to obtain a cooling curve of cerium. About 60 grams of the metal were melted in a magnesia crucible in an electric resistor furnace and readings were taken with a small copper-constantan couple placed in a porcelain mantle. It was thought that altho the porcelain would be attacked somewhat, an approximate value for the melting point might be obtained. However, the cooling curve showed no constant temperature period and was worthless.

A small piece of cerium was attached to two long copper wires by means of small copper bolts and nuts, such as are used by watchmakers. Good electrical connection was obtained in this manner. The cerium was placed in a long Jena glass tube, sealed at one end and closed at the other by means of a rubber stopper, and so arranged that the tube could be evacuated. This was then placed in a tube furnace containing a calibrated thermocouple. A small amount of current was passed through the cerium, and when connection was severed, an electric gong sounded. This scheme of obtaining the melting point did not work, as the rubber stopper connection did not give a perfectly air-tight joint. The small amount of air in the tube combined with the cerium as the temperature increased. This caused a higher vacuum to be produced, with the result that more air entered the tube, and, upon subsequent repetition of this process, all the cerium was oxidized before the melting point was reached.

The approximate melting point was determined by heating a small quantity of cerium in a magnesia-lined graphite crucible and reading the temperature at which the metal softened by means of a thermocouple placed just above the metal. This crude method gave the approximate melting point as about 700°.

The real melting point of cerium was determined as follows: A small piece of cerium foil was fastened to two bent platinum wires by means of small copper bolts and nuts, and placed in a small glass bulb and the platinum wires sealed through the glass. The bulb was then evacuated by means of a mercury rotary pump, and sealed. A small incandescent lamp was connected in series with the cerium, which was heated in an electric muffle furnace. The temperature was read by a calibrated thermocouple. The melting point of the cerium was very definite, and occurred at a temperature of 635° C. The tube collapsed somewhat, but the method gave satisfactory results.. The melting point obtained by the writer corresponds fairly closely with the value 623° C. given by Muthmann.[58] Hillebrand[57] says the melting point lies between those of antimony and silver.

9. Ultimate Strength. The same test bar was used for these determinations as in the electrical conductivity measurements. The ultimate strength was determined in an Olsen testing machine. The average diameter of the test bars was 0.212 in. (0.55 cm.). There was no elongation with constant load at 350 pounds (159 kg.). The test bar broke with a snap (like cast iron) at 495 pounds (225 kg.). The ultimate strength was equal to 12,900 pounds per square in. (9 kg. per sq. mm.).

10. Specific Heat. The specific heat was determined in a Joly differential steam calorimeter. The principal difficulty encountered was to get a suitable method of protecting the cerium from attack by the steam. The cerium was sealed in a glass tube, but this method was unsatisfactory, owing to the time necessary for exchange of heat due to the small conductivity of the glass. Another method employed for protecting the cerium was to coat it with a mixture of amyl acetate in collodion. However, this coating was attacked by the steam and was liable to peel. The metal was also placed in a small nickel box, but was attacked by the steam. The best method of protecting cerium, at the same time allowing for rapid heat interchange, was to wrap the cerium tightly in several thicknesses of tin foil. Blanks were run on copper and tin foil to check the accuracy of this calorimetric method. The values for the specific heat of copper obtained with this steam calorimeter was equal to 0.0925. The specific heat of cerium (20-100°) was measured and found equal to 0.0524. Mendeleef[47] gives the specific heat of cerium equal to 0.05. Dr. W. F. Hillebrand[60] determined the specific heat of cerium by means of Bunsen's ice calorimeter. He gives corrected value of 0.04479 for pure cerium, and used only about 2 grams of metal in a determination. The writer used more than 70 grams of cerium in a determination, and obtained a corrected value of the specific heat of pure cerium equal to 0.05112.

11. Heat Conductivity. No measurements were made on the heat conductivity, and no references were found in the literature relative to this property. The heat conductivity seems to be fairly high, and, if so, cerium is probably one of the exceptional metals which has a low electrical conductivity and high thermal conductivity.

12. Latent Heat of Fusion. From observations on melting cerium, the latent heat of fusion seems to be fairly high. It has not been determined to my knowledge.

13. Heat of Oxidation. The heat of oxidation was determined in a Mahler bomb calorimeter. Cerium must not be burned in contact with platinum, as it will alloy with the latter. The cerium filings were placed in a small magnesia crucible in the calorimeter. From one to two grams of cerium filings were used for each determination, under an oxygen pressure of about fourteen atmospheres. The average value of the heat of oxidation was 1,740 calories per gram, or 60,900 calories per gram equivalent (CeO_2 = 243,600). These values are probably correct within 4 or 5 percent. It is difficult to obtain an accurate value for the heat of oxidation where the products of combustion are non-volatile. The determinations in the case of cerium were unusually difficult to make, for the following reasons: The metal should be in a finely-divided form, but preferably in the shape of filings. When cerium is filed, care must be taken to prevent oxidation, owing to the low kindling point. A small amount of oxide forms in any case, and therefore makes the sample of metal taken non-uniform. If the filings are too coarse, oxide will fuse on the surface, and the metal in the interior will be unoxidized. Many of the difficulties encountered in the determination of the heat of oxidation of silicon[48] were met with here. Muthmann[59] gives the heat of oxidation of cerium equal to 1603 cal. per gram.

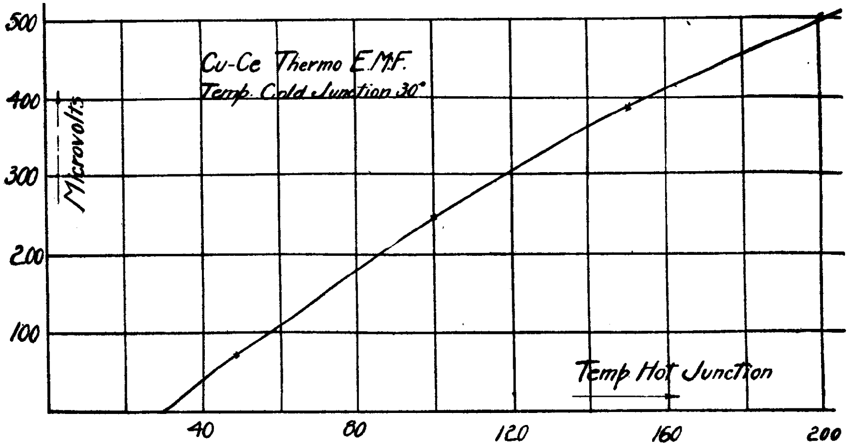

FIG. 10.

14. Single Potential. Attempts were made to measure the single potential of cerium in the alcoholic solution of cerium chloride. No reliable measurement could be obtained, owing to the rapid formation of a film on the polished surface of the metal as soon as current flowed. The potential rapidly decreased as soon as the film appeared, which is almost instantaneous with the passage of current.

Measurements on the decomposition potential of the anhydrous mixed chlorides in absolute alcohol were made, using platinum electrodes. Gas was evolved at an applied electromotive force of 3.5 volts.

As the single potential of cerium could not be measured successfully, its value was calculated from the thermal data taken from Matignon's article on the anhydrous mixed chlorides:

Heat of formation of $CeCl_3$ (per 3Cl) = 270 calories
Heat of solution of $CeCl_3$ = 33 calories

The calculated decomposition potential of normal cerium chloride in aqueous solution is equal to 4.3 volts. Therefore the single potential of cerium in normal solution of its chloride measured against the normal calomel electrode is equal to —3.16 volts.

15. Thermo-electromotive Force. Two small glass cells, protected by asbestos and fitted with wooden covers, were used. Standard thermometers with small stirrers attached were inserted through the cover. Cottonseed oil was used for the bath, and one of the cells was heated internally by means of several coils of resistance wire. The electromotive force was determined by the potentiometer method with a special piece of apparatus specially prepared for this kind of work. The thermo-electromotive force of cerium against copper is given in the table below and in the curve shown in Fig. 10. The current flowed at the hot junction from copper to cerium. The measurements are given in the following table:

Hot Junction	**Cold Junction**	**Electromotive Force**
49.2 C	29.2 C	0.000075 Volt
100.	25.	0.000770 "
100.	Red. to 30.	0.000250 "
151.	26.9	0.000399 "
151.	Red. to 30.	0.000387 "
200.5	29.7	0.000504 "
200.5	Red. to 30.	0.000502 "

16. Optical Properties. Cerium alone could not be used, owing to the fact that a thin film of oxide forms on the polished surface. Different alloys of cerium were tried, and the best ones for this purpose were found to be the magnesium-cerium alloys. The preparation of samples had to be done very carefully, as fine emery and rouge entered the soft surface of the cerium. Dry polishing with a very fine file (the finest obtainable) was the most satisfactory way of preparing the sample. For the methods of measurement of the optical properties the reader is referred to the article on the subject by Ingersoll and Littleton[49] on "A New Method of Determining the Optical Constants of Metals." The constants determined on the magnesium-cerium alloys are given in the table below:

Per cent Cerium	n	k
83	1.60	1.74
61	1.43	2.30
26	0.73	4.79
Pure Mg	0.32	12.0

CHEMICAL PROPERTIES OF METALLIC CERIUM.

Metal of approximately 98 percent cerium content was used in these determinations.

Cerium is very slightly attacked by cold water, but in boiling water a slow evolution of hydrogen gas occurs and the metal is tarnished black. At room temperature the following solvents have no action on cerium: Ethyl alcohol, amyl alcohol, chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated ammonium hydroxide, concentrated sodium hydroxide. Ethyl ether has a very slight action on the metal, as have also 3 percent and 30 percent hydrogen peroxide at room temperature. The action of dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated and dilute nitric acid, in the cold, is moderately vigorous. Ammonium chloride and potassium chloride, at room temperature, have moderate action on the metal. This may be explained by the fact that in water a small amount of cerium hydroxide forms which is soluble in potassium chloride and ammonium chloride, thus causing fresh surface of the metal to be exposed and resulting in moderate attack of the metal by the solvent. At boiling temperature the following solvents did not attack the metal. Chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated ammonium hydroxide. The metal was only slightly attacked by the following solvents at boiling temperature: Ethyl alcohol, amyl alcohol, ethyl ether and concentrated sodium hydroxide. Dilute nitric acid, ammonium chloride, potassium chloride and 3 percent hydrogen peroxide at boiling temperatures gave moderate action. Dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated nitric acid and 30 percent hydrogen peroxide gave vigorous evolution of gas at boiling temperature.

The action of various gases on cerium was studied. A small amount of cerium filings was placed in a porcelain boat in a hard glass tube. The air was displaced by the gas under test, and the tube heated gently by means of gas burners. The cerium filings heated in chlorine emitted a very bright light at a temperature of 210° to 215° C. The salt formed was tested and found to be anhydrous cerous chloride.

In bromine, cerium burned at a temperature of 215° to 220° C. with emission of less light than in the case of chlorine. The salt formed in solution in water, and was identified as the bromide.

In iodine vapors no light was emitted, altho the tube was heated to a temperature of 300° C. On examination of the contents of the tube it was found that some iodide had formed.

Cerium burned with luminescence when heated in air to a temperature of 160° C. If a lump of cerium is sealed in a glass bottle and kept warm for some time, a black powder is seen to form upon the surface of the cerium, and when the bottle is opened this powder ignites at room temperature. This is probably due to the formation of a highly pyrophoric suboxide of cerium.

When cerium filings are heated to 345° in hydrogen gas, the hydride forms without emission of light. The hydride has been described and studied by Muthmann.[50]

Cerium filings were heated in nitrogen to a temperature of 1000° C. No luminescence was observed, but some nitride was formed. This nitride is a black powder, and has been studied and described by Matignon.[51]

When the nitride is heated in potassium hydroxide solution, evolution of ammonia gas occurs. When exposed to air the nitride gradually changes over to a brown oxide.

Cerium filings were heated in the vapors of sulphur. When the black substance which is formed is treated with dilute sulphuric acid, sulphuretted hydrogen is evolved. Cerium sulphide has been studied by various investigators.[52]

Cerium filings were heated to a temperature of 500° C. in an atmosphere of carbon monoxide. There was no visible reaction, but part of the filings appeared oxidized.

ALLOYS.

A number of different alloys of cerium were studied, and are described below. In most cases the alloys were high in cerium, usually containing about 70 percent cerium. The metals were weighed out in the proper proportions, using from five to ten grams of cerium. The cerium was first melted in a small porcelain crucible under a layer of sodium chloride, and the other metal added in small pieces. The porcelain crucible was, of course, attacked by the cerium, but it was found that a thin layer of silicide of cerium forms, and this protects the crucible from further attack. The metal can in most cases be removed without breaking the crucible if care is exercised, and therefore one crucible serves for several melts. The silicide does not appear as a contaminant in the alloy. Porcelain crucibles were used except in cases where especially pure metal was desired, when magnesia crucibles were employed.

The work on the alloys of cerium is presented below in an epitomized form. The time at the writer's disposal was such that a complete study of each alloy could not be made. However, specimens of all the alloys described have been preserved and will be used for future references.

Muthmann and Beck[24b] have described some of the alloys of cerium with zinc, aluminum, magnesium and mercury.

Silver. Silver alloys with cerium quietly, and the thermal change appears to be small. The alloy has a silvery-white luster, and is hard and brittle. From all appearances, a compound is probably formed between cerium and silver.

Gold. When gold was added to molten cerium there was a slight flash from the crucible, but the reaction was not violent. The alloy was fairly soft, and had a reddish appearance. It disintegrated somewhat on ageing, forming a purplish-black powder.

Platinum. The reaction between cerium and platinum appeared to be endothermic. The alloy was fairly hard and was pyrophoric. It disintegrated to a slight extent when aged.

Copper. The cerium-copper alloy was hard and brittle, altho the two component metals were soft and malleable. A compound is probably formed. The alloy disintegrated to a powder.

Tin. This alloy was formed with the evolution of much heat. When first made, the alloy was pyrophoric, but on standing for a few months a powder formed, showing that the alloy disintegrated slowly when exposed to the air.

Antimony. There was considerable evolution of heat on the formation of this alloy. The alloy was very soft and was non-pyrophoric. It did not oxidize or disintegrate on ageing.

Arsenic. The reaction appeared to be exothermic. The alloy was fairly soft and somewhat pyrophoric. It did not decompose on being kept.

Carbon. Carbon and cerium combine directly when heated together. The carbide has been referred to and described earlier in this article.

Silicon. Cerium and silicon form the silicide $CeSi_2$. This compound may be formed by the reduction of the oxide of cerium. Large amounts of the mixed silicides have been prepared by the writer. The following mixture is recommended for their preparation:

M_3O_5	1,000	grams
Powdered graphite	200	"
Powdered silicon	450	"

The silicide of cerium is somewhat brittle, and may easily be pulverized to a fine powder. It is a splendid reducing agent. When the silicide is added to cerium so that the silicon content is about 15 percent, a good pyrophoric alloy is obtained.

Sulphur. The preparation of the sulphide has been referred to earlier in this article.

Selenium. Some reference is found in the literature to the selenide of cerium. Mosander reduced the selenite in a stream of hydrogen and obtained a brown substance of a disagreeable odor. Moissan has shown that the selenides may be obtained by the action of selenium fumes on cerium carbide.

Selenium was added to molten cerium. The reaction was very vigorous, and was accompanied with the evolution of reddish fumes. The melt consisted of two portions, a powder and a metallic alloy. The powder was impure cerium selenide, and the alloy, which was pyrophoric, apparently consisted of the selenide dissolved in excess cerium.

Tellurium. No reference was found in the literature to the telluride of cerium. Tellurium combined vigorously with molten cerium, giving a brownish pulverent mass, which was probably the impure telluride. When treated with dilute acids, the well-known odor of hydrogen telluride was detected.

FIG. 11. × 200

Lead. When lead was added to molten cerium, a violent reaction occurred, causing a portion of the contents to be ejected from the crucible. The alloy was very soft, and emitted sparks of a reddish color when scratched with a file. The alloy disintegrated slightly on ageing.

Calcium. Calcium alloyed with cerium quietly, without evolution of much heat. The alloy was white and was harder than either constituent. When scratched with a file it emitted a cluster of bright sparks. It is stable in air, oxidizing very slowly. The alloy did not disintegrate.

Sodium. Sodium alloyed with cerium quietly. The alloy was hard and slightly pyrophoric. It oxidized somewhat when exposed to air.

Aluminum. Aluminum alloyed with cerium fairly quietly. The alloy was very hard and brittle. It disintegrated without oxidation. A compound of aluminum and cerium was probably formed. This alloy was not pyrophoric. Muthmann[61] describes a compound $CeAl_4$.

Zinc. The combination of cerium and zinc was accompanied by a vigorous, in fact, almost explosive, reaction. There was a large amount of heat evolved. The alloy was hard, brittle and pyrophoric, and remained unoxidized when exposed to atmospheric conditions.

Cadmium. Cadmium and cerium combined vigorously with considerable heat evolution. The alloy was hard, brittle and pyrophoric. On exposure to air a film of oxide formed slowly, but the alloy did not disintegrate.

Chromium. The alloy was white in color, hard and brittle. It was somewhat pyrophoric. It remained unchanged in the air.

Manganese. Manganese combined quietly with cerium, forming a fairly hard, pyrophoric alloy, stable in air.

Iron. The iron-cerium alloys are very interesting, as they were the first pyrophoric alloys known, and were discovered by Dr. Auer von Welsbach. The alloys of about 70 percent cerium content are fairly hard and somewhat brittle. The microstructure of one of these alloys is shown in Fig. 11. It is seen that the structure is heterogenous, probably consisting in part of a cerium-iron compound. These alloys have been the subject of some discussion in the literature,[53] as have the reasons for the pyrophoric properties.[54] The writer believes that the question of the pyrophority depends upon the following factors: Cerium alone is soft and malleable, and when scratched with a file, small particles are not broken off. However, when the alloy is hard and brittle, small particles are easily detached from the mass, and the friction is sufficient to raise the temperature of these small particles to the incandescent point of cerium (160°). As metallic compounds (such as Cu_3Sn) are as a rule hard and brittle, the addition of such compounds to cerium usually assures a pyrophoric alloy. The alloy should be high in cerium, so that ignition occurs at a low temperature, and should contain excess of cerium above that required for the formation of a compound (such as $CeSi_2$) to act as a binder and so prevent the disintegration of the alloy, as in the case of the cerium-aluminum alloy containing about 60 percent cerium. The kindling point of the alloy may be lower than that of cerium.

Nickel. The nickel-cerium alloys made were similar to the iron alloys, but were somewhat softer. The ones high in cerium were very pyrophoric.

Tungsten. Powdered tungsten equivalent in weight to 15 percent was added to molten cerium. The tungsten dissolved fairly quickly and the reaction was quiet. The alloy was hard, brittle and pyrophoric.

Mercury. Cerium forms amalgams fairly easily. Their preparation has already been described under the methods of purification. The amalgams containing only 1 or 2 percent of cerium are liquid, but the ones of higher percentage are solid. These amalgams oxidize easily in the air, and those containing 8 or 10 percent cerium take fire in the air. Cerium will dissolve in mercury to the extent of about 15 percent.

Magnesium. The whole series of these alloys were prepared, and have been discussed under optical properties. The alloy containing about 83 percent cerium is highly pyrophoric. Most of these alloys are brittle and can be easily pulverized. Excellent flashlight powders can be prepared from the ones of higher cerium content. These alloys also form splendid reducing agents, as the combination of cerium and magnesium is an endothermic reaction, and when the alloy is oxidized, more heat is emitted than from an equivalent mechanical mixture of the two constituents. The fact that the alloys of from 60 to 75 percent cerium content may be easily pulverized in a mortar to a fineness of 200 mesh should render these alloys valuable for thermal reductions. A small amount of metallic vanadium was prepared by reducing V_2O_5 by this method. The alloys of from 75 to 85 percent cerium content can be pulverized, but they are so highly pyrophoric that it is difficult to prevent igniting them.

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DISCUSSION.

PROF. C. L. PARSONS: I cannot help rising to say a few words in praise of the work Dr. Hirsch has accomplished. Anyone who has attempted to do anything with the old Muthmann method for the obtaining of cerium knows something of the difficulties which have to be overcome to get even a very small yield of the metal; and it is certainly a very decided increase in our knowledge to understand that, with a common piece of apparatus which anyone can make readily in his own laboratory from wrought iron pipe, we can get cerium in some quantity. Also, I want to say that I hope from this paper interest will be engendered so that we may find some uses for this metal, because cerium is not anywhere near so rare a metal as many people are inclined to believe. Certainly, cerium salts can be obtained in very large quantities, and there will be no difficulty whatever in making a great many compounds of cerium, especially as cerium is now probably the most easily separated of any of the rare earths. Taking the crude material as it comes from the Welsbach Company, cerium can be separated practically in a single operation over 99 percent pure, and accordingly we may hope to see cerium metal, if uses can be found, presented at a very low price. If you take a 30 percent solution of ceric bromate, the rest being water, and simply roll up a piece of filter paper so that it looks like a firecracker, and dip that into the ceric bromate, and hold it out, it goes off like a firecracker in about half a minute. I was in my laboratory one day when Professor James was working with some of that ceric bromate which he had been making an effort to crystallize. He had it in his hand after partial evaporation in a vacuum, and while stirring it the rod went through the bottom of the beaker, and the contents went down on his shirt sleeve. There was a series of pyrotechnics that I can assure Dr. Hirsch beat that which they had with the specimen of which he spoke.

PROF. J. W. RICHARDS: Mr. Hirsch's paper on cerium is, to me, an extremely interesting one, because recently I have had occasion to look up this matter of the sparking of cerium alloys. The question has come up as to what causes the sparking of these alloys, and I have put a great deal of attention on it to find out the reason why. The very pure cerium is quite soft, like lead, and when you cut it with a knife, you get a shaving. The cutting off of the shaving does not bring it up to the ignition point. After examining a number of alloys and comparing them with the pure metal, I came to the conclusion that the spark-giving property (which is utilized so largely now in automatic sparking devices) is due to the brittleness of the material, that is, its brittleness in the sense that when it is scraped or scratched by a knife it gives off fine particles. This is not brittleness in the sense that it easily breaks, like chalk, but such that on scratching it with a knife it gives off a spray of fine particles. The energy absorbed in detaching those particles raises them to the ignition point, and then you have the ignition or sparking phenomena. I have experimented with a number of these alloys myself, and I have come to the conclusion that in every case the brittleness as thus defined is the inherent cause of the usefulness of the alloy as a spark-giving metal.

DR. J. W. BROWN: I notice that the alloy of aluminum is stated to be very hard and very brittle, and yet it does not possess this property of giving sparks, according to the theory advanced in your paper. Is this alloy an exception?

MR. A. HIRSCH: In the case of aluminum, I believe that a compound is formed containing about 55 percent of cerium, and this compound does not give the sparks, because in most cases you must have a percentage of about 70 of cerium in order to get this pyrophoric phenomenon. The silicide itself does not give sparks, but if you take that silicide and add to it enough cerium metal to bring the percentage up to about 70 or 75, you get a very good spark. If you have cerium present to act as a binder, and the percentage of cerium is about 70, you usually get the pyrophoric alloy.

Mr. C. A. Hansen: Can pyrophoric alloys be made by dissolving misch-metal carbide in various metals?

Mr. Hirsch: Cerium carbide is pyrophoric, but it decomposes.

Mr. Hansen: How about iron-cerium carbide?

Mr. Hirsch: In the presence of moisture, this also decomposes.

Mr. Hansen: The alloy, then, would not be permanent?

Mr. Hirsch: It would not.

Prof. Richards: As a matter of scientific accuracy, I would like to call attention to the fact that what we are discussing as a "pyrophoric alloy" is not pyrophoric at all in the true dictionary sense of that term. A pyrophoric material is something which takes fire spontaneously in the air. The use of the term "pyrophoric alloy" originated with Dr. Welsbach when he discovered these sparking alloys, and he used the term "pyrophoric alloys" for the cerium alloys which when scratched gave off sparks. The term "pyrophoric alloy" was thus invented, or used, by Dr. Welsbach in describing these strongly sparking alloys.

I may say that when you start with pure cerium and *increase* the amount of alloying metal, you eventually get a maximum of brittleness. As you increase the amount of alloying metal, you get a greater and greater pyrophoric quality and effect, until at a certain point it reaches a maximum, after which it decreases. That is clearly described in the fundamental Auer von Welsbach patent for pyrophoric cerium alloys.

Dr. E. F. Northrup: Did you make observations to find out whether there is any chemical action whatever of the molten cerium on quartz or silica?

Mr. Hirsch: Cerium melts at a temperature of 635°, and when heated 50° to 100° above its melting point, I believe it acts upon quartz.

Dr. Northrup: Have you made wire of it?

Mr. Hirsch: No, I have not made wire. That is, I have cut wire, but I have not drawn it with a die.

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A report of progress presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

STANDARD METHODS RECOMMENDED FOR TESTING OF DRY CELLS.

A Report of Progress by the Committee on Dry Cell Tests.

This report is presented as a tentative one, subject to such revision as may be indicated as desirable by the American Electrochemical Society and by the members of this Committee. The Committee urgently requests that a full discussion be given, as the Committee feels the necessity of securing all the assistance possible in getting this report into a final and acceptable form.

When the American Electrochemical Society voted that a Committee be appointed to formulate standard methods of testing dry cells there were, apparently, among the voters those who held an impression that the task was not a difficult one and that tests could be devised which for simplicity and convenience would be comparable to the simplicity, modest proportions and values of the dry cell itself. The difficulties, however, will be as apparent to others as they have been to the Committee, when considering the various factors which must necessarily be taken into account.

The methods of testing must in the first place be of benefit to those interested in dry cells, and the users may be divided into three classes: The average ultimate consumer, the large user, and the manufacturer.

No standard methods of testing have been devised, or, we believe, can be devised, which will be suitable at once for all of these classes, and the most serious obstacles are encountered in formulating methods suitable to the first class. This is unfortunate, since by far the larger proportion of the dry cell output is so distributed that the user is interested in one, two, six, or perhaps twelve cells as supplying his yearly requirements. This very large number of users should have a test the cost and labor of conducting which should not be out of proportion to the low values of the articles tested. There appears to be no adequate means of meeting this urgent demand for simplicity of equipment and method.[1]

The fact that there is no "X-ray" method of examining a cell to see how much energy it contains, involves the alternative method of destroying the cell to determine its energy content, and this becomes of serious moment to the ultimate consumer class. In fact, insofar as the user is concerned, your Committee must agree with Dr. Baekeland, who says that "the test for the dry cell is to use it for a particular purpose."

The large users of dry cells, such as telephone exchanges, engine manufacturers, installers of alarm and signal devices, railroads, etc., who purchase cells in large quantities, are especially interested in testing methods. Various methods of testing have been evolved by these users as a basis for purchase specifications and as a means of judging the relative merits of the various makes of cells on the market. To them the matter of elaborateness of tests is of *less* importance than to the small user.

Of even greater importance is the testing of dry cells by the manufacturer, who must necessarily adopt methods which will give him the necessary information concerning his product, no matter how elaborate.

The methods of testing which the Committee is recommending are those which are particularly suited to the second class—the large users. These tests, if extensively adopted, will be of indirect benefit to the small consumer, and will be of mutual advantage to the large users and manufacturers.

The construction of dry cells, methods of manufacture, characteristics, properties, various uses, and methods of testing are discussed in various papers presented during the past four years before the American Electrochemical Society, and these papers constitute the most important literature, at least in this country, dealing with the dry cell.

Uses of Dry Cells for Ignition Service. J. W. Brown, Transactions, **13**, 173 (1908).

Certain Characteristics of Dry Cells. C. F. Burgess and C. Hambuechen, **16**, 97 (1909).

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[1] Trans. Amer. Electrochem. Soc., **17**, 365; **19**; 32.

Dry Cell Tests. F. H. Loveridge. **16,** 109 (1909).

Some Characteristics of the Modern Dry Cell. D. L. Ordway, **17,** 341 (1910).

Dry Cell Testing. W. B. Pritz, **19,** 31 (1911).

It has been suggested to this Committee that the methods for testing should include, aside from electrical measurement, methods of physical and chemical analysis, such that judgment may be made thereby of the merits of a cell, and that what constitutes a satisfactory product should be described in these terms so that they might form a basis of specification. There is a striking similarity between the various cells on the market as far as materials used and general structure are concerned. Exceedingly slight variations, however, which introduce large variations in the quality of the product, are not capable of detection by physical and chemical examination, and what is of even greater importance in determining the quality are the methods of assembling, such as methods of mixing, grading as to size of the particles which constitute the cell mixture, and methods of tamping, factors which cannot be easily determined by physical or chemical inspection of the resultant product.

The art of dry cell manufacture cannot be considered as having been worked out to a finality; improvements are being made and will continue to be made. One maker may discover a simple method of neutralizing the effects of an impurity on his product which may have a detrimental influence in another product, and a judgment based upon the detection of such impurity would thereby work an injustice. The tests, therefore, should be such as determine the ability of the cell *to produce results,* and these can be determined only by tests involving electrical measurement. The dry cell, in all of its multitudinous uses, is merely a source of electrical energy, and its ability to deliver this energy, in the quantity and at the times desired, constitutes the principal measure of value.

Dry cell tests may be conveniently divided into three main groups, viz.:

I. Tests to determine whether or not a cell is in good condition before being placed in service.

II. Tests to determine the actual or comparative service capacity of cells.

III. Tests to determine the rate of deterioration of cells on open circuit.

This classification is followed in this report. Long discussions of the points brought out have been avoided as much as possible, references to the literature where such discussions may be found being given instead.

TESTS TO DETERMINE THE CONDITION OF A CELL BEFORE USE.

I. Electromotive Force:[2]—The electromotive force of a cell may be read by connecting a voltmeter directly across the terminals.

Notes:—In new cells of various types the electromotive force may vary from 1.5 to 1.6 volts. If a cell of the type now in general use gives an E.M.F. five or more hundredths less than 1.5 volts it is an almost certain indication either of serious deterioration due to age, or of the external short-circuiting of the cell, or of some defect such as an internal short-circuit, which will soon render the cell unfit for service.

It is seldom necessary to measure the open circuit voltage of cells, since they are seldom deficient in this respect. It is a test which may be considered as secondary in nature, and should be applied when it is suspected that the cells are below standard, for example, when cells are received with wet jackets, when the terminals are corroded, when the electrolyte leaks from under the seal, or when the cells are abnormally low in short-circuit current.

An accurate or carefully calibrated voltmeter should be used, the resistance of which is sufficiently high to render the current flow through it inappreciable. A two-scale Weston instrument of 300 ohms resistance with 3-volt maximum deflection and 1,500 ohms with 15 volts maximum deflection has been found very satisfactory for both cells and batteries. Cheap pocket instruments are often so inaccurate as to make their indications of open circuit voltage worse than useless.

The effect of temperature on electromotive force is very slight, amounting to only a few hundredths of a volt between all ordinary

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[2] Trans. Amer. Electrochem. Soc., **16**, 103 (1909); **17**, 345 (1910).

temperature ranges. The voltage returns to normal with the temperature.

II. Short-circuit Current:—The short-circuit current of a cell may be obtained by connecting an ammeter directly across the terminals of the cell.

Notes:—The short-circuit current of a cell is of value only when coupled with a familiarity with the brand of cell in question. If the reading is normal for that brand of cell, it is reasonably certain that the particular cell is in good condition, and that it will probably give as good service as others of the same make. This applies only to cells of the same brand and make. That the short-circuit current of a cell of a new and unfamiliar brand is as high as that of another brand is no indication whatever of the equality of the service capacities of the two cells.[3] The short-circuit current bears no relationship to service, and when measured without reference to temperature or other conditions may be entirely meaningless and misleading.

The ammeter for reading short-circuit current should be dead-beat, and with its leads should have a resistance of 0.01 ohm, to within 0.002 ohm. Two 30-inch lengths of No. 12 lamp-cord make very convenient leads. The maximum swing of the needle should be taken as the short-circuit current of the cell.

The ammeter should be connected across the brass terminals of the electrodes. Low readings are apt to be obtained if the ammeter is applied to the carbon electrode directly.

In order to avoid high contact resistance, the terminals of the cells and of the ammeter leads should be brightened. It has been found very convenient to fit the ammeter leads with small terminals of lead. The contact on the cell terminals is greatly improved, and with such leads it is unnecessary to brighten the contacts.

For accurate measurement of the short-circuit current of a new cell, cheap instruments of the pocket type should be avoided.[4]

The effect of temperature on the short-circuit current[5] is quite pronounced. Between 10 and 80 degrees centigrade, the amper-

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[3] Trans. Amer. Electrochem. Soc., **13**, 178 (1908); **16**, 110 (1909); **17**, 346 (1910); **19**, 33 (1911).

[4] Trans. Amer. Electrochem. Soc., **16**, 117 (1909).

[5] Trans. Amer. Electrochem. Soc., **17**, 356 (1910); **19**, 37 (1911).

age of cells is raised on an average of about 1 ampere for each 10 degrees centigrade rise in temperature. This value varies considerably with different cells, and is somewhat greater at the lower (colder) end of the scale and less at the higher. At very low temperatures the effect is very pronounced, and it is often noted that cells received in extremely cold weather read but one or two amperes. On bringing them to room temperatures, however, the short-circuit current becomes normal and the cell is not impaired by the freezing.

III. Internal Resistance:[6]—This value is usually determined by applying the formula—

$$\text{Int. Res.} = \frac{V - V'}{C}$$

where V is the open circuit voltage of the cell, V' the closed circuit voltage, and C the current drain to which the cell is subjected in order to make the determination.

Notes.—The above formula gives a compound value, composed partly of the sum of the resistances of the various parts of the cell, and partly of the resultant of the various electromotive forces in operation during the action of the cell. The value obtained varies with the current flowing, the age of the cell, and the temperature.

For these reasons we advise against the use of this test. It indicates nothing in regard to the service capacity, nor does it give an exact value of the actual internal resistance of the cell.

SERVICE CAPACITY TESTS—GENERAL DISCUSSION.

Requirements for a satisfactory test:—In general there are but two reasons for desiring a service test upon dry cells:

1. To ascertain what life may be obtained from a brand of cells in a certain service.

2. To ascertain which one of several brands will give the longest life in that particular service.

With the former object in view the knowledge is best obtained by actual use of the cells in connection with the appliance. In some

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[6] Trans. Amer. Electrochem. Soc., **17**, 348 (1910).

cases this is the only feasible way in which the definite information sought can be obtained. The great majority of tests are carried on, however, with the second object in view, viz., the comparison of two or more brands of cells for use in a particular service. Where the amount of testing is large, it is impossible, even were it expedient, to use the actual appliances for testing cells, and it becomes necessary to devise special testing methods and apparatus such that results obtained therefrom shall be comparable to the results obtained from the cells when placed in actual service. This is, we take it, the one necessary condition which dry cell tests must fulfil.

There have been tests devised which seek to go further and make the operating conditions not only comparable, but as similar as may be to the operating conditions of the service for which the test is intended. Upon this point there is some diversity of opinion. Some authorities claim that a test is of greater value and is more reliable the more nearly the conditions of test approach those of service, and, following out these claims, have devised certain tests which are rendered quite complicated, requiring much attention and apparatus for their continuance, by the introduction into the method of some of the irregularities to be expected in service. It is questionable, however, if results of greater meaning are obtained from such strict adherence to service conditions. At best, such a test is but an approach to actual service, which must be continually varying from time to time and from locality to locality. Again, the apparatus necessary to carry on an irregular, intermittent test is very complicated and requires much careful attention. This feature limits its use to the large consumers and manufacturers.

Testing cells in series:—It has been suggested that cells of various makes be tested by connecting them in series and discharging them simultaneously through any suitable resistance, thereby assuring that the cells are discharged at the same rate and under identical conditions. There are several objections to this method[7] and we therefore advise against the testing of cells in this manner.

Judging Results:—In interpreting the results obtained from a test of various grades of cells, we wish to caution against

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[7] Trans. Amer. Electrochem. Soc., **19**, 36 (1911).

drawing definite conclusions from the outcome of a single test or of a small number of tests. When the matter of choosing a brand is of much importance, it is necessary to run a series of tests over a period of six months or a year. In this way a very good idea may be obtained of the average service results which may be expected.

In the following table are given the results of ten monthly tests completed during 1910 on two brands of dry cells. The values represent the length of service given:

Tests	1	2	3	4	5	6	7	8	9	10	Average
Brand A....	42	35	38	33	60	45	48	35	66	48	45.0
Brand B....	30	37	24	25.	27	40	48	42	40	40	35.3

It is very evident from a comparison of the averages of these tests that Brand A is much superior to Brand B, yet had the consumer only the results from tests 2 or 8, he would have undoubtedly arrived at a very erroneous conclusion regarding the real merits of the two brands.

SERVICE TESTS RECOMMENDED.

I. Telephone Service:[8]—Discharge three cells, connected in series, through 20 ohms resistance for a period of two minutes, each hour, during 24 hours per day and seven days per week, until the closed circuit voltage of the battery at the end of a period of contact falls to 2.8 volts.

The following readings are taken:

1. Initial open circuit voltage of the battery.
2. Initial closed circuit voltage of the battery.
3. Closed circuit voltage at the end of the first discharged period.
4. Closed circuit voltage at the end of a discharged period after three days, and weekly thereafter.

Report the results as the number of days during which the closed circuit voltage remains above the limiting value of 2.8 volts.

Notes:—Fig. 1 shows in diagrammatic form a very convenient and inexpensive method of carrying on this test.

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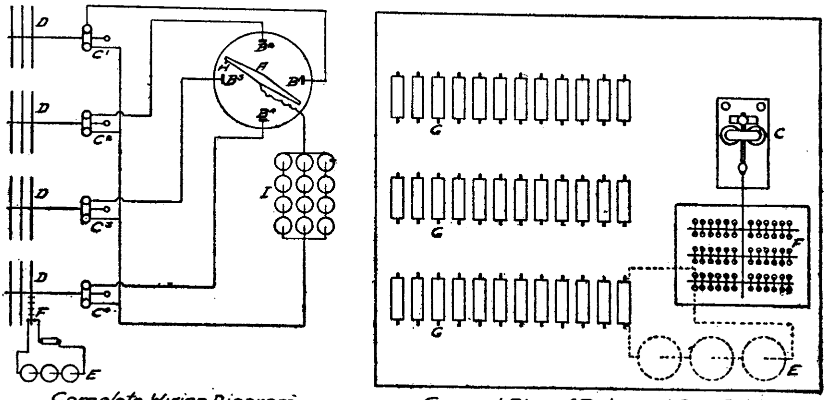
[8] Trans. Amer. Electrochem. Soc., **17**, 358 (1910); **19**, 41 (1911).

The left hand portion indicates the apparatus necessary and its arrangement. The hand of the clock *A* revolves once per hour, closing, by means of a suitable contact *H*, the circuit of the battery *I* in turn through the contacts B_1, B_2, B_3 and B_4, on the face of the clock. This current magnetizes in turn the cores of the relays C_1, C_2, C_3 and C_4, causing the extended armature arms *D* to fall, bringing the inverted *U* shaped fingers *F* into mercury cups, to which the terminals of the individual test circuits are connected. Each contact plate *B* is of such length that two minutes are required for the passage of the contact *H*.

At the right of the figure is shown one testing unit, consisting of the relay *C*, the mercury cups into which dip the contact fingers *F*, and the arrangement of the 20-ohm resistance coils *G*.

Telephone Test For Dry Cells.



Complete Wiring Diagram. General Plan of Relay and Coil Table.

FIG. 1.

The batteries *E*, are stored under the table on which the various parts are fixed. One complete test battery circuit is indicated by the dotted lines.

Fig. 2 shows a representative discharge curve obtained from a battery of three 2½ x 6 inch (6 x 15 cm.) cells of a well known brand. The curve passes through the values of the closed circuit voltage at the ends of the contact periods.

The test should be conducted in a dry place, and normal room temperature should be maintained as closely as possible.

II. Ignition Service:—Discharge six cells connected in series through 16 ohms resistance for two periods of one hour each per day, seven days per week. The periods should be eleven hours apart, but in cases where the circuits are not automatically controlled, the first and the last hour in the working day may be chosen for the discharge periods and the discharge omitted on Sunday, without materially affecting the results.

The following readings are taken:

1. The initial open circuit voltage and short-circuit current of the battery.

2. The initial closed circuit or working voltage, and the initial impulse of current which the battery is capable of forcing through a 0.5-ohm coil connected in series with an ammeter, and in parallel with the 16-ohm coil.

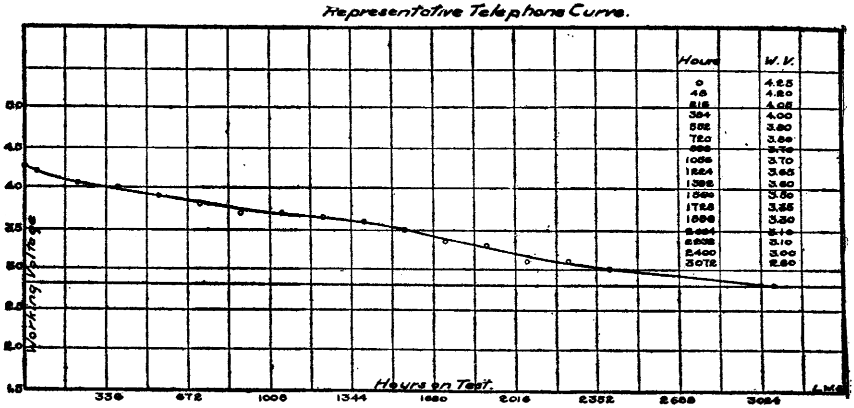


FIG. 2.

3. Closed circuit voltage and impulse current through the 0.5-ohm coil at the end of the first period of closure, at the end of the sixth period, at the end of the twelfth period, and after every twelfth period thereafter.

The test is considered completed when the impulse current at the end of a period falls below four amperes. Report the results as the number of hours of actual discharge to the limiting value of impulse current.

Notes:—Fig. 3 shows diagrammatically the arrangement for a single test.

When the number of tests is not large the circuits may easily be closed by hand. When a great many tests are to be made, it is convenient to arrange a clock-operated automatic circuit closing device.

By varying the length or number of discharge periods, the test may be made representative of any special cases of ignition. For a good comparison of the fitness of various cells for general ignition service however, the test as given above is to be recommended.

Particular care should be taken to keep the temperature of ignition test batteries as nearly constant as possible, as the service obtainable is greatly influenced by this factor, as shown by the following table in which are given the averages of five separate tests conducted at 5, 25, 35, 45, 55, 65, and 75 degrees centigrade.

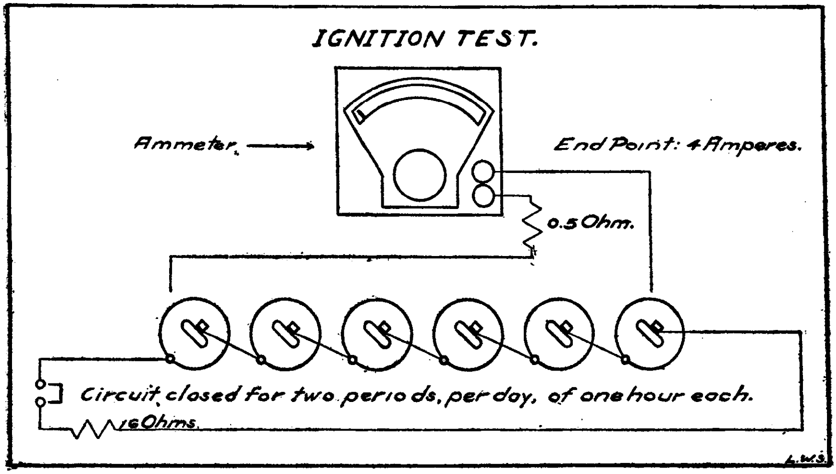


FIG. 3.

Temperature	5°	25°	35°	45°	55°	65°	75°
Hours service	31.9	46.3	50.4	46.2	35.6	29.3	26.6

The reasons for the adoption of the various constants of this test, viz., number of cells, resistance in main circuit, end point, and resistance in ammeter circuit, is fully described in the Trans. Amer. Electrochem. Soc. **13**, 178 (1908); **17**, 361 (1910), **19**, 43 (1911).

III. Flash-light Batteries:—Discharge the battery to be tested through a resistance of four ohms for every cell in series, viz., eight ohms for a two-cell battery and 12 ohms for a three-cell battery, for a period of five minutes once each day until the closed circuit voltage at the end of a discharge period falls to 0.75 volt per cell, viz., 1.5 volts for a two-cell and 2.25 volts for a three-cell battery.

The following readings are taken:

1. Initial open-circuit voltage and short-circuit current.
2. Initial closed-circuit, or working voltage.
3. Closed-circuit voltage at the end of the first, third and seventh periods of closure, and after each seventh period thereafter.

Report the results as the number of minutes during which the battery was discharged through the resistance to the given end point.

Notes:—In case the circuits are not operated mechanically, the results are not materially changed if the batteries are discharged only on working days.

Four ohms per cell is chosen for the resistance in circuit, since the tungsten bulbs generally used with a three-cell battery have a resistance of approximately 12 ohms.

Miscellaneous Services:—In addition to the telephone and ignition services, which are by far the most important services in which dry cells are used, there are numerous other services, among which may be mentioned the operation of automobile horns, sewing machine motors, small fans, toys, massage vibrators, cigar lighters, bells, buzzers, etc. In the aggregate these miscellaneous services consume enormous numbers of cells, but they are so numerous, and there are such variable conditions prevailing in each kind of service, that it would be useless to attempt to develop standard tests covering them.

It is not difficult for anyone particularly interested in any special service to arrange a suitable test for himself. Care should be taken to make the conditions of test, viz., number of cells, resistance in circuit, period of drain, etc. approximate those of the service in question.

RATE OF DETERIORATION ON OPEN CIRCUIT.

The voltage and short circuit current of the cells for test are read initially in order to insure that the cells are in good condition. The cells are then stored in a dry place of normal room temperature.

The following readings are taken:

1. Initial voltage and short-circuit current.
2. Short-circuit current at the end of four weeks, eight weeks and each eight weeks thereafter.
3. Voltage at the end of six months.

The cells are kept on the shelf until the short-circuit current has fallen below 10 amperes. This point is arbitrarily chosen, as it represents a point below which it would be difficult to market the cell. For practical purposes, the results are expressed as the number of months during which the short-circuit current remains above this cut-off point. Much more meaning, however, is attached to the rate at which the current falls, generally reported as the drop in amperage for a given period expressed as a percentage of the initial amperage. This is especially true when investigation of the quality of cells is the object. For practical purposes, however, the first rating given, i. e., months to 10 amperes, is perhaps preferable.

Notes: The results from this test are largely indicative of increase in internal resistance, and bear no definite relation to the service which the cells may give. However, this information, coupled with familiarity with a brand of cells, becomes a very good indication of its quality. It also serves to indicate any serious defects of manufacture.

The ammeter for reading short-circuit current should be dead-beat, and with its leads should have a resistance of 0.01 ohm. Two 30-inch lengths of No. 12 lamp cord make very convenient leads.

Particular attention should be given to the temperature at which cells are stored, as the rate of deterioration is influenced to a marked degree by the temperature of the cells.[9]

The ideal method for an open-circuit deterioration test would be the determination of the decrease of service capacity due to

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[9] Trans. Amer. Electrochem. Soc., **17**, 357 (1910); **19**, 39 (1911).

storage over definite periods. This practice, however, would entail much labor and expense where the amount of testing to be done is large.

THE ADAPTABILITY OF TESTS TO THE NEEDS OF THE VARIOUS CLASSES OF CONSUMERS.

The question may arise in the mind of the consumer as to what extent the cells he purchases should be tested. It obviously would not be practical for the small consumer to conduct tests on the same scale as those carried on by a consumer using many barrels of cells per year. It is impossible to formulate any set rules for sampling and testing for any consumer or group of consumers, as the amount of testing done must be regulated by the relation of the cost of testing to the value of the cells purchased. However, we present here suggestions as to the adaptability of these methods to several roughly classified groups of consumers.

The Small User:—In this class may be included the great percentage of consumers. The man who buys a few cells at a time for purposes of ignition, bell ringing, etc. Obviously it is out of the question for this class of consumers to conduct any sort of service test. The only safe course is the purchase of a reputable brand of cell. We would advise that, perhaps, every cell purchased thereafter be read for short circuit current, although as stated previously, this reading gives no direct indication of the service capacity of the cell, yet, if the reading is normal for that brand, it may be reasonably certain that the cell is in good condition and that it will probably give as much service as those of the same brand formerly purchased.

It would be impractical for the small user to provide himself with an expensive ammeter, as, for his purpose, a good make of pocket instrument will give readings sufficiently accurate. Such instruments, however, should be checked up occasionally with a standard meter.

The Small Dealer:—This class comprises those dealers who may dispose of from a few hundred to a thousand or more cells per year. The dealer is particularly interested in keeping the quality of his stock up to the standard. As cells are received a representative sample, *e. g.*, 10 percent chosen at random throughout the lot, should be read with a reliable make of ammeter. If the readings are normal it would scarcely profit to make any further tests. For his protection all cells should be read with the ammeter before being delivered to customers.

The Jobber:—The jobber buys and sells dry cells largely by barrel lots, and in many cases conducts no tests whatever. If he is desirous of keeping his quality strictly up to standard it would be well to open several barrels in each shipment and test with an ammeter a dozen cells chosen at random throughout the barrel.

If the large jobber wishes to carry the best grade of cell for any service, it would probably pay him to conduct the recommended telephone and ignition tests on a small scale. The consumer however has more interest in the service to be obtained from cells than has the jobber, but as noted above the small average number purchased by the consumer prohibits tests of any magnitude. Therefore if the jobber takes up dry cell testing seriously it would be with the ultimate aim of protecting, and building up the reputation of the small consumer.

Telephone Companies:—

1. The small telephone company consuming say less than ten barrels of cells per year could install a standard telephone test of small capacity by fitting suitable electrical contacts on a clock and connecting these with a telegraph relay in such a way as to cause the latter to open and close the dry cell circuits. We would advise that such a test be maintained by each company and that periodical tests (at least four per year) be made on the shipments of cells received and also on small lots of other brands purchased from time to time for the purpose of test. The small company should also test a representative sample (say 10 percent) of all consignments received, with a good ammeter.

2. The large telephone company using many barrels of cells per year can well afford to install an apparatus for carying on the test suggested in this report. We would advise that a battery of three cells from each consignment received be placed upon the telephone test. We would however, consider two such tests

per month as a safe maximum number of tests. In addition the short-circuit current and open-circuit voltage should be read upon a representative sample of all cells received.

It would be profitable for the large telephone company to conduct regular telephone tests, not only upon the batteries used with their equipment, but also batteries composed of the different makes of cells, in order to compare their relative merits on telephone service.

Gas Engine Manufacturer:—To the gas engine manufacturer it is important that the batteries furnished with his engine be the best cells obtainable from an ignition standpoint. As the apparatus necessary for carrying on the ignition test is quite inexpensive and as the test requires very little attention, the manufacturer of such engines purchasing a considerable number of cells should conduct the ignition test not only as a check upon the cells he is receiving, but as a basis for judging the merits of the different grades of ignition cells on the market.

An ignition test upon six cells from every fifth barrel received with a maximum of two tests for a single consignment of cells, would probably be sufficient. Before being sent out with an engine the short-circuit current on all cells should be read and those reading abnormally low (*e. g.*, 5 amperes or more below the average for the brand and grade) should be rejected.

C. F. Burgess, *Chairman,*
J. W. Brown,
F. H. Loveridge,
C. H. Sharp,
Committee on Dry Cell Tests.

DISCUSSION.

Prof. C. F. Burgess presented the paper, and in doing so said: This report is devoted to a consideration of methods of testing a piece of electrical apparatus to which very little attention has been paid, although a type of apparatus of great importance.

The members of the Society and the members of the committee have been familiar with the dry battery test largely from the standpoint of the manufacturer, but in formulating this report we have attempted to look at the matter from the standpoint first, of the small user, and then, from the standpoint of the larger user, and finally, from the standpoint of the manufacturer.

We hope the report will bring out a free discussion, not only orally, but communicated, and we will not feel at all displeased if this discussion is of an adverse nature. Any one who looks at this matter of dry battery testing will see that it is a complicated problem, there are so many different factors entering into it that it is difficult to devise perfectly satisfactory methods of testing, and we will welcome criticism of our report.

This report is presented, not with the idea that it will be accepted as a final report on the question at this time, but with the hope that it will, at least, be put into print under the auspices of this Society, and that it will go into the hands, in some way or other, of the battery users, that there will be attention paid to the matter of testing dry batteries during the coming year, and that we will have a record of tests presented giving the results of dry battery performance. This is, then, a tentative report, with the hope that at some future day this committee, or some other committee, will present a final report, which will be accepted by the Society.

MR. F. H. LOVERIDGE (*Communicated*): With reference to the E. M. F. test to "*determine the condition of cell before use,*" the writer is of the opinion that no reliance can be placed upon such test made with a high resistance voltmeter. The resistance of the instrument is so high compared to the cell itself that a cell which has seen considerable service might not give any indication of its condition.

Furthermore, cells that have shown excellent results in service and on shelf have shown voltage readings that varied in amount from less than 1.45 to over 1.60, thus indicating that the E. M. F. of cells is no safe criterion of what may be expected in service.

It should be added that these observed voltages were readings from cells that had not been sent out from the factory, and also that readings were taken after the regular time for the cells to settle down to normal had elapsed.

It is generally recognized that the effect of service on a dry cell is an increase in its apparent internal resistance rather than the loss of E. M. F.; it is not at all uncommon to find cells that will give a high voltage reading on a high-resistance voltmeter, but which are capable of giving only a very feeble short-circuit current. It then seems logical to assume that E. M. F. readings are of no particular value taken by themselves, but must be accompanied by some data as to current flowing. This naturally leads to the idea of ignoring E. M. F. and depending on current readings with a suitable resistance in circuit to represent the class of service for which the cell is to be used. The factor of length of time on closed circuit would also be dependent on the class of service. This plan is applicable to life-tests, and would have the advantage of somewhat simplifying them. It would have its best application, however, in the testing of cells in service, to ascertain their condition at any particular time.

For such a test an ammeter, having, in series, a resistance equaling that of the circuit in which the cell is used, would be the best arrangement. The ordinary pocket instrument would not be found satisfactory for this test, for the reason that the deflection of the ordinary instrument will remain at a fixed point and not show a change as the current diminishes. The only satisfactory instrument would be one in which changes of current would produce corresponding changes in deflections. A test of this nature would also be much more consistent for cells that had deteriorated to a certain extent in storage, than the test made with a low-resistance ammeter for instantaneous short-circuit current.

The internal condition of a dry cell in service is known to be dependent on a number of influences, but I believe it will be conceded that the factors of greatest importance are amount of current flow, ratio between open- and closed-circuit periods, and the arrangement or distribution of these periods over the day.

It being granted that this is the case, it follows that the more nearly we can approach actual service conditions the more nearly we will have accurate information as to results that may be expected, although it does not necessarily follow that accuracy of results is strictly proportional to the approach to actual conditions of service. This is true whether tests are made for purposes of ascertaining what may be expected from a particular make, or for comparison between various makes (each possessing more or less individuality), to determine which is best adapted for a particular purpose.

For the above reason, I would be strongly in favor of recommending that wherever practical, all battery life tests either duplicate the conditions of average service or else that readings from cells in actual service be taken, if conditions are such that there is a uniformity of service requirements for all cells.

This last condition is seldom met with except where cells are employed with some uniformly operating mechanism, but, even in this case of uniform conditions of circuit closure, other factors, such as temperature, are liable to enter.

Following the above recommendation, it would be desirable to describe specific tests to meet the requirements of the different general classes of service.

MR. W. B. PRITZ: It is true that the internal resistance of cells increases during service, and that the voltage, decreased by polarization, will recuperate greatly when the circuit is broken. End points in service tests cannot therefore be determined by open-circuit voltage readings.

The voltage measurements referred to in the report, however, are those taken while the circuit is closed, *i. e.*, while the cell is discharging. As these readings measure that part of the total E. M. F. of the cell used in forcing the current through the external circuit, such readings give precisely the same information as would be obtained from the readings suggested by Mr. Loveridge, *viz.*, readings of the current flow in the circuit. However, in the ignition test recommended in the report, the end point is determined by a current impulse value, for reasons fully stated in papers which have been presented before this Society and referred to in the report.

Relative to Mr. Loveridge's suggestion that the conditions of test be made to conform as closely as possible to the conditions of service, it may be said that this is in some cases most desirable. However, as brought out in the report, when simply a comparison between cells is wanted, a close approach to service conditions is fully satisfactory. Tests which will conform strictly to actual service conditions, could they be devised, would, in most cases, be very complicated and would require a great deal of expensive apparatus and for most purposes would be unnecessary, since simpler tests will serve to classify the different brands of cells according to their service capacities.

Conditions surrounding service in which dry cells are used, in the main, vary from time to time and also between different installations, so that in the majority of cases it is impossible as well as unnecessary to duplicate such conditions in a test. As close an approach as possible to operating conditions, at the same time retaining simplicity, is to be desired.

MR. J. FRANKLIN STEVENS (*Communicated*): In the "Report of Progress by the Committee on Dry Cell Tests," Section 2, page 279, after reciting several excellent reasons why the short-circuit current test is meaningless, without mentioning, however, the damage done the cell by short-circuiting it, full directions for making such tests are given. The directions state: "The ammeter for reading short-circuit current should be dead-beat * * *. The maximum swing of the needle should be taken as the short-circuit current of the cell." Further on it is stated: "For accurate measurement of the short-circuit current of a new cell, cheap instruments of the pocket type should be avoided."

Without attempting to discuss the advisability of the short-circuit current test, which is both harmful to the cell and meaningless as to results, I would call attention to the fact that, if the Committee decides to retain this test, the reading obained by noting the maximum swing of the needle gives no quantitative measurement of the current and a qualitative measurement only when the same ammeter is used on cells of the same capacity, that is cells giving approximately the same short-circuit current.

Indicating or direct-reading ammeters are not designed for use as ballistic galvanometers, in fact they are designed to be as aperiodic or dead-beat as possible, but in this respect no two are alike. Even ammeters of the same make and of the same range will differ sufficiently in their aperiodic qualities to prevent the overthrow of the needle giving an accurate relative measure of the current. This difference will be far greater when results are compared between ammeters of different makes and different ranges, at various parts of the scales.

The Bureau of Standards recently completed a series of tests on eight makes of American direct-current voltmeters and ammeters (see Bulletin of the Bureau of Standards, **7**, No. 3), in which they determined, among other things, the damping or dead-beat qualities. Testing voltmeters of 150 volts maximum range on a circuit of 120 volts, the time required for the pointer or needle to come to rest after closing circuit varied from 0.8 to 4.8 seconds. In the ammeter tests, employing a current of 160 amperes on instruments of 200 amperes maximum range, the time required for the pointer or needle to come to rest after closing circuit varied from 1.1 to 5.8 seconds.

The damping or dead-beat qualities of any direct-reading instrument depends upon a number of factors entering into the design and construction, such as torque, weight of moving element, friction, strength of field, and moment of inertia of the moving element, while the overthrow or maximum swing of the needle depends not only on these factors but also upon the momentum given the needle when the circuit is closed. This momentum is also directly proportional to the ratio of the current through the instrument to the total maximum current capacity of the instrument, that is, for example, the actual amount of overthrow of the needle will be greater at 2/3 of full scale than at 1/3.

Since the overthrow reading is in no sense quantitative, it is a matter of indifference whether the ammeter employed for such a test is a high-grade accurate and aperiodic instrument or a cheap type of pocket ammeter.

A consideration of the facts above makes it apparent that a measurement of short-circuit, or any other, current based upon the "maximum swing of the needle" is entirely valueless as a measure of the current or even as a basis of comparison between cells of different capacities.

DR. JOHN W. BROWN: The discussion, as I take it, deals with fractions of a second, that is the taking of readings in a small limit of time. The present way of measuring the short-circuit current of a dry cell usually requires a contact of one or two, or perhaps three seconds, and in that time it gets down to a perfectly definite reading. We are not interested in general in readings taken as indicated in that discussion.

PRESIDENT WHITNEY: It seems to me that the Society should only support a report which is practical. If we get out a report which covers a method of testing dry cells which the users will not recognize, then there is little use in our getting it out. The object of our Committee has been to study the different uses of the dry-cell battery in the various fields, to secure the best method whereby the test can be made, and to recommend a form of test which will be practicable and will be used.

It was my hope that the discussion this morning, by men who know more about it than I do, would lead to suggestions of methods for making the test in a practical manner.

PROF. JOS. W. RICHARDS: I move that this report be received and the Committee continued, to report at a subsequent meeting.

DR. CARL HERING: I second the motion.

(The motion was put to vote and carried.)

PRESIDENT WHITNEY: I think that this is a good move. Many people who are using dry batteries may be led to test them under the conditions presented in the report of the Committee, and report their conclusions to the Society.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

PERFORMANCE OF DRY CELLS.

By Carl Hambuechen.

Since 1908 the writer has made examination and tests on several thousand dry cells for the purpose of determining their characteristics and performance as judged by methods of testing in common use. The cells examined included the products of various leading manufacturers supplying the American market. This work has done for the French Battery & Carbon Company, of Madison, Wisconsin, and it was through the courtesy of this company that permission was secured to draw upon the records for information which may be of some general interest to dry-cell users.

There are three important characteristics of dry cells by which merit is judged, these being commonly designated as the "flash" or "short-circuit current," the "shelf life" and the watt-hour output or "service capacity."

The first is of the least importance and the last is the most important, as determining the actual merits of the product, but as to the frequency of use this order is reversed, and it is by the flash test that the largest proportion of dry cells sold are judged. The dealer tests the barrel of dry cells when received by means of the ammeter, the customer in turn goes over the dealer's stock and picks out cells which show the "most amperes." To those who have given the matter some thought it is evident that the merits of the cell cannot be determined solely by the initial amperage, but the test is nevertheless in general use and is an important factor. The principal reason for this test is apparently its simplicity and rapidity, coupled with the fact that it does tell whether the cell has a high or low internal resistance and whether it is alive or dead. This test being used as an indication, it is natural that the purchaser would choose cells which show the highest test, that the dealer therefore finds it easier to sell a higher testing product, and that this influence extends to the maker in prompting him to turn out a high-testing product.

That there has been a tendency in this direction during the past few years, of increasing the flash test, is indicated by the curves in Fig. 1. These were compiled from many observations of the standard size 6 inches (15 cm.) high by 2½ inches (6 cm.) diameter dry cells of the most prominent makes.

Thirteen years ago comparative tests were made on twelve different brands of dry cells on the American market; these tests being carried out in the Applied Electrochemistry Laboratory, of the University of Wisconsin. They indicated that the flash test or initial amperage of cells at that time varied between two and ten amperes. There has been a gradual upward tendency since that time, and that this upper tendency is still continuing is shown by the curves above referred to. An attempt has been made to separate the 6 in. (15 cm.) dry cells into two classes, namely, those intended for telephpone service, door bell and signal work and the like, and those intended for gas-engine ignition. It will be seen that since 1908 the initial amperage of the ignition type has been raised from 20 to over 30 amperes, while with the telephone type the amperage has been raised from 15 to nearly 30 amperes. In considering this decided upward tendency it is interesting to speculate how much further it will be carried, and as to whether the other and more important characteristics of dry cells are being likewise improved.

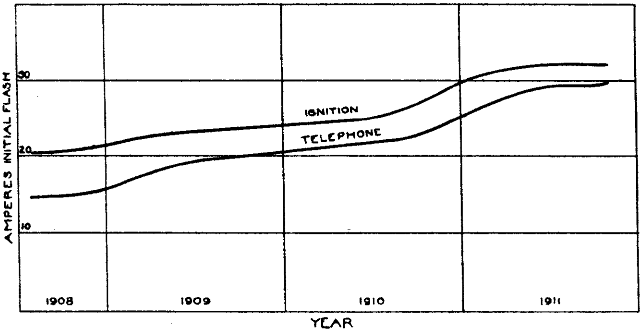

Fig. 1.

There are various methods by which the initial amperage may be increased, including the use of graphite and higher conductive carbon, the increase in the percentage of this material with a corresponding decrease in the manganese and other constituents, by the use of various chemicals which increase the activity, by the use of thinner and more porous lining for the cells and by the density and hardness of tamp, etc.

The question naturally presents itself as to whether in the attainment of a high flash some of the other desirable characteristics may not be sacrificed, and from the writer's observation it appears that during the past three years there has been little if any improvement in the cell durability or shelf-wear or in the watt-hour capacity; in fact there is some evidence that these important qualities have been sacrificed in the attainment of high amperage.

There is an impression which is becoming more generally recognized that high amperage alone is a false criterion, and that a cell possessing it is likely to suffer more rapid deterioration either in storage or for long time service. In all probability the adoption of certain simple and standard methods of testing will result in more attention being given to the more important characteristics of long life and energy output.

While there are certain classes of service in which the dry cell is naturally expected to run down within a few weeks, there are larger fields for usefulness where the service must be extended over many months and even a year, and in which deterioration when the cell is not in use naturally plays a prominent part. These classes of service include telephone, signal and alarm service, and where the dry cells are used as an emergency reserve in the failure of other sources of electrical energy supplied.

A question of great importance and upon which there is little published information is this, "What is the rate of normal shelf-deterioration for a standard well made cell under normal temperature conditions?" From statement by Mr. D. L. Ordway, Transactions of the American Electrochemical Society, **17**, page 349 (1910), the shelf life of a cell may be taken as the number of months before the short-circuit current reaches 10 amperes. This 10 amperes is taken not because it indicates a corresponding decrease in the output capacity of the cell, but because it represents a value such that the dealer could not dispose of the cell to the average consumer. The best cells in the market have a shelf life on this basis of 12 to 15 months, while 10 to 12 months is given as more nearly the shelf life obtained with the high-grade cells now on the market. Mr. W. B. Pritz, Transactions of American Electrochemical Society, **19**, 39 (1911), gives data showing the variation of shelf deterioration at various temperatures. At 25° C. at 22-ampere cell will drop 10 percent in amperage in ten weeks on open circuit.

From a large amount of data the writer has endeavored to compile a curve which will show a normal deterioration of the more prominent types of cells on the market during the past year. This is difficult on account of the wide variation in performance, not only as among cells of different makes, but even as among cells of any one make. Basing judgment upon the results obtained from over a thousand cells made in the latter part of 1910 and during 1911, the curves in Fig. 2 may be taken as representative of the better grades of 6 in. (15 cm.) dry cells. These curves express the percentage of the original flash which cells should show after various intervals of storage up to one year. It has been observed that cells made with higher initial amperage show a more rapid deterioration than those made initially of the lower flash test as indicated by the three curves for cells having initially 20, 25 and 30 amperes respectively. It has been pointed out by Messrs. Pritz and Ordway that the falling off in flash tests does not by any means indicate a corresponding

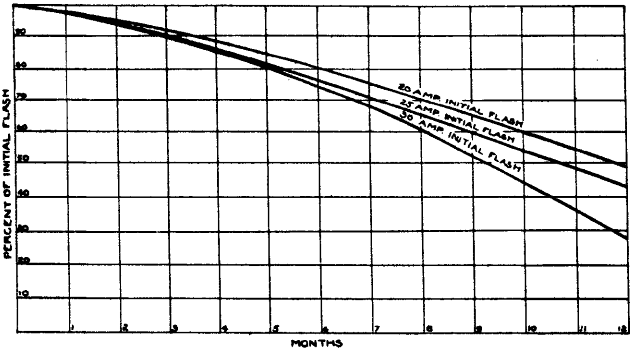

FIG. 2.

reduction in useful service capacity, and the writer wishes to confirm these observations. Nevertheless, it is desirable that cells be improved for shelf wear and the above curves indicate that marked opportunity for improvement exists.

It is hoped that more attention may be given during the coming year to dry-cell testing, especially along such standard lines as may be recommended by the American Electrochemical Society, and that later results may be presented by various observers through which more accurate knowledge concerning dry cells may be derived.

Northern Chemical Engineering Laboratories,
Madison, Wis.

DISCUSSION.

President Whitney: It seems to me that we might get a flash test which would partly ruin the cell, and our Committee should do what it can to get a proper kind of test. The "flash test" is such an easy thing that there is a possibility of its being abused.

Prof. C. F. Burgess: The flash test is used on millions of cells and by many users throughout the country. It shows them something about the apparatus, at least whether the battery is alive or dead. The battery manufacturers use a flash test on the cell to show something as to its characteristics. Most people who buy a 15-cent or 25-cent dry-cell cannot afford to have a $10 instrument to test it with, so that we are forced to face the necessity of $1.50 pocket instruments, and it is in some respects rather out of the question to say they cannot be used, because they are used and will be used. The best thing we can do is to find out what such readings mean, and thus help the situation to a certain extent.

Dr. J. W. Brown: Some companies, the National Carbon Co. included, have tried for a long time by means of an educational campaign to convince the people of the limited amount of information which is derived from the "flash test," but, nevertheless, the flash test is made and we are obliged to accept that fact. Accepting that fact, we want to point out the dangers of too broad a conclusion from a test of that sort. In talking with a great many persons personally, I have found some difficulty in persuading them that if a cell shows at the outset 25 amperes, and on a later test shows 12.5 amperes, or thereabouts, that less than half the energy has disappeared from the cell. It seems self-evident to most people that a 50 percent loss of energy has occurred. This point was brought out and emphasized at considerable length in the report of the Committee, and, confirmed by the Society, should have considerable influence with the users of dry cells.

PRESIDENT WHITNEY: In practice, any test short of a life test is not a good test. It is not true that a man must make the test on every new battery. It seems to me that the test should be made by an organization like the Bureau of Standards, and random samples taken from large consignments for test.

DR. CARL HERING: Exactly; and a parallel case is the testing of incandescent lamps.

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THE MAKING OF MAGNESIA CRUCIBLES.

OLIVER P. WATTS.
Assistant Professor of Applied Electrochemistry.

In the preparation of the thousand alloys of electrolytic iron, which have been made and tested in the Department of Chemical Engineering during the last few years, it was necessary to melt the material without contamination by carbon. Since suitable crucibles could not be purchased it was necessary to make them, and at the end of four months of constant experiment, the first successful crucible was turned out.

In view of the difficulties to be overcome, and the inquiries received from time to time in regard to the method of making these crucibles, it has seemed advisable to publish the results of our experiments along this line.

At the outset Dixon graphite crucibles, as well as crucibles turned from bars of Acheson graphite, were lined with calcined magnesia to which some binder, such as a solution of sodium silicate, magnesium chloride or tragacanth was added. The lined crucibles were allowed to dry, and were then heated in a gas oven to drive off all moisture before use. They were then charged with the desired metals, and the melt made in an electric arc furnace. After months of experimenting with these materials, fifty per cent or more of the linings failed in the electric furnace. Success was finally achieved through modifying our process in three particulars, viz.: the elimination of all binding materials, except water, the baking of the magnesia lining *in situ* to a temperature as high as that at which it was to be used, and finally the substitution of an electric furnace of the resistance type for the arc furnace.

The process as finally worked out is very simple. The calcined magnesia is moistened with water, and tamped around a core of wood set in a crucible turned from a bar of Acheson graphite. The core is withdrawn and the crucible set in an oven heated by gas, until thoroughly dry. It is then covered by a thin graphite cap, buried in a granular carbon resistor, and heated to a tempeature a little above that required to form any of the alloys. After so baking, the magnesia linings are readily removed from the crucibles. They are hard and stone-like, and show a crystalline fracture. For use, they are replaced in the graphite crucibles, charged with the desired metals, covered with a thin disc of magnesia, and the graphite cap placed on top, when they are ready for the electric furnace. A description of the furnace used has already been published.[1]

Commercial calcined magnesite was found to vary greatly in the amount of iron oxide, and carbon dioxide contained, no two lots proving alike in these respects. The iron oxide is detrimental, because in baking the linings, it distils out, is reduced to iron in contact with the inner wall of the crucibles, and this iron is then likely to corrode both the crucible and the lining by carrying carbon from one to the other.[2] Any considerable amount of carbon dioxide indicates insufficient calcining, and such material will show excessive shrinkage in baking, and in extreme cases the lining may crack. Average linings, 6 inches high and 3⅛ inches in diameter, showed a shrinkage of 12 per cent in both outside and inside diameter, and 17 per cent in length. One lot of magnesia contained so much carbonate that it was impossible to use it without calcining it. This was done in the electric arc, and the fused magnesia produced was then pulverized for use. Linings made from it shrink so little that it was sometimes difficult to remove them from the crucibles after baking. This may be remedied by the addition of 2 to 10 per cent of magnesia which has not been fused.

The extreme temperature at which such magnesia linings may be used in graphite crucibles is fixed, not by the melting of the magnesia, but by its reduction by the graphite. On account of this action, the granular resistor should never be allowed to come in contact with the magnesia linings.

In view of the hardness, mechanical strength, and high melting point of such magnesia linings, it would seem that they needed only to be given the form of commercial crucibles, to replace completely the latter for very high temperature use. Unfortunately magnesia loses its strength at a white heat to such a degree that the crucibles will not bear handling; hence

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[1] Electrochemical and Metallurgical Industry, 4, 273.

[2] Trans. Amer. Electrochem. Soc. 11, 279.

they can be used only as linings when the crucibles must be handled at, or near, a white heat. The writer has tried additions of various other refractory materials to magnesia in hope of increasing its strength at high temperatures, so that crucibles full of melted metal may be handled directly, without the use of a graphite casing, but so far these experiments have not been successful.

A similar method of manufacture is outlined in U. S. patent 1022011, recently issued to G. Weintraub, and assigned by him to the General Electric Co. Carbon or graphite cores are, however, used instead of wooden ones, and these are left in place during the baking, which is carried only to a temperature of 1500° C. To prevent the breaking of the crucibles by the contraction which occurs during cooling, several layers of paper are wound over the cores before these are put in place. The process is applied to crucibles of magnesia, alumina, and thoria.

For magnesia at least, the patented process appears to have no advantage over the earlier method evolved at Wisconsin, while it involves the additional expense of a considerable number of carbon cores, and the likelihood of the cracking of many crucibles during cooling, in spite of the cushion of paper put around the unyielding cores.

A good market awaits the manufacturer of a crucible free from carbon, which shall be as cheap and refractory as magnesia, and strong enough to be handled when full of molten metal.

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A paper presented at the Twenty-first General Meeting of the American Electrochemical Society in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE VOLATILITY OF ZINC OXIDE.

By O. L. Kowalke.

Several years ago, in connection with some experiments on the electric smelting of zinc ores, the question arose whether zinc oxide was volatile or not. In the literature there seemed to be only general statements as to the temperatures at which zinc oxide was volatile, but no record of definite tests was found. Stahlschmidt[1] says: "Zinc oxide is infusible and is notably volatile at 970° C., and about 15 percent more at 1054° C., and is rapidly volatile at a high heat."

After the present investigation had been completed, it was found that this question had been studied by Messrs. Doeltz and Grauman.[2] Their methods are about the same as in this work, but the results are somewhat different, as will be explained later.

APPARATUS.

Pyrometer: A carefully standardized and properly protected thermocouple of platinum and platinum-10-percent-rhodium and a galvanometer of Keiser & Schmidt served as the means of determining the temperatures attained.

Zinc Oxide: The zinc oxide employed was "Zinc Oxide, C. P.," obtained from E. H. Sargent & Co., and was not tested for its purity.

Furnaces: The first furnace used was of the granular carbon resistor type. The treating chamber was a magnesia crucible 4¾ inches (12 cm.) long, 1¾ inches (4.3 cm.) in diameter, walls ¼ inch (0.6 cm.) thick, closed at one end, and surrounded by a shell of Acheson graphite. All of it was imbedded in the resistor in a horizontal position, with the opening of the crucible through the wall of the furnace. This arrangement allowed the introduction and removal of the zinc oxide from the furnace in a

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[1] Ingall's "Metallurgy of Zinc and Calcium." p. 5.

[2] "Metallurgie," 1906, 212, 233.

convenient manner. The mouth of the crucible was closed with a magnesia disk through which the pyrometer and sight tube were inserted, and the whole was cemented up with asbestos fibre.

This type of furnace was very convenient, but trouble lay in the fact that there was danger of reducing gases coming through the wall of the magnesia crucible. This did happen, and the results were of no value.

The only type of furnace that did not introduce any reducing material was a tube furnace of the Heraëus form, wound with some high melting-point metal, such as "nichrome" or platinum. Such a furnace consisted of a tube of porcelain or "Marquardtsche Masse," about 1 inch (2.5 cm.)in diameter and 10 inches (25 cm.) long. A spiral of resistance wire was on the tube and connected to the terminals at the ends of the furnace. The annular space of about 3 inches (7.5 cm.) between the tube and the casing of the furnace was filled with fossil flour to serve as heat insulator.

The electric current from a 110-volt circuit used for heating the spiral of resistance wire was regulated by means of a bank of incandescent lamps, which proved to be a convenient method for control of the current and hence of the temperature.

The "nichrome" ribbon does very well for temperatures below 1100° C., but temperatures above this can not be maintained very long, as the metal oxidizes rather rapidly. The platinum foil can, of course, be heated to a higher temperature, but in this case the foil was so thin that it was not safe to go above 1400° C. In this connection it might be of interest to state that a thin platinum foil does not work well with alternating current, as the vibrations resulting from this power break the foil. Direct current is entirely satisfactory.

PROCEDURE.

The zinc oxide was placed in a boat about 3/8 inch (0.9 cm.) wide, 3/8 inch (0.9 cm.) deep and 3½ inches (9 cm.) long. Before using a new boat or fresh zinc oxide for any test they were both first ignited in a Bunsen flame to a constant weight.

The boat with the weighed amount of zinc oxide was then put in the furnace, and the pyrometer so placed that the junction of the couple was at the middle of the boat. The end through which the pyrometer was inserted was cemented up with loose asbestos, and the other end was provided with a tube about ⅜ inch (0.9 cm.) diameter, open at both ends, which served as a sight tube.

The furnace with its contents was now slowly heated to the temperature desired, kept there, and then finally allowed to cool slowly to the original temperature. The period of cooling was usually over night, after which the boat with its charge of zinc oxide was removed and weighed. The loss of weight was considered due to the voltilization of the zinc oxide. The weight of the porcelain boat was very constant, and any variations in its weight were applied to the apparent loss of zinc oxide.

RECORD OF TESTS.

With Resistor Furnace: Several runs were made with this furnace, but in all of them the zinc oxide apparently volatilized at temperatures below 1300° C. White fumes of zinc oxide were observed at the exit at temperatures varying from 1150° C. to 1240° C. in the several runs, and it will be noted that these are about the temperatures at which zinc oxide is reduced. There seemed to be no question that the carbon monoxide from the furnace came through the walls of the magnesia crucible and reduced the zinc oxide. These tests are thus of no value so far as this problem is concerned.

With Tube Furnace Heated by Metallic Ribbon: It was clear from the above tests that even a small amount of reducing agent must be kept out of the furnace. The tube furnace satisfies these conditions, and the results obtained are much more satisfactory. Below are given in tabulated form the results of the successful tests:

No. 1		No. 2		No. 3	
Time	Temperature Degrees Centigrade	Time	Temperature Degrees Centigrade	Time	Temperature Degrees Centigrade
9.00	635	3.30	910	11.00	1075
10.00	1165	3.44	1190	12.00	1260
11.30	1210	3.48	1260	2.00	1325
12.00	1240	3.50	1290	2.30	1360
				3.30	1370

	No. 1	No. 2	No. 3
Weight ZnO taken	1.0030 grams	0.7560 grams	0.9042 grams
Loss of ZnO	0.0102 "	0.0305 "	0.9040 "
Percent loss	1.01 "	4.3 "	100.0 "

DISCUSSION OF RESULTS.

It appears from these tests that zinc oxide can be completely volatilized at temperatures from 1370° C. to 1400° C. In all of these tests the zinc oxide was exposed to the high temperatures for a considerable period of time, a condition not exactly comparable to smelting conditions.

The loss of zinc oxide increases rapidly with temperature rising above 1300° C., as shown in these tests. The loss seems, however, to be of a nature similar to the slow evaporation of water below the boiling point, but at temperatures above 1400° C. it appears reasonable to say that the volatilization proceeds rapidly.

This view is supported by the work of Doeltz and Grauman, who find that at 1400° C. a series of nine treatments, for periods of 10 minutes each, produced a loss of 13 percent of zinc oxide. However, when zinc oxide was dropped on a platinum wire heated by a current of electricity to a bright red heat, the zinc oxide adhered tenaciously, and upon heating the wire to a white heat, above 1400° C., and near its melting point, a rapid volatilization of zinc oxide took place.

The painstaking assistance of Mr. Albert R. White in obtaining these data is hereby acknowledged.

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University of Wisconsin.

DISCUSSION.

DR. JOSEPH W. RICHARDS: There has been a good deal of uncertainty as to whether zinc oxide itself was volatile at a moderate temperature or not, and this paper finally settles the question. If we had the complete vapor tension curve we could draw some further conclusions.

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A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE EFFECT OF VARIOUS SUBSTANCES ON THE RATE OF CORROSION OF IRON BY SULPHURIC ACID

By Oliver P. Watts.

In Vol. 8 of the transactions of this society, C. F. Burgess called attention to the remarkable reduction in the corrosion of iron by sulphuric acid, brought about by the addition of a small amount of arsenious oxide to the acid. Later[1] he explained the protective action as follows: "The explanation which has been offered for this phenomenon is that the iron receives, by contact with the solution, an extremely thin coat of arsenic which resists the action of the acid and protects the underlying metals." He also gave experimental proof that the iron was coated with arsenic.

It has long been known that by dipping clean iron into solutions of suitable composition and concentration thin coatings of gold, silver, platinum, copper, and several other metals may be deposited on the iron. It is generally conceded that such coatings are not sufficiently continuous and impervious to protect the underlying metal from corrosion, even though the metal forming the coating may itself be thoroughly resistant to the corrosive agent. Instead of being a protection, such coatings are usually considered to be stimulators of corrosion.

Since all metals which thus deposit upon iron when it is immersed in a solution of the metallic salt are electro-negative to iron, a short-circuited voltaic cell is formed, of which the iron is anode and the metal deposit is the cathode. So long as any iron remains in contact with the electrolyte, it would seem, except for certain considerations which will be presented later, that the corrosion of the iron ought to be stimulated by this condition, and that the only way in which such a coating could afford good

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[1] For references see list at end of paper.

protection would be by covering the iron completely, so that no electrolyte could come in contact with it.

Speaking of the effect of other metals in contact with iron, W. H. Walker says,[2] "Tin is a metal which, like copper, accelerates the corrosion of iron by aiding in the oxidation of the hydrogen set free by the reaction." M. P. Wood[3] calls attention to the injurious action of metals, "The use of anti-corrosive, or anti-fouling paints, containing salts of any metal, is attended with the greatest danger to the coated (iron or steel) structure. These pigments are extremely sensitive to the presence of saline elements in moisture, their action being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way."

It appears then, that arsenic is unique among the metals which precipitate themselves upon iron from solution, for arsenic protects iron almost completely from powerful corrosive agents, while the other metals are generally considered to aggravate corrosion and rusting. The protective action of arsenic cannot be due to any superior power of resisting attack by sulphuric acid, for silver, platinum and gold are even more resistant, and yet accelerate the corrosion of iron. It is evident that these other metals do not form continuous and impervious coatings over the iron, else they would protect it. It is difficult, perhaps impossible, even with the aid of the electric current, to deposit from solution a thin coating of one metal upon another so perfectly as to protect the underlying metal from corrosion by an acid ordinarily capable of attacking it. It is almost incredible that a thin yet perfect and non-porous metallic coating should be deposited by a process which depends for its operation upon the dissolving of the underlying metal. The protective action of coatings of copper, silver, etc. thus deposited on iron is about as effective as would be expected from a knowledge of their method of formation. They are continually being undermined by the corroding of the iron anode at points not yet covered, until the copper or silver becomes detached, to have its place taken by a new coating, and so on, as long as any of the salt of the depositing metal remains in the solution. If the coated metal be removed to an acid, the corrosive action is similar, except that the renewal of the coating can take place only at a rate not greater than that at which the detached metal redissolves in the acid.

If the coating of arsenic is so porous and imperfect as the action of acids shows the coating of copper, for example, to be, how can the arsenic protect the iron any better than copper does? It occurred to the writer that the explanation lay in a high overvoltage or excess potential of hydrogen on arsenic, and the experiments which follow were undertaken to discover whether this is the explanation of the singular and mysterious protective action of arsenic. If the above explanation is correct, among the metals which deposit upon iron when it is immersed in a solution of their salts those having a high overvoltage for hydrogen should protect iron, and those of very low overvoltage should aggravate corrosion.

If an electrode of platinum coated with platinum-black be immersed in normal sulphuric acid the electrode will be electronegative to the solution by about 1.14 volts. If now a small but slowly increasing electromotive force be applied between this electrode and an insoluble anode it will be found that the platinized cathode becomes progressively electronegative with regard to the solution. When a certain difference of potential between the cathode and the solution is reached, bubbles of hydrogen begin to appear on the cathode. If a cathode of smooth platinum is used, hydrogen will not appear on this until it has become 0.09 volts more positive than the other cathode was when hydrogen first appeared on it. Similarly zinc must be 0.70 and mercury 0.78 volts more positive than the platinum-black before hydrogen appears upon them. This excess of potential required to cause a visible liberation of hydrogen upon a cathode of any particular metal, over the potential required for the liberation of hydrogen upon platinum coated with platinum-black, is known as the overvoltage of hydrogen upon that metal. In Table I are given the single potentials in normal solutions of the sulphates of the metals, and the overvoltage of hydrogen as stated by different observers.

TABLE I.

		Overvoltage in normal sulphuric acid			In 5 per cent. KOH.
	Single Potential	Caspari[4]	Foerster[5]	Harkins[6]	Nutton and Law[7]
Mercury	—0.98	0.78	0.43	0.74	
Zinc	+0.524	0.70		0.71	0.70
Lead	—0.095	0.64	0.35	0.62	0.57
Tin	—0.085	0.53	0.43	0.55	0.61
Cadmium	+0.162	0.48	0.48		0.52
Arsenic	—0.550			0.39	
Bismuth	—0.490			0.38	
Iron	+0.093				0.15
Copper	—0.515	0.23	0.10	0.25	0.41
Cobalt	—0.019			0.22	
Nickel	—0.022	0.21	0.10	0.15	0.37
Silver	—0.947	0.15		0.13	
Platinum	—1.140	0.09	0.07	0.07	
Gold	—1.356	0.02	0.055		

On the theory that the protection of iron by a deposit of arsenic is due to the high overvoltage of hydrogen on the latter the action would be as follows: Iron dissolves and by so doing deposits arsenic upon the surface of the iron. Since the arsenic is deposited simultaneously with the dissolving of the iron, and only as a result of this dissolving, it is hardly possible that the iron should be perfectly covered by arsenic, but here and there holes will exist, allowing the iron to make contact with the electrolyte. Voltaic cells are thus formed. From the single potentials of iron and of arsenic, + 0.093 and — 0.550, these cells should have an electromotive force of 0.64 volts, and the corrosion of the iron ought to be very vigorous. It is here that the overvoltage of hydrogen comes in play. The iron is anode and the arsenic cathode, and, just as in any other primary cell with sulphuric acid as electrolyte, hydrogen is deposited on the cathode. But when hydrogen is liberated on arsenic the potential of the latter is raised 0.39 volts higher than — 0.277, the potential at which hydrogen is liberated on platinum-black. This would raise the potential of the arsenic to + 0.113 volts, or higher than the potential of the iron anode. This means that in our iron-arsenic cell there can be no visible evolution of hydrogen on the arsenic, for before this can occur the potential of the cathode has become equal to that of the anode, and corrosion of the iron ceases, in other words, this particular primary cell polarizes so badly that after a few seconds of action its electromotive force has fallen to zero.

If the above explanation is correct, protection should be afforded by those metals which plate out on iron by immersion, and whose overvoltage for hydrogen is great enough to raise their potentials to at least equal the single potential of iron. The potentials of the following metals are far enough below that of iron to expect that they will deposit on iron even in moderately strong sulphuric acid: antimony, arsenic, bismuth, gold, lead, mercury, platinum, silver and tin. Potential measurements made by students in the writer's laboratory indicate that chromium should be included in the list. Omitting lead, on account of the insolubility of its sulphate, mercury, tin, and arsenic show the highest overvoltage; compounds of these metals were therefore used in a preliminary experiment, by A. C. Shape.

Specimens of mild sheet steel of 22 gauge, 5 centimeters square, were pickled in sulphuric acid to remove the scale, dried, weighed, and corroded in sulphuric acid to which three volumes of water had been added. The amounts of the reagents added were 4 c.c. of twice normal stannous chloride, the same volume of twice normal sodium arsenate, and 16 c.c. of half normal mercuric chloride. The results are shown under Test 1.

Test 1.

Specimen	Reagent Added	Original Weight	LOSS	
			In 24 Hours	In 48½ Hours
A	None	16.38 g.	6.64 g.	10.32 g.
B	$SnCl_2$	16.53	0.09	0.11
C	$HgCl_2$	16.48	0.42	1.37
D	Na_3AsO_4	16.93	0.07	0.10

Tin and arsenic gave equal and excellent protection, but the action of mercury was not so satisfactory. The failure of the mercury may have been due to its gathering in drops and leaving exposed considerable areas of the iron. It has been pointed out by Cushman[8] that the protective action of a piece of zinc in contact with an iron surface extends but a very short distance from the zinc. The corrosion of specimen *C* was very peculiar, and was confined to deep pits about the diameter of a pin. The pitting was especially noticeable upon the edges of the sheet. In view of these facts, the writer did not consider the imperfect protection afforded by mercury to be fatal to his theory as to the nature of the protective action, and he decided to investigate the matter more fully.

The specimens used were as previously described. Corrosion was carried out in covered glass tumblers containing 200 c.c. of solution. The acids used in the following tests were sulphuric acid of specific gravity 1.140 at 15°C. corresponding to 19.6 percent acid, and of specific gravity 1.072 or 10.48 percent acid, hydrochloric acid of specific gravity 1.095 or 18.8 percent and hydrobromic acid of specific gravity 1.145 or 18 percent acid. In future these acids will be referred to by their approximate percentage composition.

In Test 2 the reagents added were in such amount as to make the solutions one hundredth normal with regard to the reagents. Since antimony is closely related chemically to arsenic, it was hoped that this might give the same degree of protection, and, on account of its less poisonous nature, prove useful commercially for this purpose.

Test 2.

For 21 h. 45 m. at room temperature (21°C.)

Specimen	34.9 per cent. H_2SO_4	Reagent Added	Weight	Loss
1	"	None	16.08	11.50
2	"	$Ni(NH_4)_2(SO_4)_2$	16.42	12.25
3	"	$CuSO_4$	16.12	11.36
4	"	$AgNO_3$	16.59	11.37
5	"	$Sb_2(SO_4)_3$	16.44	12.15

On examining the specimens at the end of the time specified they were all found to be covered with crystals of ferrous sulphate to such an extent that further corrosion was prevented. To avoid this difficulty weaker acids were used in all other tests.

Test 3.

In 19 percent sulphuric acid for 24 hours.

Specimen	Reagent Added		Weight	Loss
6	None		16.13 g.	5.47 g.
7	0.75gNa_3AsO_4	=0.20g.As	16.52	0.08
8	$As_2(SO_4)_3$	=0.20g.As	16.61	0.02
9	$SnCl_2$	=0.47g.Sn	15.92	0.02
10	0.678g.$HgCl_2$	=0.50g.Hg	16.14	1.40

The results of this test in the more dilute acid confirmed those of the previous test, except that the mercuric chloride showed less protective action.

In Test 4 various additions were made to the acid. As in Test 3 the various solutions were one twenty-fifth normal as regards the metallic salts added.

Test 4.

In 19 percent sulphuric acid for 20 hours 15 minutes.

Specimen	Reagent Added	Weight	Loss
11	None, No. 11 was amalgamated........	15.88	6.36
12	$Co(NO_3)_2$	14.87	9.87
13	$Bi_2(SO_4)_3$	15.79	14.36
14	$Sb_2(SO_4)_3$	16.39	8.67
15	K_2CrO_4	16.21	12.40
16	$HgNO_3$	16.20	13.61
17	$Cr_2(SO_4)_3$	16.04	2.21
18	$CuSO_4$=0.47 g. Cu	16.06	13.96
19	$AgNO_3$=1.617 g. Ag	16.31	16.31+

Specimen No. 11 was thoroughly amalgamated. At the end of 15 hours it was found that No. 19 had completely dissolved. Only one reagent, chromium sulphate, showed any protective influence. Silver nitrate, bismuth and copper sulphates and potassium dichromate accelerated corrosion. The effect of antimony sulphate, cobalt nitrate and of amalgamation is in doubt. A few hours from the start much spongy silver had collected in the solution and on the iron of No. 19, metallic copper was evident as a powder in No. 18, and bismuth powder in No. 13. In No. 14 antimony was deposited on the iron in loosely adherent flakes, which peeled off from time to time. No silver nitrate remained in solution 19 at the end of the test. The insoluble residues left after removing the specimens were washed, dried and weighed. In 13, 14, 18 and 19 the residue was equal, within a few milligrams, to the weight of bismuth, antimony, etc., originally contained in solution, plus the amount of insoluble matter calculated for the iron dissolved in each case. Chromates and dichromates have often been recommended[9] for the prevention of the rusting of iron and steels when exposed to the air, or in sea water. The great increase in corrosion caused by the addition of potassium chromate was therefore rather surprising. A comparison of No. 15 and No. 17 suggests that the protective action heretofore ascribed to chromates may really be due solely to the chromium which they contain, and not to the chromate as such. The marked increase of corrosion by mercurous nitrate is noteworthy.

It is stated by Burgess[10] that the protective effect of arsenic in hydrochloric acid is much less than in sulphuric acid, and Test 5 was arranged to learn the effect of several substances upon corrosion by hydrochloric acid.

Test 5.

In 19 percent hydrochloric acid for 24 hours.

Specimen	Acid	Reagent	Weight	Loss
20	19% H_2SO_4	None	15.92	13.92
21	19% HCl	None	16.46	1.89
22	“ “	$CrCl_3$, about 3 g.	15.99	2.42
23	“ “	K_2CrO_4	16.55	1.91
24	“ “	$Na_3AsO_4 = 0.25$ g. As.	15.82	0.13
25	“ “	$SnCl_2 = 0.59$ g. Sn.	16.15	2.14

Hydrochloric acid dissolved about one-seventh as much iron as sulphuric acid. Potassium chromate has no effect on the rate of corrosion by hydrochloric acid, while stannous chloride and chromium chloride act as accelerators instead of retarders of corrosion.

Test 6.

For 24 hours.

Specimen	Acid	Reagent	Weight	Loss
26	19% H_2SO_4	None	16.03	7.84
27	19% HCl	None	16.43	1.83
28	19% H_2SO_4	N/25 $Bi_2(SO_4)_3$	15.93	12.13
29	“ “	N/25 $Na_2SnO_2 = 0.51$ g. Sn.	15.98	0.68
30	“ “	N/25 $Ni(NH_4)_2(SO_4)_2$	16.08	7.29
31	“ “	N/25 $Sb_2(SO_4)_3$	15.97	4.86
32	“ “	N/25 $KMnO_4$	16.45	15.14
33	“ “	N/25 $NaCl = 0.286$ g. Cl.	16.45	4.01
34	“ “	2 g. CrO_3	16.25	15.15
35	“ “	2 g. chrome alum	16.00	8.81
36	“ “	N/25 KNO_3	16.13	10.25
37	“ “	5 g. CrO_3	15.47	15.47+

Specimen No. 37 was entirely dissolved at some unknown time during the test. Chromic acid, potassium permanganate, potassium nitrate and bismuth sulphate are accelerators, sodium stannate, antimony sulphate and sodium chloride are retarders of corrosion, while nickel ammonium sulphate and chrome alum have little effect. The oxidizing agents in 32, 34 and 37 were reduced before the end of the test.

Since the previous tests had demonstrated that chromic acid and chromates do not render iron passive in sulphuric acid, the action of these and other oxidizing agents was tried in solutions of a neutral salt.

Test 7.

For 12 days, 16 hours.

Specimen	Reagent	Weight	Loss
38	29 g. NaCl + 10 g. CrO_3	15.96	1.99
39	26 g. NH_4Cl + 10 g. CrO_3	15.54	1.99
40	29 g. NaCl + 10 g. $KClO_3$	15.68	5.22
42	29 g. NaCl + 10 g. $KMnO_4$	16.21	3.71
43	29 g. NaCl + 10 g. $K_2Cr_2O_7$	15.97	0.065
51	Water + 10 g. CrO_3	15.91	0.005
52	29 g. NaCl	15.77	0.043

The addition of the oxidizing agents strongly stimulated corrosion, except in No. 43. This result needs confirmation by further experiments.

Test 8.

For 29 hours.

Specimen	Acid	Reagent	Weight	Loss
44	19% H_2SO_4	10cc HCl = 1.99 g. Cl...	15.88	0.70
45	19% HCl	None	15.86	1.65
46	19% HCl	About 10 g. $CrCl_3$	16.01	1.92
47	19% HCl	10 g. K_2CrO_4	16.02	7.82
48	19% H_2SO_4	10 g. NaCl = 6.1 g. Cl ..	15.72	0.32

Previous tests had shown that salt and other chlorides diminished the corrosion by sulphuric acid, and the writer expected that the increased amount of salt in No. 48 would still further diminish corrosion, but was not prepared for the astonishing result obtained in No. 44. Previous tests had shown that in 24 hours the sulphuric acid dissolved from five to seven times as much iron as the hydrochloric. Now the substitution of 10 c.c. of the hydrochloric acid for an equal volume of water in the sulphuric acid reduces the corrosion to less than half that of hydrochloric acid.

Up to this time all experiments had been carried out upon the laboratory table, subject to whatever variations there might be in room temperature during the twenty-four hours. A study of the results showed that different tests were not comparable. All the tests which follow were carried out in a water bath maintained at 30° C.

Test 9.

In a water-bath at 30° C.

Specimen	Acid	Reagent	Weight	Loss	Time Hours
53	19% H_2SO_4	None	15.35	15.35+	20
54	19% H_2SO_4	22 cc. HCl = 3.98 g. Cl	15.78	0.93	24
55	19% H_2SO_4	5 g. NaCl = 3.06 g. Cl	15.70	1.24	24
56	19% H_2SO_4	None	15.65	14.92	22
57	10% H_2SO_4	None	15.75	6.62	24
58	19% HCl	None	15.74	5.06	24
59	19% H_2SO_4	None	15.14	14.84	22
60	19% H_2SO_4	5 g. KNO_3	15.63	15.63+	20
61	19% H_2SO_4	5 g. resorcin	15.84	10.36	24
62	19% H_2SO_4	5 g. hydrochinone	15.74	7.48	24

Specimens No. 53 and No. 60 were found to be entirely dissolved at the end of 20 hours, but how much earlier complete solution occurred is not known. A comparison of No. 53 and No. 54 shows that the restraining effect of chlorine is about the same, whether it is added in an acid or in a chloride. The reducing agents in No. 61 and No. 62 retard corrosion somewhat, but since an alkaline solution is needed to make them energetic reducers, it is hardly to be expected that they would have much effect in a strongly acid solution.

The lack of temperature control in previous tests tended to exaggerate differences in the rate of action of the various solutions, for the more rapid action of any solution at the outset gave it a higher temperature, which still further increased its rate of action. This is plainly seen in comparing the rates of corrosion by sulphuric and hydrochloric acids. Without the water bath, sulphuric acid dissolved six to seven times as much iron as hydrochloric acid, but with temperature control it dissolved only three times as much.

Test 10.

In water-bath at 30° C. in 19 percent H_2SO_4.

Specimen	Reagent	Weight	Loss	Time
63	3 g. K_2SO_4	15.78	15.78	24 hours
64	5 g. $(NH_4)_2SO_4$	15.81	15.81	24 "
65	5 g. NH_4Cl = 3.27 g. Cl	15.67	2.06	24 "
66	1 g. NH_4Cl = 0.67 g. Cl	15.77	10.28	24 "
67	5 g. KBr = 3.36 g. Br	15.62	0.24	24 "
69	1 g. $PbCO_3$	15.54	15.54+	22 "
70	None	15.22	15.22+	22 "
71	2 g. H_3BO_3	15.37	15.37	24 "
72	2 g. citric acid	15.34	15.15	24 "

Before twenty-two hours had elapsed No. 69 and No. 70 were dissolved. Potassium and ammonium sulphates, boric and citric acids, and the small amount of lead sulphate contained in its saturated solution, were without marked effect. Potassium bromide is a strong restrainer of corrosion, and ammonium chloride acts similarly, but far less effectively.

Test 11.

19 percent H_2SO_4 in water-bath at 30° C. for 20 hours.

Specimen	Reagent	Weight	Loss
73	0.94 g. $Na_3AsO_4 12H_2O$ = 0.25 g. As....	15.44	0.53
74	0.47 g. $Na_3AsO_4 12H_2O$ = 0.125 g. As....	15.32	0.77
75	0.094 g. $Na_3AsO_4 12H_2O$ = 0.025 g. As....	15.80	13.62
76	0.016 g. $Na_3AsO_4 12H_2O$ = 0.004 g. As....	15.81	14.56
77	1 g. $Na_2SnO_3 3H_2O$ = 0.44 g. Sn....	15.80	1.29
78	0.5 $Na_2SnO_3 3H_2O$ = 0.22 g. Sn....	15.74	2.44
79	0.1 $Na_2SnO_3 3H_2O$ = 0.044 g. Sn....	15.63	4.43
80	0.05 $Na_2SnO_3 3H_2O$ = 0.022 g. Sn....	15.84	7.18
80	2 g. $Na_2SnO_3 3H_2O$ = 0.89 g. Sn....	15.73	0.68
82	None	15.74	15.13

The amount of sodium arsenate required for effective restraint of corrosion by 19 percent sulphuric acid lies between 0.47 and 0.09 g., or 0.125 and 0.025 g. arsenic, per 200 c.c. E. Heyn and O. Baur[11] find that 0.0069 g. As_2O_3 in 250 c.c. of 1 percent sulphuric acid diminishes the corrosion by one-third. Two grams of sodium stannate are required to produce equal protection.

In Test 12 the accelerating effects of copper, silver and platinum were compared, and also the relative corrosion by hydrochloric and nitric acids of about equal molecular strengths.

Test 12.

In water-bath at 30° C. for 24 hours.

Specimen	Acid	Reagent	Weight	Loss
83	10.5% H_2SO_4	Ag_2SO_4 = 0.2 g. Ag ...	15.73	8.15
84	10.5% H_2SO_4	Ag_2SO_4 = 0.1 g. Ag ...	15.49	7.50
85	10.5% H_2SO_4	Ag_2SO_4 = 0.02 g. Ag ..	15.61	5.06
86	10.5% H_2SO_4	$CuSO_4$ = 0.15 g. Cu ...	15.40	7.23
87	30% HNO_3	None	15.83	15.83+
88	19% HCl	None	15.88	7.78
89	10.5% H_2SO_4	$PtCl_4$ = 0.025 g. Pt	15.81	12.52
90	10.5% H_2SO_4	$PtCl_4$ = 0.075 g. Pt.	15.29	12.77
91	10.5% H_2SO_4	$HgSO_4$	15.33	4.43
92	10.5% H_2SO_4	None	15.80	5.89

Specimen No. 87 was attacked violently, and was entirely dissolved in a few minutes. The excessive activity of nitric, as compared with sulphuric or hydrochloric acid, can only be due to its strong depolarizing action in removing hydrogen from the iron. Silver and copper both accelerate corrosion, as was expected from the low overvoltage of hydrogen on these metals. Equal weights of metal show about the same effect, but in chemically equivalent quantities the effect of silver is much the greater. The small amount of silver in No. 85 seemed to diminish corrosion. Platinum had a tremendous effect at the start, and even at the end of the test was a more powerful stimulator than the other metals.

Test 13.

In 10.5 percent H_2SO_4 at 30° C. for 24 hours 15 minutes.

Specimen	Reagent	Weight	Loss
93	3 g. KI = 2.3 g. I	15.67	0.04
95	5 g. $K_2Cr_2O_7$	15.81	8.62
96	4 g. $MnCl_24H_2O$ = 1.43 g. Cl...........	15.17	1.34
97	2 g. KF = 0.65 g. F....................	15.84	3.46
98	20 cc. of 31% HF = 6.5 g. F...........	15.69	0.44
99	1 g. $Cr(OH)_3$ = 0.52 g. Cr.............	15.61	0.56
100	5 g. K_2CrO_4	15.45	8.17
101	None	15.76	5.55
102	4 g. chrome alum = 0.42 g. Cr.	15.81	3.88

The protective action of hydrofluoric acid and of potassium fluoride are nearly proportional to their fluorine content. The stimulative action of potassium chromate and dichromate is in striking contrast to the protection afforded by chromium sulphate. Chrome-alum is a much less efficient protective agent per unit of chromium than chromium sulphate. These experiments indicate the possibility of a revision in our ideas of the manner in which chromates protect iron from rusting, and may lead to the substitution of chromium salts for the chromates heretofore used to render iron "passive."

Test 14.

In water-bath at 30° C. for 20 hours 45 minutes.

Specimen	Acid	Reagent	Weight	Loss
103	19% H_2SO_4	5 g. KI = 3.83 g. I...........	15.56	0.03
104	19% H_2SO_4	1 g. KI = 0.76 g. I...........	15.57	0.06
105	19% H_2SO_4	None	15.60	13.10
106	10.5% H_2SO_4	2 g. KNO_3	15.54	5.17
107	10.5% H_2SO_4	2 g. $KClO_3$	15.64	9.97
108	10.5% H_2SO_4	None	15.31	4.40
109	19% H_2SO_4	25 cc. of 18% HBr = 5.1 g. Br	15.29	0.31

Potassium iodide proves an excellent protective agent, and hydrobromic acid acts similarly. Of the two oxidizing agents, potassium chlorate stimulated corrosion much more than did potassium nitrate, as was to be expected from its larger amount of available oxygen.

Test 15 was made to compare the effects of very small additions of several metals. At the end of a few hours the specimens were removed, brushed, dried, weighed and returned to the acid.

Test 15.

In 19 percent H_2SO_4 at 30° C.

Specimen	Reagent	Weight	Loss at end of time in hours		
			2.25	5.72	8.3
110	5 g. $K_2Cr_2O_7$	15.27	3.06	5.71	15.27+
111	$PtCl_4$ = 0.016 g. Pt.........	14.88	6.76	8.85	14.88+
112	$AuCl_3$ = 0.016 g. Au	15.78	0.19	0.85	11.33
113	$Bi_2(SO_4)_3$ = 0.020 g. Bi	15.83	0.17	0.92	12.12
114	$Sb_2(SO_4)_3$ = 0.020 g. Sb ...	15.60	0.20	1.04	11.82
115	$CuSO_4$ = 0.020 g. Cu	15.86	0.27	1.42	12.76
116	Ag_2SO_4 = 0.020 g. Ag	15.33	0.18	1.00	12.22
117	None	15.41	0.28	1.38	13.40
118	2 g. $Cr.(OH)_3$ = 1 g. Cr....	15.60	0.06	0.12	0.73
119	None	15.40	0.25	1.08	13.12

Only platinum chloride and potassium dichromate produced marked acceleration. Specimens No. 110 and No. 111 had entirely disappeared. Most of the salts, at this very low concentration, exhibited a slight protective action, as was noticed for silver sulphate in Test 12.

To test the permanence of the protection afforded by coatings of arsenic and tin, specimens Nos. 7, 8 and 9, of Test 3, after having stood in the air 41 days, were immersed in 10 percent sulphuric acid.

Test 16.

At 30° C. for 3 hours 35 minutes.

Specimen	Metal Coated by	Weight	Loss
7	Arsenic	16.44	0.29
8	Arsenic	16.59	0.20
9	Tin	15.90	0.20

For continued protection it is apparently necessary that some salt of the protecting metal be present in the acid.

In view of the conflicting statements in regard to the effect of the presence of copper sulphate in acid used for pickling iron, a direct comparison was made between sulphuric acid, copper sulphate and a combination of the two.

Test 17.

At 30° C. for 3 hours 35 minutes.

Specimen		Weight	Loss
120	19% H_2SO_4	15.81	2.84
121	19% H_2SO_4 + 20 g. $CuSO_4$	15.68	14.89
122	20 g. $CuSO_4$	15.55	4.22

For these particular concentrations the rate of corrosion by the mixture was twice as great as that by the two substances separately. Although the molecular concentration of the sulphuric acid in No. 120 was greater than that of the copper sulphate in No. 122, the latter proved the more active corrosive agent. In this connection it should be noted that the electromotive force of the primary cell, consisting of iron and copper in sulphuric acid, is 0.61 volts, computed from the data of Table I, while that of the iron-hydrogen cell is only 0.37 volts, minus the unknown overvoltage of hydrogen on iron in sulphuric acid. Platinum salts ought to be still more vigorous corrosive agents.

From the experiments given above, certain definite conclusions can be drawn and other generalizations now appear probable, but may require revision or rejection in the light of future experiments.

The writer's hypothesis, that the protective action of arsenic is due to its high overvoltage, has been in a general way confirmed. Other metals of high overvoltage have had a protective influence, while all metals of low overvoltage which deposit on iron are accelerators of its corrosion. So far as overvoltages are known, bismuth alone fails to conform to the hypothesis. Theoretically it should retard corrosion; actually it is an accelerator. Unless redeterminations of the overvoltage of bismuth and the single potential of iron shall reconcile theory with fact, the writer's hypothesis fails. The overvoltage of bismuth was presumably measured on a solid electrode. Bismuth deposited as a powder. If there is the same difference in overvoltage for bismuth as between smooth and spongy platinum, this correction would put bismuth in the list of accelerators.

The statements which follow are intended to apply only to the corrosion of iron by sulphuric acid.

Tin, chromium and mercury retard corrosion; of these, tin alone is as effective as arsenic. The protective action of mercury is very slight.

In studying the effect of different reagents on corrosion it is necessary to consider both the metal and the non-metal or acid radical, since each may have an effect of its own.

The binary salts and acids of the halogens are very good protective agents when used in considerable amounts. To combine most effectively the protective effects of a metal and a halogen, *e. g.*, tin and chlorine, much stannous chloride should not be added, for a large amount of the salt of any metal which precipitates on iron in an acid solution is likely to act as a corrosive agent; only a small amount of stannous chloride should be added, and the extra chlorine added as sodium chloride.

Oxidizing agents are in themselves accelerators of corrosion by acids, although in dilute solution this may be masked by a protective action which supervenes when the oxygen has been used up, as might happen with chromates.

Reducing agents should show more or less protective action, but this fact remains to be confirmed by further experiment.

In general, the whole subject as here presented is but a preliminary study which opens many possibilities for future investigation. It is hoped that the data appended may prove of service to those wishing to pursue the subject, and that the writer's conclusions may meet with confirmation from independent sources.

For convenience in comparing the effects of different reagents, an index is appended.

RETARDERS OF CORROSION

	No. of Specimen
Acid, hydrobromic	109
“ hydrochloric	44, 54
“ hydrofluoric	98
Arsenate of sodium	7, 24, 73, 74, 75, 76
Arsenic sulphate	8
Bromide of potassium	67
Chloride of ammonium	65, 66
“ “ manganese	96
“ “ mercury	10
“ “ sodium	33, 48, 55
“ “ tin	9, 25
Chrome alum	35, 102
Chromium sulphate	17, 99, 118
Fluoride of potassium	97
Hydroquinone	62
Iodide of potassium	93, 103, 104
Mercury chloride	10
Mercury sulphate	91
Resorcine	61
Stannate of sodium	77, 78, 79, 80, 81

ACCELERATORS OF CORROSION

Acid, chromic	34, 37, 38, 39, 51
Bismuth sulphate	13, 28, 113
Chromium chloride	22, 46
Copper sulphate	3, 18, 86, 115
Gold chloride	112
Mercurous nitrate	16
Platinum chloride	89, 90, 111
Potassium chlorate	40, 107
“ chromate	15, 47, 100
“ dichromate	95, 110
“ nitrate	36, 60, 106
“ permanganate	32, 42
Silver nitrate	4, 19
“ sulphate	83, 84, 85, 116

OF NO EFFECT OR DOUBTFUL

Ammonium sulphate	64
Antimony sulphate	5, 14, 31, 114
Boric acid	71
Citric acid	72
Potassium sulphate	63

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DISCUSSION.

PROF. C. F. BURGESS: Thousands of tons of acid are used annually for pickling purposes, and it is surprising that, in view of the tremendous application of these pickling processes, there has been comparatively little published on the action and the constitution of sulphuric acid itself. Dr. Watts points out that certain substances like arsenic retard the rate of corrosion. It is of especial interest to note that adding a little hydrochloric acid would not increase the rate of corrosion, but, on the contrary, it retards it very greatly. Other chlorides do the same thing. Adding salt to sulphuric acid will retard the action. There are certain other substances which will increase the activity of the acid, one of them being the bichromates, which are frequently called "inhibitors."

PRESIDENT W. R. WHITNEY: A great deal has been done in attempting to produce iron which will have less tendency to corrode. I would like to see this paper discussed at length.

DR. CARL HERING: Dr. Watts' suggested explanation, based on over-voltage, is very interesting, and seems to me plausible, It recalls the question I asked before this Society some years ago: What is the physical meaning of this over-voltage? If, for instance, two cells for decomposing water are made exactly alike except that the cathodes are of different metals, then in sending a current through them in series exactly the same quantity of water will be decomposed in both, yet one will consume more energy than the other. The question therefore arises: What is the physical explanation of the consumption of this extra energy and what becomes of it? I presume it is safe to guess that it will appear somewhere as heat.

Another remark of interest was that the over-voltage is probably considerably less when the electrode is rough than when it is smooth. It seems, in other experiments also, that gases liberate themselves much more freely from small particles than from flat surfaces. There is an illustration of this in the typical champagne glass, with its deep tube in the stem of the glass. This tube always has some particles of dirt at the bottom because it can not be cleaned like other portions of the glass, and it is at the bottom of this that the gas always prefers to be liberated. In a really clean glass the champagne would probable appear flat, although as a fact it would really be retaining more of its gas, because that property which seems to correspond with "over-voltage" is greater.

DR. ALLERTON S. CUSHMAN (*Communicated*): Mr. Watts' paper opens up an interesting field of inquiry, although it should be pointed out that it is one in which the controlling factors are exceedingly complex and, up to the present time, but little understood.

The phenomenon of over-voltage is unquestionably but one of the factors which controls the rapidity of corrosion (or solution) of a metallic surface immersed in a more or less dilute mineral acid. But even the phenomenon of over-voltage is profoundly influenced by a number of variables. Caspari used the designation "over-voltage" to express the excess voltage required to begin the disengagement of hydrogen from a metallic surface, as compared with a platinized-platinum electrode. It has been shown that the fact as to whether or not hydrogen is absorbed by the metal to a great extent governs the over-voltage. All metals which, like iron (steel), absorb hydrogen in large amounts have low over-voltages, and *vice versa*.[1] In addition to this, the smoothness or condition of the metallic surface is an important factor.

A piece of cold-rolled sheet steel will have a lower solubility and higher over-voltage than the same sample which is annealed without subsequent cold-rolling. Moreover, a very slight change in the chemical constitution of the steel, in respect to the number and quantity of impurities which may be present, brings in a number of additional variable factors.

We have still to find an entirely satisfactory explanation of the following anomalies, over which I have pondered from time to time for a number of years. If a specimen of sheet iron or steel is immersed in dilute sulphuric acid containing a very small quantity of arsenic, the solution of the metal is retarded. If, on the other hand, we alloy a small quantity of arsenic with iron and roll the material into sheet form, the solubility is accelerated. In the case of copper we find just the reverse to be true; a little copper dissolved in the acid will increase the solvent action of the acid on iron, but a little copper alloyed with steel will reduce the solubility in acid to a remarkable degree.

I have attempted to explain the action of alloyed copper, at least to my own satisfaction, by supposing that its presence called for a higher over-voltage, and that the immersed metal was protected by a film of un-disengaged or ionized hydrogen. If, however, we are dealing with a steel free from copper, and put copper into solution in the acid, we get the usual depolarizing effect produced by copper unequally plated out on the iron, and thus a stimulated solvent action.

The arsenic problem presents new difficulties, and while I do not take issue with Mr. Watts' conclusion that the protective effect due to arsenic in solution is occasioned by over-voltage phenomena, I am free to confess that I am considerably at sea in respect to the explanation, and am glad to take refuge with the author in the perhaps vague assertion that "arsenic is unique among metals which precipitate themselves upon iron from solution."

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[1] See Mott: Over-voltage as a Factor in the Corrosion of Metals. Trans. Am. Electrochemical Society, **15**, 569 (1909).

I have sometimes surmised the possibility of catalytic phenomena being an important factor in the solution of metals in acids, and whether or not the presence of arsenic acted as an anti-catalytic or "poison," as Bredig found it to be in his classical researches on the catalytic reactions produced by colloidal solutions of metallic platinum and gold.

Mr. Watts has pointed out another curious anomaly which requires explanation, *viz.*, that whereas it is well known that solutions of chromic acid and its salts will protect samples of iron and steel from corrosion when immersed in liquids containing them, on the other hand, when we are dealing with a fairly strong acid-immersion test, the addition of chromic acid increases the corrosion effect. I have worked on problems similar to this, as have also Friend in England and Heyn and Bauer in Germany, and it has frequently been pointed out that when mixtures of inhibitors and stimulators are present at the same time in a solution, the effect produced will depend upon the special conditions of equilibrium present in the system. I first pointed this out in a paper on the "Inhibitive Value of Certain Pigments," presented before the American Society for Testing Materials, at its annual meeting in 1908. Heyn and Bauer and Friend have shown that there is a critical concentration for each substance dissolved in water, as far as corrosion phenomena are concerned. If, however, we have mixtures of materials in the solution, it is hard to predicate the results which will be obtained. The fact that Mr. Watts has found that chromic acid stimulates corrosion under the conditions of his experiments in nowise interferes with the value of the observations that chromic acid and its salts act as strong inhibitors of corrosion under neutral as well as under very slightly acid and alkaline conditions, provided the concentration of the chromic acid ions is sufficiently great.

I have found Mr. Watts' paper an extremely interesting one, suggestive in many ways, and it is, in my opinion, a valuable contribution to studies of corrosion.

MR. E. B. SPEAR: In regard to the rusting of iron in the presence of potassium dichromate, we have devised an experiment in our laboratory to show that the rate of corrosion is a function of the concentrations of the oxidizing agent and of the hydrogen ion. Iron becomes passive in concentrated solutions of dichromate containing little free acid, while it corrodes much faster in very dilute solutions of the oxidizing agent than it does in water containing the same amount of acid. As the acid is increased, however, the concentrated solutions of the dichromate attack the iron very rapidly.

MR. WALTER A. PATRICK: In order to study the effect of the concentration of the sulphuric acid, the following experiment was carried out. Two pieces of steel were secured, one of which had a high oxygen content (*i. e.*, was a poor steel), while the other was normal steel, but contained about 0.2 percent copper. Both were mild steels. Carefully cleaned pieces of these two steels were then placed in solutions of sulphuric acid, the concentration of which varied from about 25 percent down to 1 percent. In the strong acid the poor steel dissolved about 50 times as fast as the steel containing the small amount of copper, but in the more dilute acid solutions the difference between the two steels became less and less until in a 1 percent acid the poor steel was dissolving only 3 times as fast as the other steel. If the acid corrosion test were carried out upon the above samples with 20 percent acid, it would show that the copper steel was 50 times as good as the other steel; but with 1 percent acid the relation between the two steels would be only 3 instead of 50, which is probably much nearer the true value for practical purposes.

MR. WATTS (*Communicated*): Experiments in the corrosion of alloys of iron and arsenic, carried out in the chemical engineering laboratories of the University of Wisconsin, gave results opposite to those cited by Dr. Cushman. The samples containing arsenic were somewhat more resistant both to atmospheric oxidation and to corrosion by dilute sulphuric acid than the original iron. The maximum amount of arsenic in any of the alloys tested at the University of Wisconsin was 4 percent. The different results obtained by Dr. Cushman may have been due to the use of higher percentages of arsenic. But little information has been published concerning the constitution of the arsenic-iron alloys, so that it is impossible at present to predict their behavior throughout the whole series toward a corrosive agent such as sulphuric acid. Definite compounds of iron and arsenic appear to be present in some of the alloys.

Stead[1] says: "Arsenic and iron most readily combine to form arsenide of iron. * * * We find that on solution of arsenical steel in dilute hydrochloric or sulphuric acid practically the whole of the arsenic remains as a black, insoluble arsenide of iron."

This indicates that iron is the anode in the voltaic cell formed by the contact of iron with its arsenide in sulphuric acid, and the considerable electromotive force of this cell may be responsible for an increase in the rate of corrosion of the iron when such compounds are present.

Since this alloyed arsenic is not dissolved by the acid, it fails to exert the well-known protective action produced when a little arsenic has been previously dissolved in the acid.

The iron-copper alloys, up to a content of 8 percent copper, consist of solid solutions of copper in iron.[2] They are homogeneous, and any differences in the rates of attack of such alloys by sulphuric acid, as compared with the rate at which the acid attacks pure iron, must depend upon the inherent nature of the two materials. In binary alloys which are solid solutions we would naturally expect a mean between the properties of the elements of which the alloy is composed. Copper is attacked only slowly by sulphuric acid. It is therefore to be expected that alloys which consist of solid solutions of copper in iron will resist corrosion by sulphuric acid better than iron. This proves to be the case.

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[1] J. Iron and Steel Inst. 1888, I, 180.

[2] J. E. Stead. J. Iron and Steel Inst. 1901, II, 112.

A Paper read at a Joint Session of Sections Xa: Electrochemistry, and Ve: Paints, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912. Dr. W. H. Walker in the Chair.

THE RATE OF RUSTING OF IRON AND STEEL

By James Aston and Charles F. Burgess.

An editorial review of chemical progress in 1911 says:[1]

"The rusting of iron has received its usual amount of study and controversy, but the question remains as ragged and dubious as it has been for years. Part of the difficulty arises from some of the investigators falling in love with a neat, trim, complete theory, blinding their eyes to its defects, and rejecting the contributions of other workers who do not worship their own idol."

In spite of the vast amount of study which has been given this subject, it is a regrettable fact that there is but a limited amount of information and data available bearing upon the practical phases of the question. The painstaking and detailed work which has been devoted to proving or disproving a theory that carbonic acid is the cause of rusting is illustrated by the fact that one of the prominent workers in this field asserts that in spite of boiling and other methods of purifying there still adhered to the inner walls of a glass vessel in which corrosion tests were made enough CO_2 from the glass blower's breath to make the results of tests of doubtful value. On the other hand the controversy on the intensely practical question as to the relative durability of iron and steel is still unsettled; there is no reliable information as to how durability is dependent upon purity and as to the quantitative influence of various impurities. There are no standard methods of testing, by means of which the corrosion determinations made by one investigator may be compared with those made by another.

For a number of years experimental work has been carried on in the Chemical Engineering Laboratories of the University of Wisconsin on various phases of iron corrosion, and the purpose of this paper is to present some of these results as far as

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[1] The Engineer (London), Jan. 12, 1912.

they deal with commercial forms of iron and steel. Various grades of commercial materials were subjected to corrosion tests during 1910 and 1911, and in presenting these results the purpose is not to draw an accurate comparison of the relative merits of various commercial materials at present available, but rather to give some data on testing methods. In view of marked advances which have recently been made, the samples which were selected early in 1909 probably do not include representative samples of some of the high purity materials at present available.

No attempt is made to classify the results in accord with any theory, but rather to submit them in such manner that they may serve as a record containing some information of general usefulness, and to which results of further measurements which are under way may be compared.

While appreciating the limitations upon corrosion data as generally submitted, and while desiring to make our tests standard as far as possible, we must recognize serious limitations on our own results—limitations due partly to lack of foresight and partly to lack of facilities, time and financial resources.

Samples were prepared from six different classes of materials as representative of the range of materials obtainable on the market. These comprise several grades of open-hearth iron of high chemical purity, Swedish iron, open hearth mild steel, open hearth mild steel subjected to special hot working process, Bessemer rail steel, and gray cast iron. Some of these materials were chosen both from bar and sheet stock.

The list of materials thus chosen comprise twelve in number, and six samples of each were prepared for and subjected to various corrosion tests, there being 72 test specimens in all.

The twelve materials are described in the following list:

1. Open-hearth high purity iron from bar stock.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) ground to smooth surface on emery disc.

2. Open-hearth high purity iron.—Samples 1 x 2 x ¼ in. (2.5 x 5 x 0.65 cm.) ground to smooth surface.

3. Open-hearth high purity iron.—Samples 3 x 3 in. (7.5 x 7.5 x 0.16 cm.) from 16 gauge sheet. Samples were used with black annealing scale.

4. Same as 3, but ground smooth on emery disc to remove scale.

5. Swedish wrought iron.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) ground smooth.

6. Open-hearth steel—from plate stock.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.)—taken as representative of good quality low carbon steel of the better grade used in boiler plate.

7. Open-hearth steel sheet—16 gauge.—Samples 3 x 3 in. (7.5 x 7.5 x 0.16 cm.) with annealing scale. From designation by the manufacturer it is representative of very mild, annealed, high grade open hearth product.

8. Same as No. 7, but with scale removed and surface ground smooth.

9. Open-hearth special sheet steel, 20 gauge.—Samples 3 x 3 in. (7.5 x 7.5 x 0.1 cm.) with annealing scale. It is represented as a special steel, by reason of, a mechanical treatment of the ingot during working down with the idea of eliminating surface heterogeneity and blow holes.

10. Same as No. 9, but with scale removed and surface ground smooth.

11. Bessemer steel.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) cut from the flange of a steel rail. Analysis not determined, but may be taken as representative of material having carbon content of 0.50 to 0.60.

12. Cast iron.—Samples 1 x 2 x ½ in. (2.5 x 5 x 1.25 cm.) cut from a medium-grained, gray-iron casting. Analysis not determined, but representative of average iron casting, except that the scale or surface chill has been removed.

Six samples of each of the above listed materials were subjected to tests for corrosion; these are indicated by *a, b, c, d, e,* and *f* respectively; *a, b* and *c* were exposed to the weather conditions on the roof of the Chemical Engineering building, at the University of Wisconsin, and *d, e* and *f* were placed at the ventilator outlet on the roof of the Chemistry Building, where together with the weathering conditions additional corrosive action was exerted by the gaseous fumes from the chemical laboratory. It is believed that in the former case we have typical atmospheric corrosive conditions uninfluenced by smoke and fume, while in the latter case the atmospheric corrosion is considerably aggravated by fume. The former will be designated as "atmospheric corrosion," and the latter as "fume corrosion." The fume corrosion was not, however, excessively severe, since the ventilating fan discharged the heated air at a high velocity, with conditions favorable for the rapid drying of specimens after wetting from atmospheric conditions.

All samples were ground or polished to a uniformly smooth surface on a fine emery disc. However, with the sheet material, duplicate sets were exposed without removal of the rolling or annealing scale. The bar samples were set in wood racks, and the sheet samples suspended in frames, all edge up; the racks were built to allow for as good drainage as possible. All specimens were first exposed on December 22, 1910, after weighing. On March 8, 1911, one of each of the three making up the various sets was taken in, the rust removed by ammonium citrate solution, and the loss determined. These samples were then exposed (without altering the surface conditions) a second time, on March 8, 1911. On May 21, 1911, the above mentioned samples, together with one of each set which had been out for the total period from December 22, 1910 to May 21, 1911, were taken in, and the amount of corrosion determined.

All of these specimens were then ground to a smooth finish, weighed and subjected to 20 percent sulphuric acid corrosion for one hour, according to the specifications suggested by the American Society for Testing Materials. This loss was then determined. Finally, after regrinding and weighing, the bar samples were again exposed to the previous weathering conditions on June 1, 1911. The sheets were too much corroded by the acid to be available for this test. On October 18, 1911, all specimens, including three of each bar sample, and one of each sheet sample, were taken in and the corrosion loss determined.

At the completion of these tests, all of the bar samples, Nos. *1, 2, 5, 6, 11* and *12*, were examined as to character and depth of pitting. This character of pitting is shown photographically. The depth of pitting was determined by carefully grinding down one of the faces of each specimen, until the pit marks just disappeared, and the amount of metal thus removed was noted. To these values were added the losses by corrosion, and the sum gives a value called for convenience the "equivalent corrosion" per square inch. Then by dividing the "equivalent corrosion" by the actual corrosion we have values which we choose to designate as the "pitting factor."

The diagram, Fig. 1, will illustrate perhaps somewhat more clearly the various steps through which each set of samples passed.

In making the acid tests at the end of the second period the average of *a* and *b* and of *d* and *e* were taken—it being found that close agreement existed between the two samples of each pair, though not between the two pairs.

DIAGRAM I.

	Atmospheric			*Fume*		
	a	*b*	*c*	*d*	*e*	*f*
Dec. 22, 1910:	......	......	......	......	......	......

March 8, 1911:

End of 75 days—*a* and *d*, freed from rust—loss determined and replaced.

May 21, 1911:

End of 150 days—*a, b, d* and *e* had rust removed, loss determined and ground to smooth surface. Then subjected to acid test. Then ground again to smooth surface, and exposed for 139 days.

June 1, 1911:	......	......	......	......	......	......

Oct. 18, 1911:

End of 300 days—all samples taken in and loss determined.

From analysis of the data thus obtained certain conclusions of interest and of possible value may be drawn as having a bearing upon the important problem of corrosion. The question which is perhaps of the greatest importance and of interest to the greatest number is "What is the relative durability of the various materials on the market under various corrosive conditions?" This is a question which we do not attempt to answer. Although some of the tables presented herein appear to give numerical expression to the corrodibility of various grades of materials, they cannot be used as a guide, since it is by no means certain that the small samples employed were truly representative of the classes of materials from which they were drawn. In fact, recent microscopic analysis seems to show that in one instance at least especially inferior samples were employed in these tests. However, it is believed that the figures represent some concrete idea of the possible ranges of values which may be encountered in commercial materials as judged from the durability standpoint.

Other and more reliable conclusions can be drawn from these tests. It is shown that atmospheric corrosion depends upon the seasons of the year and upon the gaseous impurities in the air; that these impurities affect different grades of iron and steel in different degrees. Much interest attaches at the present time to the usefulness of the accelerated acid test as a means of judging the durability of the metal under various corrosive conditions, and some conclusive evidence is given to show that there is little relationship. The accelerating influence of an initial rust formation upon subsequent rusting is demonstrated. The black scale on sheet iron is shown to have little, if any, retarding influence upon deterioration by rusting. A peculiarity is apparently pointed out that iron after exposure to severe atmospheric corrosive conditions undergoes some deep-seated change, which is evidenced by a notably decreased resistance to attack by acid. It is well known that the damage to iron by rusting is not measurable alone by the loss of weight of the metal, but the depth of pitting produced by the rust is an important factor. An attempt is made to give a numerical expression to this factor.

In Tables I and II the results are given as "corrosion factors," the reference unit being taken as the rate at which material No. 1 rusted per day under normal atmospheric exposure during the winter period. The use of the "corrosion factor" is in accordance with the practice recommended by Friend.[2] In making measurements, all of the corrosion losses were reduced to loss per square inch per day, and the ratio of that loss compared with the sample chosen as standard constitutes the corrosion factors. In order that these corrosion factors can be converted into actual loss of weight per day, there is given the "corrosion constant," which is 0.00092 g. per sq. inch per day, or 0.01426 g. per sq. dcm.

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[2] The Corrosion of Iron and Steel, J. Newton Friend, p. 276.

Table I is of greater practical importance, since the "fume test" represents only a special artificial condition not capable of reproduction.

The influence of the seasons upon corrodibility is marked. The average of the corrosion factors of the twelve materials for winter is 118, for the spring 169, and for the summer and autumn 60.

TABLE I.

Corrosion Factors Atmospheric Test

Material	(a) 1st Period 75 days Winter	(a) 2nd Period 75 days Spring	(b) Combined Period of 150 days	(a) 139 day Period Summer	(b) 139 day Period Summer	(c) Total Period of 300 days
1. High purity iron ½" bar	100	134	154	74	79	79.6
2. High purity iron ¼" bar	94.5	100	143	67	59	63.2
3. High purity iron sheet with scale	148	135	149	..	..	109
4. High purity iron sheet without scale	124	124	135	..	..	90.5
5. Swedish iron ½" bar....	82.5	96	141	48.5	73.5	73.5
6. Open hearth steel boiler plate	97	123	135	48.5	51	99
7. Open hearth steel sheet with scale	141	193	177	..	..	186
8. Open hearth steel sheet without scale	169	175	185	..	..	150
9. Special sheet steel with scale	121	460	307	..	..	160
10. Special sheet steel without scale	137	276	254	..	..	149
11. Bessemer rail steel......	91	95	123	51	59	63.5
12. Gray cast iron..........	113	105	91.5	59	54	93

Corrosion constant = 100 = 0.00092 g. pr. sq. in. per day = 0.01426 g. sq. dcm.

It is unfortunate that the tests did not cover a 365 day run—but the figures given in the 300 day column may be taken as representing approximately the behavior of the metals when exposed to a year's atmospheric attack. The average 300 day corrosion factor is 111. The corrosion constant being 0.01426 g. per sq. dcm. per day, the amount of corrosion per year is 365 x 1.11 x 0.01426 = 5.777 g. per sq. dcm. of surface per year.

Assuming a uniform corrosion without pitting, the thickness of iron removed by rust per year would be according to the above figure, and with the specific gravity of iron taken as eight, 0.00722 cm. or 0.00284 inch.

On this basis a 16-gauge sheet, having a thickness of 1/16 in. (0.16 cm.) when exposed to atmospheric corrosion on both sides, would have a life of 11 years. This is a longer life than would actually be attained, because of pitting and other disturbing factors. It is, of course, not demonstrated by these tests whether there is an accelerating or retarding action during succeeding years.

TABLE II.

Corrosion Factors **Fume Test**

Material	(*d*) 1st Period 75 days	(*d*) 2nd Period 75 days	(*e*) Combined Period 150 days	(*d*) 139 day Period Summer	(*e*) 139 day Period Summer	(*f*) Total Period 300 days
1. High purity iron ½" bar...	147	305	211	134	132	189
2. High purity iron ¼" bar..	146	325	207	117	108	183
3. High purity iron sheet with scale	157	305	193	...	...	160
4. High purity iron sheet without scale	128	299	200	... ...	... ...	216
5. Swedish iron ½" bar......	133	244	144	88.5	95	122
6. Open hearth steel boiler plate	138	251	179	107	124	111
7. Open hearth steel sheet with scale	116	280	134	...	...	108
8. Open hearth steel sheet without scale	163	337	377	...	...	148
9. Special sheet steel with scale	185	303	250	...	...	101
10. Special sheet steel without scale	173	307	340	...	...	135
11. Bessemer rail steel	97	140	87	93.5	83	63.5
12. Gray cast iron	117	150	115	73.5	83	67.2

Corrosion constant = 100 = 0.00092 g. pr. sq. in. per day = 0.01426 g. sq. dcm. per day.

As to the relative durabiltiy of different grades of materials, no absolute conclusions are possible, since the samples chosen may not be truly representative, but on the assumption that they are, we have a range from 63.5, as representing the most resistant, to 186 for the least resistant, or a variation of over one hundred percent.

That a commercial material, even though it may be of a uniform and constant composition and structure, cannot be assigned a definite "corrosion factor" is shown by comparison of Table I with Table II. The more resistant metals under atmospheric corrosion become the less resistant under another kind of corrosive atmosphere. That is, the corrosion conditions are important as affecting the relative durability of a given list of materials. Following this line, then, the "atmospheric" corrosion to which these samples were subjected is not necessarily the same as atmospheric corrosion in other sections of the country, and the data obtained cannot be used therefore without reservation.

TABLE III.

Acid Corrosion.—Relative Losses by Standard Acid Test.

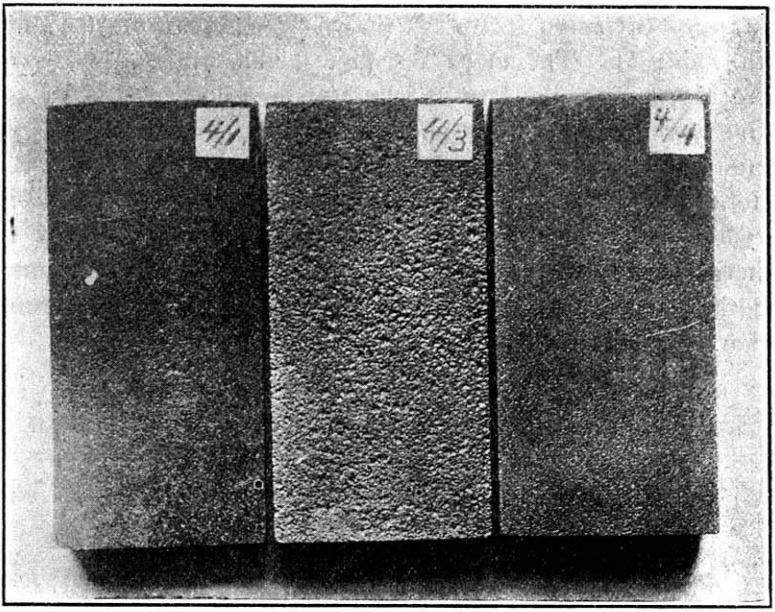
	(*A*) Samples first exposed to atmospheric corrosion	(*B*) Samples first exposed to fume corrosion	B/A
1	100	140	1.40
2	79	142	1.80
3	67	168	2.54
4	80.5	136	1.69
5	320	361	1.13
6	1,960	2,210	1.13
7	5,500	9,000	1.63
8	5,150	11,500	2.24
9	6,710	7,050	1.05
10	7,770	4,450	0.57
11	2,100	3,170	1.51
12	3,330	4,080	1.23

Corrosion constant = 100 = 0.0072 gr. per sq inch surface per hour = 0.00115 gr. per sq. cm. per hour.

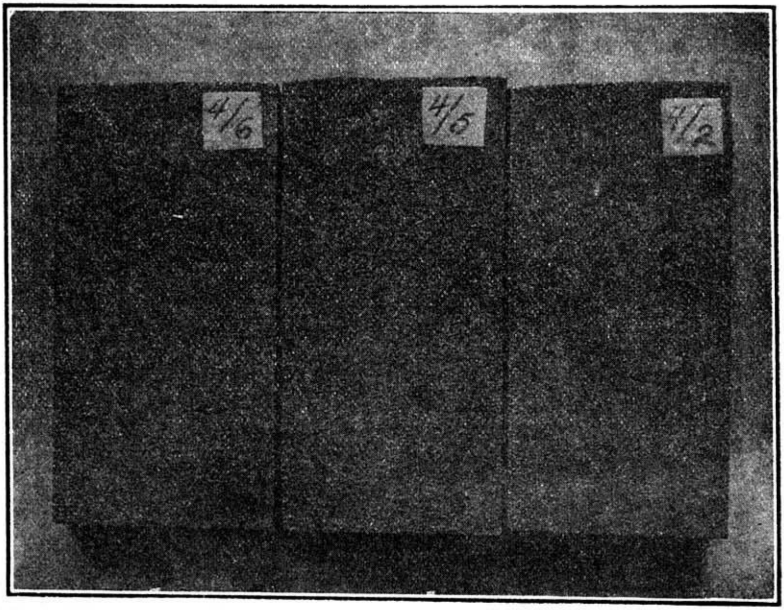
Acid Corrosion.

After having been exposed to atmospheric and fume corrosion for 150 days, the samples were ground down to a smooth, bright surface and exposed to the standard sulphuric acid test. There were duplicate samples of each material, and the results recorded in Table III are the averages of these two determinations. That there were only very small errors in measurement was shown by the close agreement between the losses of each of the two corresponding samples.

By comparison of the last column of Table I, giving corrosion factors for atmospheric corrosion, with the first column of Table III, giving the corrosion factors for acid corrosion, we had a



139 Days. 300 days. 139 days.
FIG. 2. Atmospheric Corrosion, Open Hearth Steel Plate.



139 Days. 300 Days. 139 Days.
FIG. 3. Fume Corrosion, Open Hearth Steel Plate.

means of judging something of the significance of the acid test. There is seen to be no direct relationship between the two tests. The four materials showing the highest acid corrosion were the ones showing the highest rate of atmospheric corrosion, but the sample showing the least atmospheric corrosion, the Bessemer rail material, has a high acid corrosion rate. While the high purity samples had the lowest rates of acid corrosion, and were likewise below the average in rate of atmospheric rusting, there is no direct relationship as between the respective samples of this class of materials.

TABLE IV.

Influence of Scale on Rate of Rusting.

Atmospheric Test.

Material	75 day Period		150 day Period		300 day Period	
	with scale	without scale	with scale	without scale	with scale	without scale
3 and *4*— High purity iron..	148	124	149	135	109	90.5
7 and *8*— Open hearth mild steel	141	169	177	185	186	150
9 and *10*— Open hearth special steel	121	137	307	254	160	149
Totals	410	430	633	574	455	389.5

Fume Test.

3 and *4*— High purity iron..	157	128	193	200	160	216
7 and *8*— Open hearth mild steel	116	163	134	377	108	148
9 and *10*— Open hearth special steel	185	173	256	340	161	135
Totals	458	464	583	917	429	499

By comparison of the acid corrosion with the fume corrosion tests, column 2 of Table III and column 6 of Table II, there is seen to be no utility in the acid test, since the samples most resistant to acid were among the least resistant to the fumes.

A characteristic of the acid test is its extreme sensitiveness,

× 70

FIG. 4. Low Carbon Areas with Slag.

× 70

FIG. 5. Medium Carbon Area with Slag.

the most corrodible metal being dissolved 116 times as rapidly as the most resistant. The atmospheric test shows a ratio of only 2.9 as between the most and the least corrosive. Evidently there are factors which influence the rate of acid attack which do not enter into atmospheric corrosion.

An interesting phenomenon is shown in column three of the acid corrosion table, in that the attack on the metals which had been subjected to fume corrosion was notably greater, with but one exception, than on those which had been subjected to atmospheric attack. Just why this should be is not evident, but it appears that the fume corrosion has had a deep-seated action, penetrating into the metal and making it more susceptible to acid corrosion.

Influence of Scale on Rate of Rusting.

In making quantitative corrosion determinations, and a comparison of durability of different classes of material, the question arises as to the influence of the black scale which comes on commercial sheet, and whether for sake of comparison it is important that all of this scale be removed before beginning a test. This in turn depends upon whether the oxide scale has a protective or accelerating action. There is no doubt that the protective property of mill scale is dependent upon its physical properties, continuity, etc.

It was the purpose in conducting these tests to make comparison of rusting on samples identical in every particular except as to presence of the mill scale. In the above tables, materials Nos. *3, 4, 7, 8, 9, 10,* were subjected to this comparison, the odd numbered materials being tested with the scale, while from the even numbered materials the scale was carefully removed by mechanical means before the test.

The results of this comparison are presented in Table IV. Except for the first 75-day period it is shown that the mill scale had an accelerating effect for the atmospheric test and a retardent action for the fume test.

Accelerating Influence of Rust.

It is a generally accepted belief that rust having once formed upon an iron surface, this adhering rust exerts an accelerating

FIG. 6. Swedish Iron. Junction of Medium and Low Carbon Areas with Slag Lines.

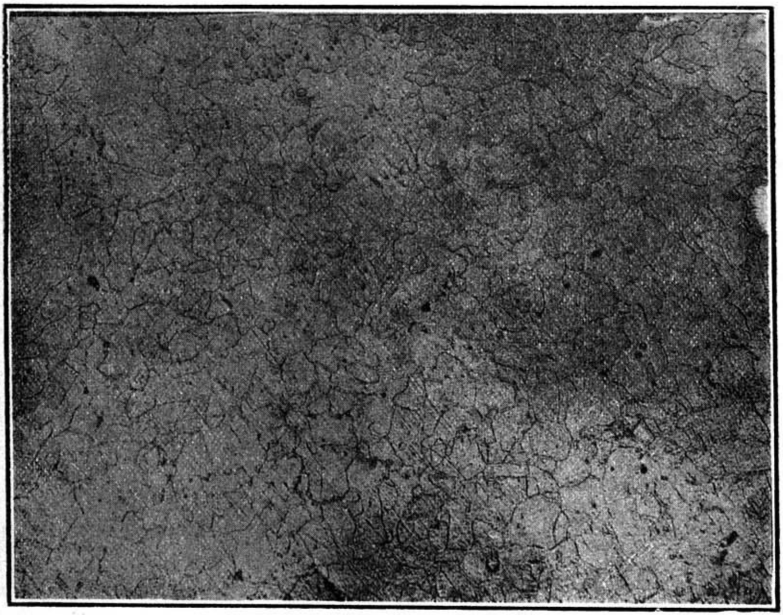


FIG. 7. High Purity Iron. Good, Clean Ferrite Structure.

influence upon the subsequent rate of rust formation; that the adherent rust, instead of acting as a protection, has a reverse influence.

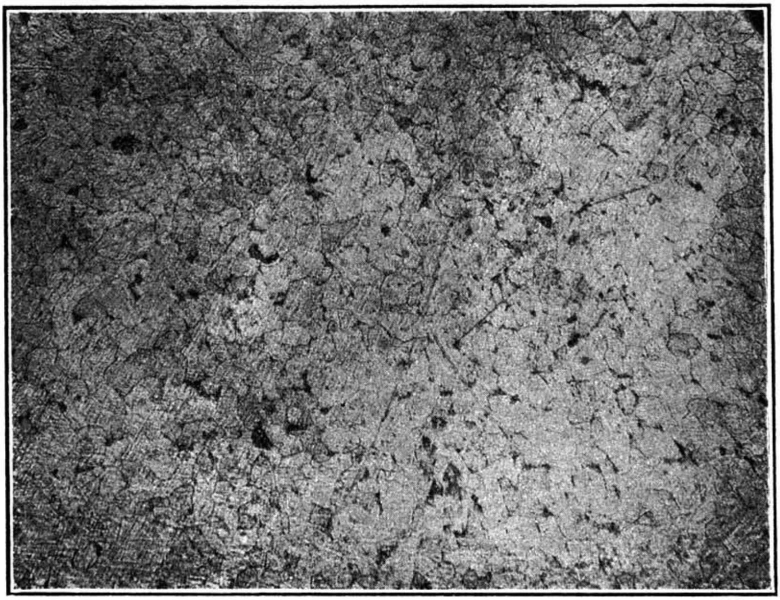
The tests above recorded present data from which a quantitative idea of the influence of this factor may be derived. Samples marked (*a*) and (*d*) in Tables I and II, were exposed to two successive periods of rusting, the rust having been removed at the end of each period. At the same time similar test pieces (*b*) and (*e*) were exposed without disturbance for the entire 150-day period. If the presence of rust exerts an accelerating action, this will result in the total amount of corrosion from the 150-day samples being greater than for the sum of the corrosion of the two 75-day periods. This relationship is shown in Table V. The first and second columns give the corrosion factors for the two 75-day periods, the third column the average of these two periods. The fourth column gives the corrosion factors for the 150-day period. The ratios of the values of the fourth to the third column give the figures for the last column, which indicates whether there has been an accelerating or a retarding influence caused by the presence of rust.

From this table it is seen, that when subjected to atmospheric corrosion, there has been an accelerating action on all materials except cast iron; while with the materials exposed to fume corrosion the presence of the rust coating seems to have exerted a protective action on all but three of the materials. It is, of course, evident that these ratios would be different, depending upon the lengths of time of exposure. The accelerating action is probably greater when there is only a small amount of rust on the surface than when the rust increases in thickness.

The deduction of particular interest from this table is that the kinds of conditions by which rusting is produced are of importance, and that external conditions as well as internal structure and purity of material must be considered in studying iron corrosion.

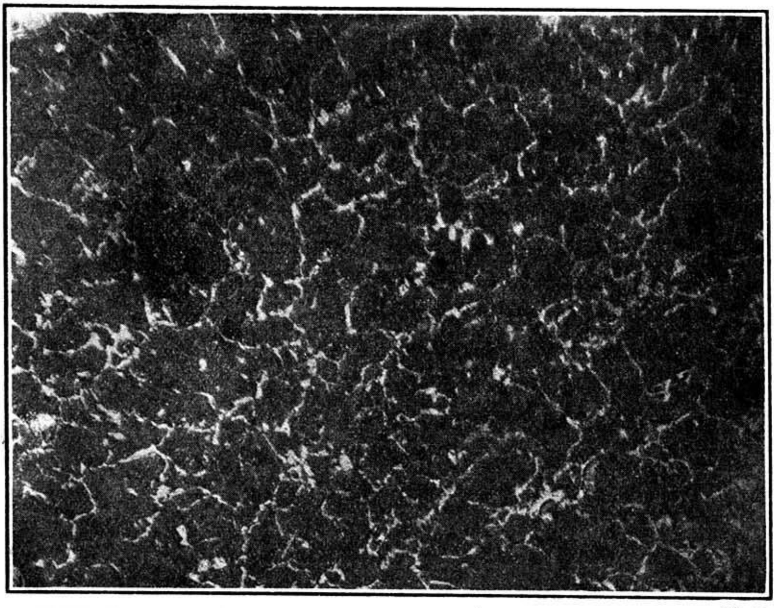
Influence of Pitting.

It is obvious that the rate of deterioration of iron is measurable not only by the loss of weight, but that the depth of pitting is a factor which must be included. An attempt is made here to give



× 70

FIG. 8. Open Hearth Plate.
Ferrite and Small Pearlitic Areas, Indicating Low Carbon Content; Few Inclusions, Indicating Good Material.



× 70

FIG. 9. Bessemer Rail Steel.
Normal Structure of Rail from Reheated Billet and Rolled Hot.

a quantitative idea of this factor. It is unfortunate that all of the samples could not be tested for pitting effect. The thin sheet samples had been rendered too thin to be subjected to accurate grinding for removal of the pit marks and only the bar samples were examined.

TABLE V.

Accelerating Influences of Rust on Rusting.—Relative Corrosion Factors.

Atmospheric Corrosion.

Material	1st Period 75 days	2nd Period 75 days	Average	Combined Period 150 days	Accelerating factor (percent)
1	100	134	117	154	131
2	94.5	109	101.7	143	140
3	148	135	141.5	149	105
4	124	124	124	135	109
5	82.5	96	89.2	141	158
6	97	123	110	135	122
7	141	193	167	177	106
8	169	175	172	185	108
9	121	460	290.5	307	106
10	137	276	206.5	254	123
11	91	95	93	123	132
12	113	105	109	91.5	84

Fume Corrosion.

1	147	305	226	211	93
2	146	325	235.5	207	88
3	157	305	231	193	83
4	128	299	213.5	200	94
5	133	244	188.5	144	76
6	138	251	194.5	179	92
7	116	280	198	134	68
8	163	337	250	377	151
9	185	303	244	256	105
10	173	307	240	340	142
11	97	140	118.5	87	74
12	117	150	133.5	115	86

The materials, Nos. *1, 2, 5, 6, 11* and *12*, which had been rusting during the 139 and 300-day periods, were filed down and ground smooth until the pit marks had just disappeared and the amount of metal removed by this mechanical operation was determined. This was reduced to weight per square inch and

× 70

Fig. 10. Grey Cast Iron, Unetched, showing Graphite Distribution.

× 70

Fig. 11. Low Carbon Steel. Special Mechanical Treatment.

added to the corrosion loss per square inch. This combined value is taken as representing the combined deterioration by rusting and pitting, and the ratio of this amount to that due to rusting alone is indicated by what we choose to call the "Pitting Factor." The results are recorded in Table VI.

TABLE VI.

Influence of Pitting.

Atmospheric Corrosion.

Description of Material	139 Day Period			300 Day Period		
	Corrosion loss g. per sq. in.	Corrosion and Grinding loss g. per sq. in.	Pitting factor	Corrosion Loss g. per sq. in.	Corrosion and Grinding loss g. per sq. in.	Pitting factor
1. High purity iron ½ in. (1.25 cm.) thick.	0.1014	0.4874	4.8	0.2193	1.0433	4.70
	0.095	0.456	4.8			
2. High purity iron ¼ in. (0.65 cm.) thick.	0.0752	0.4072	5.41	0.230	0.885	3.86
	0.0853	0.4523	5.30			
5. Swedish wrought iron.	0.093	0.423	4.55	0.1995	0.9105	4.57
	0.0623	0.404	6.52			
6. O. H. steel boiler plate.	0.0658	0.3398	5.16	0.272	1.022	3.70
	0.0621	0.3061	4.93			
11. Bessemer rail steel.	0.0764	0.4344	5.68	0.1756	0.9566	5.45
	0.0668	0.3638	5.44			
12. Cast iron.	0.0763	0.4223	5.54	0.253	0.888	3.51
	0.0698	0.3838	5.50			

Fume Corrosion.

1. High purity iron ½ in. (1.25 cm.) thick.	0.168	0.609	3.63	0.5219	0.9739	1.86
	0.1601	0.555	3.47			
2. High purity iron ¼ in. (0.65 cm.) thick.	0.1382	0.4483	3.25	0.507	0.855	1.68
	0.1497	0.4387	2.94			
5. Swedish wrought iron.	0.121	0.3125	2.58	0.336	0.740	2.2
	0.113	0.417	3.69			
6. O. H. steel boiler plate.	0.1585	0.5615	3.54	0.3054	0.7504	2.40
	0.1375	0.5145	3.74			
11. Bessemer rail steel.	0.1053	0.4683	4.59	0.1756	0.555	3.18
	0.1196	0.4516	3.78			
12. Cast iron.	0.0925	0.3665	3.96	0.186	0.491	2.64
	0.1064	0.3704	3.48			

The fact of interest drawn from this table is that the combined effect of rusting and pitting under atmospheric conditions is from 3.5 to 6.5 times that as measured by the rusting alone, while under the fume corrosion conditions the pitting is much less pronounced, as represented by the corresponding ratios between limits of 1.68 and 3.96. While the loss by rusting for the 300-day period is much the greater under the fume conditions, the pitting is less marked and the total deterioration is less.

Photographic records of the appearance of each of the samples after corrosion were obtained, a typical one being presented in Figures 2 and 3. This is for the open-hearth plate steel. There was a striking similarity of appearance as between the various materials and it is for this reason that only one is presented here. The fact that there has been less pitting under the fume than under atmospheric conditions is clearly shown.

Microscopic examination was also made of the various samples to determine if possible how the rate of corrosion may have been dependent upon internal structure. Some of these sections, magnified to 70 diameters, are presented in Figures 4 to 10.

It is a prevalent impression that corrosion, rusting and pitting are dependent upon the impurities in the metal, upon the internal structure, and especially upon segregation; that if there is absolute uniformity, absolute purity, and absence of slag, oxide and other inclusions, there will be minimum rusting. These impressions do not appear to be borne out by this investigation. The Swedish iron is shown in Figures 4, 5 and 6 to be markedly heterogeneous, there being some areas of pure ferrite, but others of medium carbon content and with slag inclusions. Fig. 7 shows good uniformity in one of the commercially pure irons, while other microphotographs not shown here indicate spots of impurity. In preparing these microphotographs it was the intent to make them representative of the average appearance of the samples rather than to emphasize impurities or non-uniformity.

SUMMARY.

1. The range of durability of various grades of commercial materials when exposed to a 300-day atmospheric test is represented by the ratio of about one to three. When exposed to the acid test the ratio is very much greater, being one to one hundred and sixteen.

2. The average rate of normal atmospheric corrosion under conditions found in Madison, Wis., is 5.777 g. per sq. dcm. per year. For a 16-gauge plate (0.16 cm. thick) exposed on both sides and assuming uniform corrosion this would mean a complete disappearance in about 11 years.

3. The corrosive action of the atmosphere may be influenced by fumes and smoke, so as to influence in marked degree the durability of iron, and that material most durable under one set of conditions may not necessarily be the most durable under others.

4. Since the service conditions constitute a vital factor in determining the rust-resisting power of iron, a study of these conditions is equally important with a study of the materials themselves.

5. The seasons and the weather conditions have a marked influence on the rate of corrosion.

6. The sulphuric acid test is not a satisfactory guide for estimating the rust-resisting power of a metal. It has a certain usefulness in investigative work, but is of little value as a practical test.

7. The ordinary black scale does not appear to be a retarder of atmospheric rust. Pitting causes deterioration in a year's time approximately three times as great as would rusting if distributed uniformly over the surface.

8. While impurities in the metal undoubtedly have an influence on the rate of rusting, it is evident that, although some are detrimental, others may be beneficial. Little accurate information appears available on this matter.

9. Heterogeneity of structure of metal is generally supposed to be antagonistic to durability, but this investigation shows that if it is a factor it is one of secondary significance and overshadowed by other factors.

These results are presented as tentative only, since conclusive evidence on a problem so important and complicated as the corrosion of iron and steel can be obtained only by repeated tests upon a large number of samples.

The authors acknowledge their indebtedness to Mr. E. C. Haag in making many of the measurements recorded in this paper, and to the Northern Chemical Engineering Laboratories, in the preparation of specimens and co-operating otherwise in the work.

University of Wisconsin.

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INFLUENCE OF VARIOUS ELEMENTS ON THE CORRODIBILITY OF IRON.

By Charles F. Burgess and James Aston.

Incidentally to an extensive investigation on electrolytic iron and alloys produced therefrom, as carried out under a grant made a number of years ago by the Carnegie Institute, tests were made upon the corrodibility of a number of alloys. Acknowledgment is made to Mr. B. F. Bennett for his assistance on this particular phase of the work.

The electrolytic iron which has been used as a basis for the alloys, when compared with materials commercially available, may be taken as essentially pure, and in making up the alloys care was taken to exclude impurities as far as possible. The method of preparing the test samples consisted in first melting the electrolytic iron or the electrolytic iron alloy in closed graphite magnesia-lined crucibles heated in an electrical resistor furnace. Upon cooling down, the small ingots weighing from one to two pounds were forged into rods and strips. Only those alloys which would forge readily into shape were included in these tests.

From the forged bars samples were taken for chemical analysis, and through the courtesy of Messrs. Booth, Garrett and Blair, of Philadelphia, the determinations given in the first column of the attached table were obtained.

The corrosion test samples were about 2 x 1 x ⅛ in. (5 cm. x 2.5 cm. x 3.1 mm.). They were exposed to the weather conditions in Madison, Wis., for a period of 162 days, from July, 1909, to February, 1910. Before exposure all samples were ground to a uniformly smooth surface. After the removal of rust by the ammonium citrate method, all samples were subjected to an accelerating acid-corrosion test, using a twenty percent sulphuric acid and immersing for a period of one hour. Each sample was suspended by itself in a beaker, to avoid errors by presence of other materials.

Some results of interest were derived from these tests, though how far they may be of practical value as indicating the influence of various elements on commercial material is problematical. The materials used are practically carbon free, and with such minor quantities of sulphur, phosphorus, silicon and manganese (except where intentionally added) as would have, in all probability, little effect. There is a widely prevailing belief that the effect of any element added to iron is to increase corrodibility, by furnishing galvanic couples. A great majority of these test samples indicate the reverse; that is, a greater durability for the alloys than for the electrolytic iron base.

Comparisons between the corrodibility of electrolytic iron and certain forms of pure commercial iron on the market indicate that electrolytic iron is more corrodible both in the atmosphere and in acids. In fact, no quantitative comparisons have been attempted between the alloys produced in this investigation and commercial materials. As an approximate indication, however, ranges are given for tests on commercial materials at the bottom of the table for the experimental alloys.

Electrolytic Iron.

The electrolytic iron for which data are given in the table is not introduced as a sample of the purest that can be made, but is rather average material, serving as a good representative standard for comparison. As a matter of fact, during the course of the tests, as will be noted at the foot of the table of data, figures were obtained upon various grades of iron and steel of commercial grade and of widely varying degrees of purity; and in these results may be noted values of corrosion both higher and lower than those of the electrolytic-iron sample.

So far as this particular sample is concerned, it shows nothing especially striking in resistance to corrosion either in acid or in the atmosphere.

In the acid test, in particular, it does not fall in line with the commonly accepted view that a close approach to purity would indicate a high resistance to acid attack. On the contrary, this particular material has been attacked even more severely than most of the alloy samples tested at the same time.

Aluminum.

In this series there are not enough data to warrant definitive deductions. So far as the sample with 0.067 percent of aluminum is concerned, this may be taken as corresponding to iron free from alloying agents. The second sample, carrying 1.33 percent of aluminum, shows an even higher attack by acid than the one of the lower aluminum, but there has been a slight falling off in the atmospheric corrosion. However, there has been nothing striking in either case.

Arsenic.

In view of the fact that the presence of small amounts of arsenic in sulphuric acid pickling solutions decreases markedly the rate of the attack, it has been suggested frequently that arsenic present as an alloying constituent of steels might make such steel more resistant to corrosion, particularly to acid corrosion. This, however, appears to be an erroneous assumption, as increased corrosion in acid has been shown by Heyn and Bauer, and by Berthier. No satisfactory or conclusive work seems to have been done on the resistance of these materials to atmospheric influences.

Our results cover a series in which arsenic ranges from 0.29 percent to 3.56 percent, and we find a fair resistance to the acid attack, which resistance falls off appreciably with increase of arsenic content. On the other hand, the corrosion in the atmosphere is somewhat on a par with that of the electrolytic sample, and there would seem to be no particular merit in the use of arsenic alloys for resisting atmospheric corrosion.

From the point of view of physical qualities also, this series would not be of particular value, since the brittleness and weakness resulting from the addition of arsenic would be serious. Addition of arsenic seems to result in high magnetic qualities, but it is an element which is difficult to add, and if of service from the corrosion point of view it would have to be added in very large amounts, resulting in a structurally or mechanically poor material.

Cobalt.

In view of the close relationship in the general properties of cobalt and nickel, it might be natural to expect that the use of these elements as alloying agents would result in somewhat similar properties. The series here tested, however, in which the cobalt varies from 1.3 to 5.5 percent does not point to any close relationship. The resistance to acid of this series is not particularly striking, but does fall off appreciably with increasing cobalt content. The same general effect is noted in the atmospheric tests; but while the corrosion is fairly low, there is not the same resistance to atmospheric attack as is obtained by the addition of the same quantity of nickel. This series shows a fairly close relationship in the rates of atmospheric and acid attack.

To use cobalt for the purpose of making a material highly resistant to corrosion would seem to demand considerable quantities of this element. There would be no advantage, therefore, in the use of this metal as compared with nickel, in view of the high relative cost of the cobalt.

Copper.

The influence of copper upon the corrosion of iron and steel, and to some extent, as well, upon the other physical properties is, at the present time, a matter of controversy. So far as the resistance to acid attack is concerned, particularly to sulphuric acid, the evidence seems to be convincing that copper additions result in marked decrease in the rate of such attack. There is a tendency also, not supported by conclusive tests, to believe that copper additions will likewise increase the resistance to atmospheric corrosion.

The series herein tabulated, in which the copper ranges from 0.089 percent to 7.05 percent have the expected high resistance to acid attack and also show a low corrosion in the atmosphere. The latter is of particular interest, inasmuch as the values are consistently low throughout the series, and the markedly beneficial results seem to be obtained from even small amounts of added copper.

In view of the materially improved physical properties resulting from one to two percent of copper additions, together with the low cost of such addition and the corrosion resistance herein noted, it would seem that this series is of particular promise and worthy of extended study. The quality, both mechanically and from the corrosion point of view, is entirely comparable with that resulting from the use of corresponding amounts of nickel and, of course, there is a materially lessened cost for the addition.

The exact reason for the decreased corrosion is somewhat a matter of speculation. Considering that iron and copper form solid solutions, at least up to three percent or thereabouts of copper addition, or well within the limits of commercial utility, we should expect the structure of the resultant alloy to be one of perfect homogeneity. There should, therefore, be no internal influence tending to promote increased electrolytic action, and the effect of the dissolved copper should at the very worst be merely neutral as far as corrosion is concerned. In fact, increased resistance to corrosion might be expected, since the solid solution of the two elements might decrease the solution tendency of the iron; or if the iron finally goes into solution, it may leave a deposit of copper, forming a film and protecting the underlying metal from further attack. The presence of such a copper film has been observed repeatedly in the course of etching of samples for microscopic examination and has been noted by other investigators during acid attack of copper-iron alloys. This speculation seems to be confirmed by the tests herein enumerated.

Lead.

But one alloy of this series was tested, and that contained only 0.061 percent of this element. The acid corrosion is the same as that observed by the electrolytic iron, while the atmospheric corrosion has dropped to about half the figure of electrolytic iron. Not enough data are at hand, however, to warrant any deductions regarding the influence of lead upon the corrosion of iron.

Manganese.

The supposedly increased corrosion of modern steels as compared with the older iron has generally been ascribed to the presence of manganese, which is present in the later-day materials as a result of modern processes of manufacture. It may be, however, that the manganese is blamed for results due to the other elements associated with it, or perhaps to other factors resulting from modern conditions of manufacture.

So far as our tests show, in this series, which runs from 0.50 percent manganese to 10.42 percent manganese, there is nothing worthy of particular comment either in the acid or atmospheric corrosion. There is considerable inconsistency in the results, and the atmospheric tests in particular seem to indicate a slight increase of corrosion with increase of manganese content, though in all cases the corrosion was less than for the electrolytic iron alone.

The alloying relations in this series are those of solid solution, in this respect similar to the copper-iron alloys in the useful range. We have, therefore, a homogeneous structure and no internal causes for electrolytic action. However, in view of the very similar properties of the two metals, there would probably result but little change in the solution tendency of the alloy as compared with the iron itself. Also there would be no deposition of a protective film, as was mentioned in the copper series, since manganese is attacked very much like iron and would rust away in a similar manner. Consequently rust once formed from solution of either metal should aid rather than retard further progress of the corrosion.

Nickel.

This series shows alloys notably good both in the acid and atmospheric tests. There is a general tendency for increased resistance with increased nickel content.

Within the nickel content used in practice, about three percent, we note a marked falling off in atmospheric corrosion. The hindrance to the general use of this property is the relatively high cost of the nickel addition, and it would seem that these alloys would not be of particular merit unless the use of the material is also warranted by the increased strength resulting from the addition. The highest resistance noted lies well up in the series, at ten percent nickel and above. Such alloys would be beyond the range of general commercial utility, not only because of the high cost of the nickel, but because of the hardness and brittleness and generally disadvantageous physical properties in this region of the series.

The alloying relations of nickel and iron are those of solid solution, and it would seem that the protective effect is due perhaps to the same reasons cited in the case of the copper-iron alloys; that is, we would have very probably a markedly decreased solution tendency, and in case of any corrosion it would result in a solution of the iron and the consequent concentration of the nickel as a surface-protecting film.

Selenium.

There was tested but one alloy of this series, with the very low content of 0.017 percent of selenium, consequently no particular deductions can be drawn. The acid resistance in this particular sample is very low, while the corrosion in the atmosphere is noticeably high.

Silicon.

In this series the silicon content varied from 0.23 percent to 2.82 percent. The corrosion values are in general high and somewhat conflicting. In fact, this series seems to have suffered the greatest corrosion noted. There is a general tendency for increase in the atmospheric corrosion with increase of silicon content, but not a very material increase.

There seems to be an inclination to assume increased resistance to corrosion in the silicon steels, but the only reliable data appear to be those obtained upon acid tests, and mainly upon acid tests of the alloys of high silicon content. Here a compound of iron and silicon becomes the principal constituent, and the resistance to acid is probably due largely to this.

So far as ordinary amounts of silicon are concerned, its use seems to be disadvantageous both in acid and atmospheric corrosion. Also, silicon behaves much like arsenic and, while it results in good magnetic qualities, the resultant steels are otherwise poor physically, being brittle, weak and hard to work.

Silver.

Although alloys were made in which the added amount of silver was as high as ten percent, the resulting alloys actually indicated a maximum of 0.69 per cent retained, and the series here cited has a silver content varying from 0.28 percent to 0.69 percent. There is no particular merit in this addition so far as either acid or atmospheric corrosion is concerned, and all of the figures are closely comparable to that obtained with electrolytic iron alone. There is, of course, no particular commercial significance attached to the use of iron-silver alloys, because of the relatively high cost of the addition.

Tin.

This series has a tin content varying from 0.28 to 1.56 percent. In the lower end of the series the resistance to acid attack is particularly good, but the corrosion in acid increases perceptibly with the higher content of tin. As far as the atmospheric tests are concerned there is nothing of particular moment. There is a slight falling off however with increase of tin. The iron-tin alloys are somewhat similar in their general properties to the iron-arsenic and iron-silicon alloys,—that is, all of these additions result in improved magnetic quality of material, but at the expense of the physical, and the resulting alloys are brittle and weak and hard to work.

Tungsten.

The tungsten varied from 0.40 percent to 23.86 percent. In the acid test the results are all good, some of them very strikingly so; but there is a general irregularity in the figures. The same is true in regard to the atmospheric tests, with a seeming tendency toward decreased corrosion with increased tungsten content.

However, the general results are not especially worthy of attention, and considering the fact that any markedly decreased corrosion is obtained only after high tungsten additions, these alloys do not offer special value from the corrosion standpoint, since with the high tungsten additions we are entering the tool-steel range of alloys of high cost and extreme hardness and brittleness.

Conclusions.

These tests, covering several series of alloys of iron with other elements, do not seem to point to any quantitative relations between the acid and atmospheric corrosion.

So far as the atmospheric tests are concerned, numerous alloys can be noted in which the corrosion is less than in the electrolytic iron. The copper series would seem to offer particular advantages in view of the beneficial results obtained with small copper additions and because of the consistently low values throughout the series. Again these benefits are obtainable without prohibitive cost for the addition agent.

		Acid Corrosion	Atmospheric Corrosion	
		g. per sq. dcm.	lb. per sq. ft. per year	Kg. per sq. meter per year
Electrolytic Iron		1.30	0.1025	0.499
	Percent			
Aluminum—	0.067	0.628	0.110	0.513
	1.333	0.760	0.080	0.39
Arsenic—	0.292	0.448	0.083	0.405
	0.430	0.815	0.0703	0.343
	0.951	0.405	0.0870	0.425
	1.810	0.131	0.072	0.352
	3.862	0.086	0.064	0.312
	4.141	0.102	0.074	0.361
	3.562	0.144	0.063	0.306
Cobalt—	1.035	0.705	0.049	0.239
	2.000	1.02	0.070	0.342
	4.055	0.356	0.042	0.205
	5.052	0.257	0.042	0.205
Copper—	0.089	0.178	0.052	0.254
	0.202	0.095	0.039	0.190
	0.422	0.059	0.055	0.268
	0.592	0.112	0.050	0.234
	0.804	0.104	0.053	0.259
	1.006	0.067	0.046	0.225
	1.51	0.147	0.046	0.225
	2.005	0.091	0.051	0.249
	3.99	0.093	0.035	0.171
	5.07	0.087	0.031	0.151
	6.16	0.143	0.041	0.200
	7.05	0.186	0.033	0.161
Lead—	0.061	1.30	0.056	0.273
Manganese—	0.505	0.56	0.055	0.268
	1.00	0.52	0.080	0.390
	2.00	0.725	0.062	0.302
	3.00	1.11	0.067	0.327
	10.419	0.352	0.089	0.435
Nickel—	0.27	0.633	0.059	0.288
	0.56	0.547	0.071	0.347
	1.07	0.507	0.058	0.283
	1.93	0.192	0.023	0.112
	7.05	0.226	0.038	0.185
	8.17	0.125	0.029	0.141
	10.20	0.091	0.027	0.132
	11.29	0.123	0.027	0.132
	12.07	0.084	0.024	0.117
	13.01	0.237	0.031	0.151
	19.21	0.072	0.018	0.088
	22.11	0.0254	0.020	0.098
	25.20	0.054	0.023	0.112

		Acid Corrosion g. per sq. dcm.	Atmospheric corrosion	
			lb. per sq. ft. per year	Kg. per sq. meter per year
	Percent			
Nickel—	26.40	0.554	0.021	0.102
	28.42	0.155	0.021	0.102
	35.09	0.183	0.018	0.088
	47.08	0.160	0.0126	0.062
	75.06	0.049	0.0044	0.0215
Selenium—	0.017	0.190	0.1385	0.676
Silicon—	0.233	1.63	0.104	0.509
	0.603	1.19	0.076	0.370
	1.033	0.85	0.106	0.518
	1.897	0.80	0.124	0.606
	2.826	1.27	0.130	0.635
Silver—	0.281	1.02	0.065	0.317
	0.492	1.76	0.090	0.430
	0.581	1.34	0.073	0.356
	0.691	1.17	0.092	0.450
Tin—	0.288	0.284	0.069	0.337
	0.342	0.350	0.039	0.190
	0.686	0.386	0.049	0.239
	1.568	1.03	0.058	0.283
Tungsten—	0.406	0.363	0.076	0.371
	0.925	0.088	0.062	0.302
	2.334	0.086	0.062	0.302
	3.553	0.332	0.063	0.308
	5.982	0.304	0.060	0.293
	9.849	0.398	0.040	0.195
	13.641	0.365	0.049	0.239
	23.866	0.183	0.044	0.215

Various grades of low carbon iron and steel	0.300 to 0.73
High carbon steel	0.278
Cast iron—scale removed	0.770

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University of Wisconsin.

DISCUSSION.

Dr. A. S. Cushman: Laboratory studies such as are described in these papers are very valuable, and bring out points that are well worthy of our attention and discussion, and that, perhaps, have not been carefully enough considered heretofore. With respect to the first paper, I wish to state that it is unquestionably true that in the alloy field we have the opportunity of stumbling on combinations of metals which may prove far more resistant to corrosion than the purest iron that can be made. Whether or not such alloys can be manufactured for a cost which will be practical and attractive remains to be seen. Electrolytic iron is interesting to test because of its freedom from metallic impurities. It is, however, saturated with hydrogen, and to that extent is itself an alloy. In this respect it probably differs from iron which has been annealed in hydrogen, where the hydrogen is probably held in some form of solution or inclusion. If the electrolytic iron is melted it is probable that most of the hydrogen is driven out, but it is by no means certain that it is entirely eliminated by this treatment. This point should not be lost sight of in considering electrolytic iron as a material of standard purity.

My experience has led me to doubt the value of laboratory corrosion tests, or even atmospheric corrosion tests that depend upon cleaning off the rust and re-weighing the specimen. The fact that it has been shown pretty conclusively that all corrosion phenomena are connected with electrolytic effects which take place on the surface of the corroding metal, and since a piece of metal which is rusting is not losing weight at the electro-negative areas on the surface, it is quite possible that of two samples, the one which is losing the least weight is really suffering the most under the conditions of the test. In fact, in my experience, which now extends over quite a number of years, in observing corrosion phenomena and testing various samples I have frequently made this observation, namely, that the specimen which was rusting more evenly and losing weight very slightly from all over its surface would show up the worst on the weight records, whereas the other piece which is rusting and pit-holing through does not lose so much weight. So far nearly all acceleration corrosion tests made by different observers have depended upon making a record of loss of weight of the specimens, and I wish to point out the danger of error and being drawn to wrong conclusions by such methods of testing. To make myself still clearer, let us suppose that we are dealing with two pieces of sheet metal of exactly the same size and thickness. Now, suppose we wish to remove from these two specimens samples for analysis and at the same time destroy the specimens as little as possible by the removal of the sample. If one of the specimens was attacked with a planer, a very slight shaving might be taken off the entire surface without damaging the test piece to any considerable degree, whereas if the other specimen was attacked with a drill it would be impossible to take an equal weight off of it without actually destroying the integrity of the specimen by drilling holes through it or almost through it. With these considerations in my mind, I wish very emphatically to state that conclusions drawn from weight loss under corrosion tests are dangerously misleading, and in some cases would cause us to form an opinion diametrically opposite to the truth. I quite agree with the authors in regard to the unsatisfactory nature of the acid test, but, unfortunately, all other acceleration tests so far proposed are equally unsatisfactory. I do believe that the acid test gives some valuable information in regard to a material, if it is properly interpreted and applied. As far as exposure tests of bare specimens to atmospheric conditions are concerned, I agree with Prof. Burgess that results may vary in different parts of the world, owing to climatic conditions and depending upon the prevailing winds which blow with reference to the surface of the test piece, and upon the character of the prevailing atmosphere with regard to acid impurities. It should also be pointed out that neither iron nor steel is manufactured to be exposed to the weather without any form of protective coating. With the exception of the insides of boilers, tanks and pipes, and possibly also heavy chains, iron is not directly exposed to the corroding medium without some form of protective coating, and the condition of exposure of iron and steel in this sort of service is nothing like the attack made upon the metal by exposure, for instance, on the roof of a building. After all, the long time experience of consumers with reference to any given type of ferrous metal must continue to be of more value in forming a judgment than the results of any accelerated tests, whether in the laboratory or on exposure of bare plates or sheets to the outdoor atmosphere.

DR. W. H. WALKER: I am very much interested to learn that Prof. Burgess has found that manganese is not deleterious in iron, inasmuch as I have held this opinion from the first. In fact, manganese should decrease the corrosion of a sample of iron rather than increase it. The fact that samples of steel which corrode rapidly are frequently found to be high in manganese has been made the basis for the opinion that manganese is itself harmful. I believe that it is manganese oxide that does the harm, but not metallic manganese. A fact which may be easily observed in Boston, where the switches and frogs of the trolley system are made from manganese steel, is that after a rain the ordinary steel rails will rust rapidly, while the frogs remain perfectly bright.

MR. BRADLEY DEWEY: In connection with Dr. Cushman's criticisms of the manner in which Professor Burgess carried out his tests, I might state a few results which I have recently had the privilege of going over in some detail, although the work is not mine and is being done by Mr. D. M. Buck, who will probably describe it to the Society at some future date.

Mr. Buck has, at several places throughout the country, put up test roofs, made up of some half dozen or so full-sized sheets of each of many different grades of steels and similar products. At these same points there are small, I think 2 by 4 inches, test pieces in insulated racks. These test pieces are from the identical steels used to make up the full-sized sheet. Now, at the end of some months there are very marked differences in the condition of the various steels, those high in copper being in very good shape, while those Bessemer steels which are without copper have entirely broken down.

Recently, with the roof in this condition, and after a close examination and marking by several persons, who all checked reasonably well, the small test pieces were taken down and their loss in weight determined. In the light of Dr. Cushman's doubting that the small scale tests are ever in agreement with those carried out on a large scale, it is interesting to note that this loss in weight varied over very wide limits, and that in every case the degree of corrosion as determined in this method gave the same order of value as did the grading of the actual large scale tests by the various observers.

MR. R. H. GAINES: Prof. Burgess remarked in the course of his abstract that he had arrived at a conclusion that certain foreign elements in iron and steel were not hurtful to the metal, whereas others were certainly corrosive by their presence. I would like him to state what elements he considers as deleterious and what non-deleterious.

DR. W. H. WALKER: I would like to ask a question on the same line. I was interested to hear him state that he did not regard heterogeneity in the sample as controlling, but as rather of secondary importance. I understood from someone that Dr. Heyn, of Berlin, had given the same opinion. I would like to ask Prof. Burgess if he ever heard Heyn say that, or let us know what he said.

PROF. C. F. BURGESS: The suggestion made by Dr. Cushman, that electrolytic iron may not be comparable to other forms of iron due to hydrogen content, cannot be denied. Since the material to be melted must pass the high temperature of 1,600° C., the amount of hydrogen which remains after this treatment must be exceedingly small and, therefore, the influence of this small amount should be comparatively slight. The properties of melted electrolytic iron are probably influenced more by oxygen than by hydrogen.

On account of the high purity, as determined by chemical analysis, and, on account of the reproducible uniformity of the material, it should constitute a desirable starting point for investigating the influence of the various elements when alloyed with iron, and on this assumption the numerous alloys referred to in the paper have been prepared. The alloys were made primarily for physical and electrical tests, and it was an afterthought to subject them to corrosion tests. As a result there are not a sufficient number of samples containing some of the elements, such as sulphur and phosphorus, to determine the exact influence of such elements on corrosion. The point which appears of interest and suggestive is that the great proportion of elements seem to make electrolytic iron more resistant to corrosion, the notable exceptions being silicon and selenium. It must, of course, be admitted that the influence of these various elements on electrolytic iron may not be exactly comparable to their influence on other forms of commercial iron and steel.

DR. W. H. WALKER: Is anyone present who happened to hear what Dr. Heyn said? I always felt that heterogeneity in iron was deleterious, although I must say I always in my own mind limited it to oxide.

MR. F. N. SPELLER: I referred to Prof. Heyn's remarks in discussion earlier in the afternoon. As I remember what he said last week on this matter, it was simply that as a result of his investigations he had come to the conclusion that the influence of purity had been greatly exaggerated and that ordinary rust once formed on the surface of the iron was a greater accelerator of corrosion than any of the foreign elements commonly found in iron or steel.

MR. W. D. RICHARDSON: Several years ago I read a paper before the Chicago Section of the American Chemical Society, and later on a similar paper before the Minneapolis meeting of the American Chemical Society, concerning certain experiments which I had carried on in regard to the corrosion of iron. The gist of the ideas presented was that the surface conditions, and especially rust, overbalance all the influences within the metal itself in determining the course of ordinary corrosion after corrosion is once started. The composition of the metal influences the commencement of corrosion, but after an adherent layer of rust is formed the rust is the predominating influence, so that nearly pure iron, iron containing a small percentage of copper, mild steel, etc.; in other words, metals of different composition will, if adherent rust is present, follow nearly the same line of corrosion. Of course, to produce the adherent rust, it is necessary to have oxygen present, also to have alternate wet and dry conditions, and these are the conditions prevailing in ordinary atmospheric corrosion. The experiments which I carried out bore out these ideas in general. I also advanced the hypothesis, as a part of the general proposition, that it is only when we have a clean surface and continuously maintain a clean surface of the metal, that the composition of the metal itself becomes of predominating importance in influencing the corrosion. We have these conditions when carrying out corrosion tests in acids, and one of the great problems in corrosion was the difference in behavior between iron and steel of different composition, in dilute sulphuric acid, for example, and in the air. According to the hypothesis advanced, the differences noted in the early experiments between corrosion tests in acid on the one hand, and service tests, or tests simulating corrosion in service on the other, were due to the fact that in one case a clean surface was present, and in the other case there was an adherent coating of rust covering a part of the surface. Of course, if the rust covering were uniformly adherent all over the surface there would be no corrosion. There may be other surface factors also, but rust appears to be the most important. The hypothesis, as stated, may require considerable modification in respect to different details; probably it does. But it seemed to me then, and I have seen no evidence since to change my view, that it is true in its main aspect.

DR. W. H. WALKER: I think it is unquestionably true that there is one factor which we have not taken sufficiently into consideration in our study of the corrosion of iron, namely, the ability of a given sample to form a closely adherent protective surface of iron rust. The old bridge at Newburyport has stood for almost one hundred years, and the iron is still in a fine state of preservation, although the bridge itself has been replaced by a larger one. A piece of this iron when freed from its natural coating of rust is very heterogeneous and will corrode as rapidly in water as any sample of iron or steel I have ever seen, and yet, apparently, it is able to protect itself.

MR. EDW. WESTON: It has been the experience of the speaker with regard to water works service pipes that the character of the water has a very marked effect upon the rate of corrosion. While it is ordinarily true that after rusting is once started, due to imperfect coating of the pipe or imperfections in the coating of the pipe, it will go along very rapidly provided there is no deposit from the water on the inside of the pipe, yet if the condition occurs where the organic matter in the water causes the rust to take the form of an impenetrable film or lining, corrosion comes practically to a standstill after a few weeks or months. This has been noted repeatedly.

It is a well-known fact that very pure waters containing large amounts of carbonic acid and oxygen attack service pipes much more rapidly than surface waters containing organic matter in colloidal suspension. This matter will precipitate with the rust and form a film on the inside of the pipe. For this reason most surface waters can be used with lead pipe with impunity.

Most water works engineers are prejudiced in favor of the so-called old-fashioned wrought iron. There seems to be no scientific reason for this prejudice, but they speak in almost endearing terms of the pipe that they used to get. The speaker's own experience is that wrought iron pipe can be good and bad, and the same is true of steel pipe. It is difficult to tell by any ordinary test which pipe is iron and which is steel. If a ready test could be placed in the hands of the ordinary practicing engineer, it would be a great boon. It might help to determine which metals will resist ordinary corrosion and which will not.

In this connection some experiments by the writer with tin-lined lead pipe are of interest. Contrary to expectations, the tin lining did not protect the lead against solution; it only retarded it. No tin was dissolved from the pipe, but appreciable quantities of lead. The explanation of this lies in the well-known fact that tin crystallizes before it fully contracts, thus leaving interstices through which the water reaches the lead, and, furthermore, reaches it under electrolytic conditions very favorable to corrosion.

PROF. BURGESS: While taking part in an investigation of a stand-pipe failure last winter, a study was made of the quality of steel which entered into its construction. Certain portions of this steel were found to be badly pitted. In selecting one of the deepest pits and cutting a section it was found that the pit had a flat bottom, apparently formed by the presence of a layer of slag, or, perhaps more properly speaking, by so-called metallographic "ghost bands." The optical evidence pointed, in this case, to a retarding influence of impurity. This does not constitute absolute proof, but is suggestive that impurities producing heterogeneous material may have some merit.

Based upon extensive study and the occasional turning up of iron samples which seem to show remarkable durability, the writer believes that there is some important factor governing the rate of corrosion which is not thoroughly understood; also, that there is consequently a possibility of discovering some new line of attack on this problem of making durable iron, which will be of importance. Certain laboratory investigations which will be reported upon later seem to point in this direction.

In attempting to prevent deterioration by rust there should be recognized a difference between the problem of preventing the initial rusting and the problem of preventing the pitting action to which Dr. Cushman has just called attention. Pitting is dependent upon an acceleration action produced by rust accumulation, and if a barrier can be interposed so that a rust spot will spread out rather than become deeper, there will be a minimizing of the damaging action. The writer believes that slag and other non-conductive impurities frequently found in iron, under certain conditions, constitute such barrier. A study of the influence of impurities must recognize, not only those which are alloyed with the iron and the metallographic relationship of the same, but those impurities which exist as included non-metallic compounds.

MR. GAINES: Do you mean to suggest that a half percent of silicon in wrought iron would render it more durable?

PROF. BURGESS: In all probability silicon as an alloy with the iron has a decidedly different influence on the corrosion than has silicon in the form of included slag. Silicon in the former condition appears to be disadvantageous, while in the latter there may be some advantage.

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A paper read before Section Xa: "Electro-chemistry" of the Eighth International Congress of Applied Chemistry, in New York City, September 11, 1912.

PHYSICAL AND CHEMICAL DATA ON DRY CELLS AND DRY CELL MATERIAL.

By Carl Hambuechen and O. E. Ruhoff.

In the discussion of a paper on "Dry Batteries" presented recently before the Faraday Society, it was stated as noteworthy that the best of American cells are inferior to the best British types. Without going into the justice of this assertion, perhaps a presentation of some of the characteristics of typical American dry cells may be appropriate at this time. In presenting this paper the writers are indebted to the courtesy of the Northern Chemical Engineering Laboratories and the French Battery and Carbon Company, of Madison, Wisconsin, for permission to publish the following data obtained through a comparative study of various typical American cells.

A nearly standard method of construction appears to prevail in this country. The anode is a cylinder of sheet zinc, which serves also as the container. The electrolyte is a solution of zinc chloride and ammonium chloride held in a layer of absorbent material, usually paper, lying next to the zinc, and separating it completely from the cathode. The cathode consists of a carbon pencil surrounded by a granular mixture of manganese dioxide, carbon and ammonium chloride. Graphite is also a common ingredient. This granular mixture is saturated with electrolyte containing ammonium chloride and zinc chloride in solution.

Testing of Battery Materials.

The chemical inspection of dry cell materials should include a determination of the purity of these materials, especially as regards the presence or absence of quantities of useless inert substances, so as to indicate the percentage of the materials on which depend the usefulness of the cells. In addition to this, tests should also be made for comparatively small quantities of such impurities as exert an actively injurious effect upon the cell.

The physical properties of some of the materials are of quite as great importance as are the chemical ones. One of the most important of these is the conductivity of the crushed carbon and graphite, and that of the mixtures of these materials with manganese dioxide. The conductivities of crushed carbon and graphite depend upon the raw materials used in their manufacture, the conditions of heat treatment used, and the size of the granules in the composition.

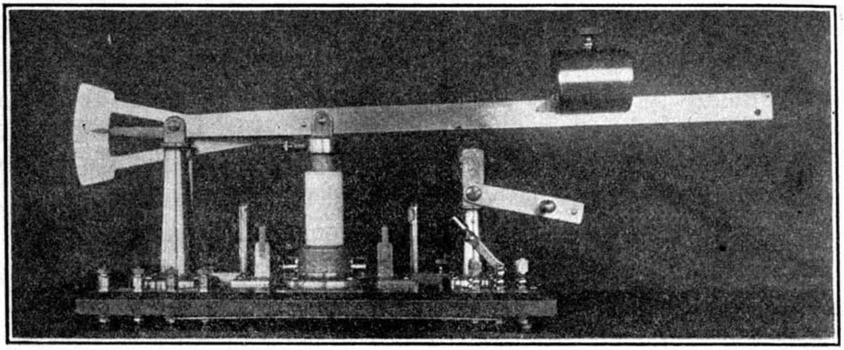


FIG. 1.

Battery carbon may be prepared from petroleum coke, retort carbon, or coke made from soft coal. The graphite which is used may be either a natural product or that manufactured by electric furnace methods. Crushed carbon and graphite may also be prepared from used furnace electrodes, or from worn out electrodes from electrolytic processes.

For the determination of the conductivities of crushed materials and mixtures, an apparatus especially devised for the purpose and shown in Fig. 1 was used. The material to be tested is placed in a porcelain tube 2 in. (5 cm.) long and 1 in. (2.5 cm.) inside diameter. The bottom of the tube is closed during the test by a removable graphite plug, and the tube is filled flush with the material to be tested. The tube is placed in an upright position and another graphite plug inserted at the top upon which a pressure of 15 pounds (6.8 kg.) is exerted, by means of a suitably arranged lever and weight. A current of one ampere is passed, the graphite plugs serving to make connection to the column of granular material. The circuit includes an ammeter and a variable external resistance. The drop in voltage between the graphite plugs is measured by a voltmeter of suitable range. If accurately checking readings are desired, great care must be taken in the manner of applying the pressure to the tube full of granular material. This same testing apparatus is also arranged to test the conductivity and breaking strength of carbon pencils.

A number of samples of crushed graphite and carbon as supplied by various manufacturers and made by various processes have been tested for conductivity. For graphite there have been obtained readings varying between 0.071 and 0.411 ohm and for carbon between 0.188 and 0.637 ohm per linear inch (2.5 cm.) of a column one inch (2.5 cm.) in diameter, equaling resistivities of 0.14 to 0.82 ohm for graphite and 0.37 to 1.27 ohm for carbon, per cub. cm. The minimum readings in each case represent a very high grade of material, while the maximum ones indicate materials which are practically useless for most battery purposes. Most of the samples of carbon tested have been crushed so as to pass through about a 20 mesh screen (8 openings per cm.) while the samples of graphite will usually pass through a 100 mesh screen (40 openings per cm.).

In comparison with carbon and graphite, the other insoluble ingredient of pulverized dry-battery filler—manganese dioxide—has a very low conductivity, so that as far as the final conductivity of the whole mixture is concerned, the manganese dioxide may be considered as practically a non-conductor. It follows, therefore, that the higher the proportion of MnO_2 in the depolarizing mixture, as compared with the conducting ingredients, the higher will be its resistance, presuming, of course, that the size of granules in the composition and the quality of materials remains the same. The curves plotted on the accompanying chart indicate in a general way how the conductivities change with variations in the proportions of conductive to non-conductive materials, and with variations of the size of granules in the composition for the same proportions by weight. Variations in the conductivity of ten to several hundred percent can be brought about by varying the size of granules in the composition of a mixture, with no change in the proportion by weight of the several ingredients.

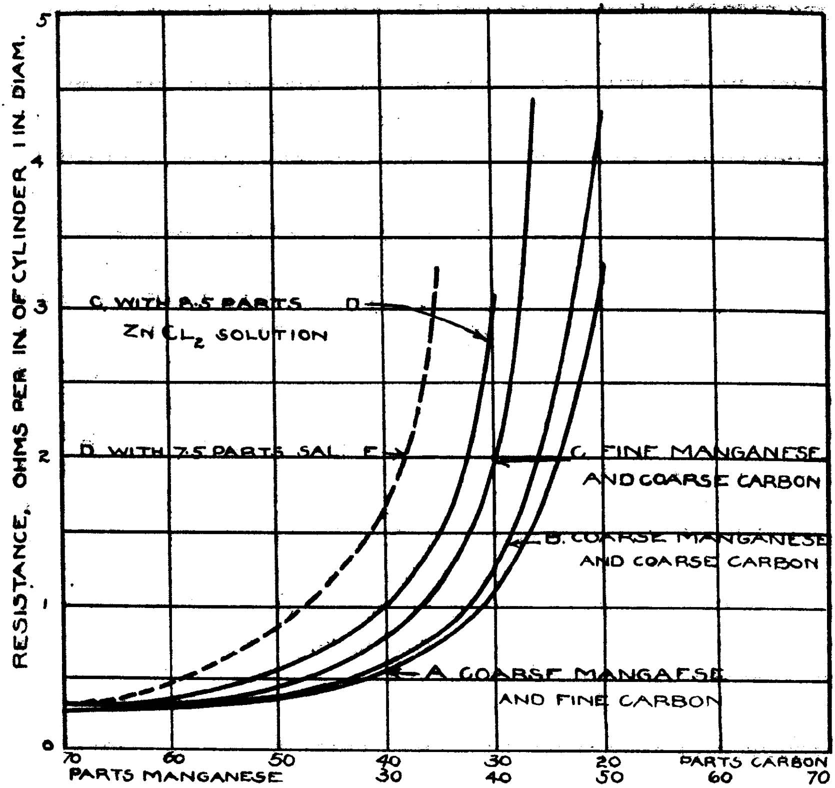


FIG. 2.

Inspection of Various Types of Cells.

Four of the typical brands of cells investigated and concerning which data are given in the tables are designated by the letters *A*, *B*, *C* and *D*.

It will be noted from the tables that there is comparatively little variation in the composition of these several makes of batteries. Perhaps one reason for this is the strong demand of the American market for a low-priced cell, compliance with which places narrow limits on the manufacturer in indulging any desire he may have to improve the quality of the battery by using more expensive materials, or by devising a more complicated structure.

Table I shows the weights, dimensions and physical properties of several types of batteries. The size of granules in the composition and the percentage of MnO_2 on the several sizes of the washed and dried mixtures is shown in Table II. In general, it seems that an increase of MnO_2 in the coarser sizes will reduce the internal resistance of the battery. On the other hand there are indications that an increase in the proportion of very finely divided manganese dioxide results in greater depolarizing power per unit weight of the MnO_2.

TABLE I.

	A	*B*	*C*	*D*
Voltage of cell	1.50	1.57	1.55	1.50
Amperes on short circuit (flash test..)	33	33	32	30
Weight of cell, grams	980	932	984	942
Weight of moist depolarizing mixture, grams	642	545	576	574
Weight of paper lining, wet, grams	61	71	65	72
Diameter of carbon pencil { inches	1	1	1	0.75
Diameter of carbon pencil { centimeters ..	2.5	2.5	2.5	1.9
Weight of zinc, grams	117	110	132	151
Resistance, in ohms, of depolarizing mixture per linear inch of a 1-inch column	0.94	1.69	1.90	0.86
Resistance, in ohms, of depolarizing mixture per cubic centimeter (resistivity)	1.84	3.31	3.72	1.69
Relative coherence of depolarizing mixture	1.9	1.7	1.5	1.6

TABLE II.

Screen Analysis of Washed and Dried Depolarizing Mixtures.

	A	*B*	*C*	*D*
On 20 mesh (8 openings per cm.), percent...	4.8	0.2	1.3	0.5
" 40 " (16 " " "), " ...	25.5	12.8	20.0	29.0
" 60 " (24 " " "), " ...	11.8	14.3	10.5	12.0
" 80 " (32 " " "), " ...	4.3	5.3	7.0	3.3
" 100 " (40 " " "), " ...	9.8	22.5	28.8	12.0
" 150 " (60 " " "), " ...	2.3	7.3	8.5	4.5
Through 150 " (60 " " "), " ...	41.5	37.6	24.2	38.7

Table III shows the quantities of zinc chloride and ammonium chloride present in the solution held in the paper, and in the solution with which the depolarizing mixture is moistened.

The quantity of water present in a No. 6 dry cell varies somewhat for different makes. The lower and upper limits are about 60 and 90 grams. Other things being equal, a better cell probably results from approaching the latter figure rather than from too close an approach of the former.

Measurements of the conductivity of the mixtures were made directly upon the depolarizing material as removed from the batteries, but previous to making the test all of the mixtures were passed through a 10 mesh (4 openings per cm.) screen. The internal resistance of the battery depends, naturally, not only on the conductivity of the mixture but also the tightness with which it has been compressed in filling the cell. Additional factors influencing the internal resistance that will result from any given mixture are the weight per unit volume of battery space and also the manner in which the packing is performed.

TABLE III.

Percentage of MnO_2 in Various Sizes.

	A	*B*	*C*	*D*
On 20 and 40 mesh (8 and 16 openings per cm.)	74.9	71.5	82.5	60.3
" 60 " 80 " (24 " 32 " " ")	53.8	61.6	46.3	45.9
" 100 " (40 " " ")	45.2	38.3	27.1	41.8
" 150 " (60 " " ")	44.4	37.0	30.8	38.1
Through 150 " (60 " " ")	31.3	38.3	50.2	31.7

TABLE IV.

NH_4Cl and $ZnCl_2$ in Papers and Mixture.

	A	*B*	*C*	*D*
Grams NH_4Cl in papers, per cell..................	10.1	13.4	12.3	12.3
" NH_4Cl in mixture, " "	36.2	42.6	25.1	30.5
" NH_4Cl, total " "	46.3	56.0	37.4	42.8
" $ZnCl_2$ in papers, " "	7.0	6.8	9.7	8.9
" $ZnCl_2$ in mixture, " "	13.8	10.3	15.8	15.5
" $ZnCl_2$, total " "	20.8	17.1	25.5	24.4

The remaining common ingredient of dry cells is the least costly of all, but it is nevertheless of considerable importance. This is the air occupying the "void" spaces in the depolarizing mixture, that is, space not occupied by water, salts, carbon, graphite or manganese dioxide. The volume of voids varies from about 3 to 15 cubic centimeters. All of the data given have reference to a standard "No. 6" cell, the dimensions of which are 2.5 by 6 in. (6.5 x 15 cm.).

Northern Chemical Engineering Laboratories,
Madison, Wisconsin.

A paper presented at a Joint Session of Section Xa: Electrochemistry and Ve: Paints and Pigments, of the VIII International Congress of Applied Chemistry, in New York City, September 11, 1912.

THE INFLUENCE OF CINDERS ON THE CORROSION OF IRON IMBEDDED IN CLAY.

By Walter B. Schulte.

Investigations of electrolytic corrosion of underground structures occasionally reveal examples of marked corrosion under certain conditions which preclude a consideration of stray currents from electric railways as the cause. Filled ground seems to be especially harmful to iron pipes, especially where the filling is composed largely of cinders, coal, and furnace products.

Of the various explanations which have been offered to account for this corrosion, the more common are that the sulphur, which is a constituent of most coals, probably forms sulphuric acid, with the resultant chemical corrosion; also that cinders and particles of conductive carbon in contact with iron produce a local couple, and the pits which are formed are attributed to this effect.

The objection to the former theory is that the high temperature of burning usually expels the sulphur from the cinder material; and that the latter explanation is not completely adequate is indicated by the fact that the corrosion occurs even where there may be an intermediate layer of clay between the cinder bed and the pipe. Certain cases of deep pitting of iron pipe have been called to the attention of the writer where an overlying bed of cinder filling out of direct contact with the pipe seemed to be in a measure responsible for the damage noted.

It is well known that if a mass of carbon and a mass of iron are imbedded in an electrolytic conductor, such as in moist earth, a difference of potential is established between these two bodies, the iron being electrochemically positive to the carbon. This potential does not establish a flow of current unless metallic contact is made between these two bodies. While a layer of carbon material may be separated from an iron pipe in one locality by a bed of sand or clay, corrosion may be produced at that locality by reason of contact between the iron and the carbon bed at some other position, such, for example, as occurs where a service pipe or other portion of the underground system may pass through the carbon bed. It is evident, therefore, that contact between the cinders and the iron is not necessary at the exact location where the corrosion is observed in order to account for such corrosion.

An active couple produced by carbon and iron results in the iron being the anode and the carbon being the cathode. Polarization tends to reduce the flow of current, but this polarization is minimized if air has ready access to the carbon bed; therefore the nearness of the carbon bed to the surface of the earth is a factor which influences the corrosion caused by such material.

The object of the investigation here described was to reproduce in the laboratory conditions which were found in the field, and to make laboratory measurements of potential and current flow and determination of the amount of corrosion. The experiments were carried out in the Chemical Engineering Laboratories of the University of Wisconsin.

Apparatus.

The apparatus as set up in the laboratory included a sheet of iron, buried in a bed of clay, on the top of which rested a layer of granular graphite, which represented the cinder bed. Electrical contact between the plate and cinders was provided for by a wire connecting them. The arrangement of the apparatus is shown in Fig. 1.

It is, of course, evident that the conductive layer of carbon here used has a higher electrical conductivity than that produced by cinder filling, as found in practice; and the reason for using this was to accelerate the action so as to produce measurable results within a short time.

The iron plate was of No. 24 sheet iron, pickled, dried and weighed before being placed in the clay, which was taken from a fresh excavation and was moist when placed in the box. The layers below and above the plate were well tamped in place. The carbon, which had been used as a resistor in electric furnaces, was granular, the particles ranging from ¼ to ½ inch (6 to 12 mm.) in diameter. A graphite block with a stem was placed in the carbon to make electrical contact between the carbon and external connections, and insulated wire connected to the plate was brought out through the clay. The carbon lead was connected to a switch also connected to the iron plate terminal, so that by closing it the cell was short-circuited. The switch was provided with short leads, so that an ammeter or voltmeter could be connected to them and measurements be made with the switch open. The carbon was covered by a ½-inch (12 mm.) layer of sand at the beginning of the test, but this was removed on the fourth day.

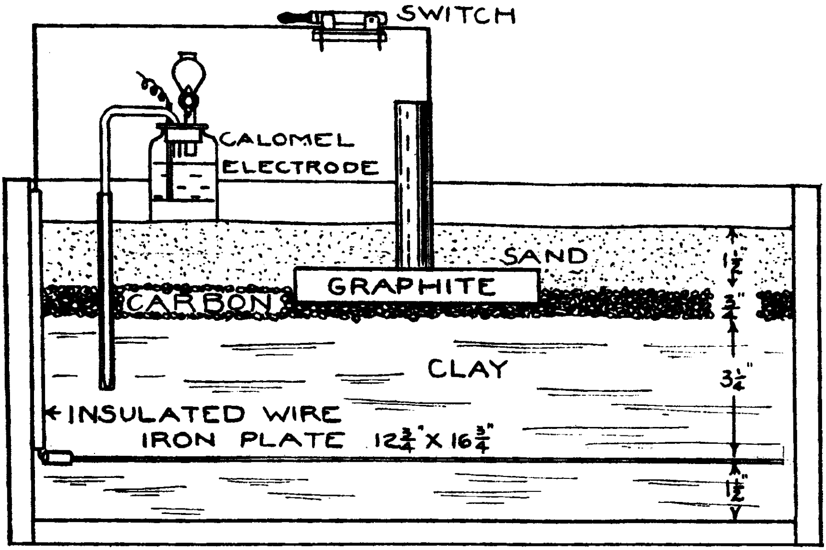


Fig. 1.

To measure the single potentials of the iron and carbon against the clay a calomel electrode was employed, with a long nose reaching down through a glass tube into the clay half way between the carbon and iron. A few drops of normal KCl were poured into the bottom of the glass tube to moisten the clay and assure good contact between the clay and electrode.

Measurements.

Before closing the switch the potentials of the iron and carbon against the clay were determined by the potentiometer method, taking —0.56 volt as the potential of the calomel electrode. The results are given below:

Total E. M. F. ....0.842 volt, carbon cathode
Clay to carbon .....—0.638 volt
Iron to clay ....+0.204 volt

Total ....0.842 volt
A voltmeter indicated 0.83 volt.

After making the single potential measurements the circuit was inadvertently closed for a minute or two, after which the voltage, as indicated by a voltmeter, had fallen to 0.72 volt. Further short-circuiting caused the voltage to drop from 0.68 to between 0.45 and 0.50 after a few minutes. One and one-half minutes after opening the switch the voltage increased to 0.68 volt.

The cell was short-circuited for twenty minutes and the switch then opened, after which single potential measurements were made at various intervals.

After being on short-circuit for seventeen hours, similar single potential measurements were made, during which time the average current, as measured by a milliammeter, was 0.0515 ampere. The data of these measurements, as tabulated in Table I and plotted in Fig. 2, show that the rate of depolarization is decreased after the cell has been short-circuited for the longer time.

The cell was then allowed to stand short-circuited, and readings were made of the voltage and current at various times and during the run, the results of which are tabulated in Table II. The instruments were of standard make and in good calibration and of the following scales and resistances:

Voltmeter 0-15 volts; 53.5 ohms resistance
Ammeter 0-500 milliamperes; 0.09 ohm resistance

During the fourth day the layer of sand above the carbon was removed, as noted in the table. The clay began to dry out, so that beginning with the tenth day about half a liter of water was sprinkled over the carbon and allowed to soak in before a set of readings were made. No readings were taken between the thirty-third and fifty-eighth days, nor was the cell moistened, with the result that the current on the fifty-eighth day was almost nil, and the potential 0.22 volt. Three minutes after the cell had been moistened the observed values increased to 0.0175 ampere and 0.32 volt.

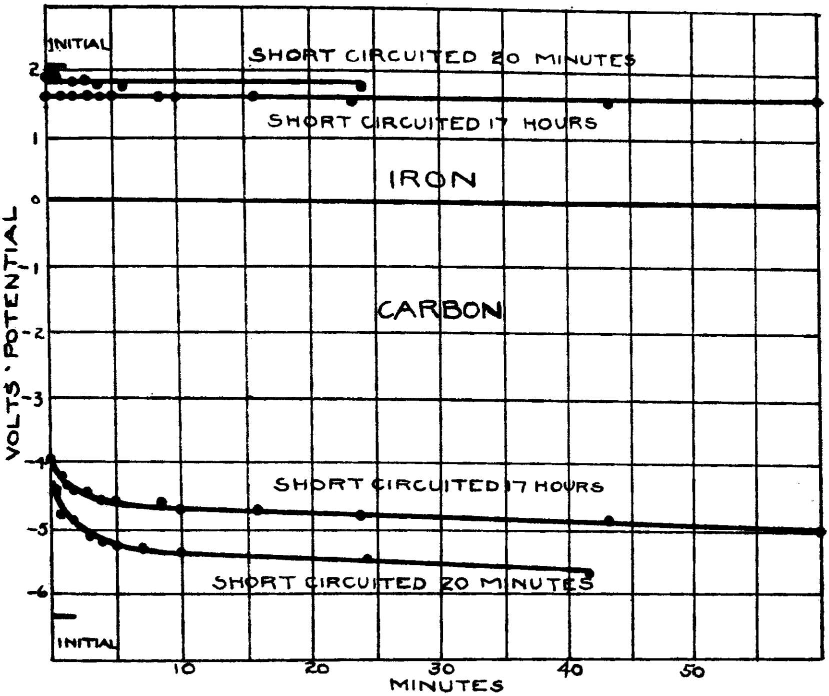


FIG. 2.

Rough integration of the curve plotted between current and days, with the current as zero on the fifty-eighth day, gives 35 ampere-hours. If the cell had been moistened regularly each day throughout the test it is fair to assume that the average current would have been 0.03 ampere; 0.03 ampere for 58 days is equivalent to about 42 ampere-hours. The average voltage over this period can be taken as 0.35 volt.

The interesting point to be noted is that as long as the clay was moist a current flowed continuously from the iron to the carbon, the depolarization, due presumably to the action of the air on the carbon, taking place at a constant rate.

The corrosion of iron by one ampere-year is about 20 pounds, so that 0.03 ampere, the assumed average current with the clay moist, would corrode about 20 × 0.03 = 0.6 pound.

The area of the plate was 1.45 square feet (12 sq. dm.), or 2.9 square feet (24 sq. dm.) total surface, so that the theoretical corrosion per square foot would be 0.23 pound (12 grams per sq. dm.) per year. This loss, or about one-quarter pound, on a plate would destroy the equivalent of a No. 30 sheet in one year, or half of a No. 24 sheet. If this corrosion were concentrated in six square inches area on every square foot (on 4 percent of the surface), the metal would be pitted to the depth of 0.15 inch (4 mm.), which would pierce a 3-inch (75 mm.) cast iron main in a little over two and one-half years.

TABLE I.

Depolarization.

Single Potentials of Carbon				Single Potentials of Iron			
Short-circuited 20 Minutes		Short-circuited 17 Hours		Short-circuited 20 Minutes		Short-circuited 17 Hours	
Time Min.	E. M. F.	Time Min.	E. M. F.	Time Min.	E. M. F.	Time Min.	E. M. F.
½	—0.432	0	—0.394	0	+0.184	0	+0.162
1	—0.478	1	—0.424	¼	+0.184	1	+0.160
2	—0.485	1½	—0.434	¾	+0.186	2	+0.160
3	—0.508	2	—0.438	2	+0.180	3	+0.160
4	—0.510	3	—0.442	3	+0.182	4	+0.160
5	—0.516	4	—0.452	4	+0.180	5	+0.160
7	—0.524	5	—0.452	6	+0.178	8	+0.158
10	—0.530	8	—0.458	24	+0.180	10	+0.158
24	—0.540	10	—0.468			16	+0.158
42	—0.564	16	—0.470			23	+0.156
		23	—0.474			43	+0.156
		43	—0.484			60	+0.158
		60	—0.499				

Corrosion of Plate.

After the fifty-eighth day the cell was dismantled. Examination of the clay near the plate showed that the rust had penetrated into it as much as ¼ inch (6 mm.) in some places. The plate was spotted with oxide and greenish iron compounds. Corrosion was noticed both on the upper and lower sides of the plate, and the corner diagonally opposite the wire connection was eaten through.

TABLE II.

Current and Voltage Readings.

Day	Amperes	Volts	Remarks
1	0.052	0.45	
2	0.0518	0.50	
3	0.050	0.45	
4	0.051	0.45	Sand removed from top
5	0.051	0.44	
7	0.0495	0.38	
8	0.035	0.40	
9	0.030	0.20	
10	0.040		Began wetting
11	0.035	0.40	
12	0.0475	0.42	
14	0.0475	0.42	
15	0.040	0.42	
17	0.041	0.40	
24	0.030	0.35	Dried out since last reading
25	0.0375	0.36	
29	0.023	0.30	
30	0.020	0.20	
31	0.035	0.40	
32	0.028	0.35	
33	0.028	0.35	
58	0.015	0.32	

The plate was washed, the greater part of the rust scraped off, and the remainder then dissolved off by hot ammonium citrate, after which it was weighed. The data follow:

Weight of plate before test.......... 401.6 grams
Weight of plate after test.......... 346.5 grams

Loss .... 55.1 grams

Thirty-five ampere-hours theoretically would corrode 36.4 grams of iron so that the efficiency of corrosion in this case would be about 150 percent. That is, it may be said that two-thirds of the loss by corrosion was due to the current produced by the difference of potential between the carbon and the iron.

These experiments were intended as preliminary work for further investigation, which, however, was not undertaken; but a description of this first, rather incomplete work, it was thought, would prove of interest and draw attention to the influence of carbon and cinders on the corrosion of iron, and perhaps lead to further experimenting on the subject. Further work along this line should be undertaken with the conditions more closely approaching those actually found, that is, using cinders instead of carbon, and putting them, with the iron plate, in the earth. Similar plates not connected with the carbon should also be buried so that the amount of natural corrosion can be determined. Under these conditions, with the higher resistant cinders, it is to be expected that less current would be produced.

An interesting case of corrosion of a gas pipe, which may be explained by action similar to that discussed above, has been observed recently by the writer. Along a certain street the gas mains were paralleled by a water main buried a short distance beneath. The soil is mainly clay or silt, but at the lowest portion of the street the water main dipped into a peaty layer. The gas main lay in the clay above the peat at this point, and was corroded through at several places. The main apparently was in a locality not subjected to stray currents from the street railway or grounded power circuits, so that the currents causing the corrosion must have come from other sources.

A length of gas main about 400 feet long was disconnected from an adjoining portion. Potential measurements between this disconnected length and an iron rod driven in the black layer showed that the gas main was 0.3 volt positive, and readings between gas and water connections showed that current was flowing from the gas to the water main through the earth. The corrosion can be explained by the fact that peat sets up a different potential toward an iron surface than does clay, and connections between the gas and water services on the consumer's premises make the couple electrolytically active, thereby producing electrolytic corrosion.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

MR. J. O. HANDY: Has the composition of the cinder any influence? There is a greater amount of sulphur in some cinders than in others.

PROF. C. F. BURGESS: Of course a cinder body such as locomotive cinders and different furnace ashes has very poor conductivity. Sulphur does not seem to play any part.

MR. HANDY: I made some comparative corrosion experiments, having samples of different kinds of steel embedded in coke of a maximum size of a quarter of an inch and kept moist for a period of about three weeks. The pitting during that time was very marked.

Report of Committee on Calorimetry

Written for the Seventh Annual Meeting of the American
Gas Institute, October, 1912

by J. B. Klumpp, Chairman

INDEX

REPORT OF COMMITTEE ON CALORIMETRY.

WRITTEN FOR THE SEVENTH ANNUAL MEETING OF THE AMERICAN GAS INSTITUTE, OCTOBER, 1912, BY J. B. KLUMPP, CHAIRMAN.

The main purpose of the investigation which has been carried on during the past two years was to study calorimetry with the idea of determining as far as possible the factors which influence the accuracy of measurements. These factors have been studied in connection with the use of several of the more important types of calorimeters available. While the tests which have been made and which will be described, show some of the relative characteristics of these different instruments, it is not the specific purpose of this report to show the relative merits or to present this as being a complete report covering all makes of calorimeters in existence. In the previous reports results were given of tests made upon the following list of calorimeters:

Simmance-Abady, Boys, Junkers and Sargent.

The results of this past two years' work have shown various factors which were not given full recognition in the former tests, and while this did not, apparently, lead to any erroneous conclusions the results from the former tests of calorimeters are not strictly comparable to those which are now presented. The diagrams or tables to be presented give an idea of the performance of the various types of instruments which have been studied during the past year. This does not include the Simmance-Abady, Boys, or Sargent calorimeters previously investigated.

The two former instruments have not been available to the committee and it is known that marked improvements have been made upon the Simmance-Abady which are said to have improved its accuracy.

Special attention has been given to the calorimeters of the continuous flow type with independent gas metering equipment, and also to the newer types of calorimeters recently placed upon the market such as the Doherty, the Parr, and the Sarco. These three calorimeters embody entirely different methods of construction and operation.

The laboratory investigations upon which the prior reports of this committee have been based have been carried out largely in the Chemical Engineering Laboratories of the University of Wisconsin, the laboratories of The United Gas Improvement Company, Philadelphia, and the laboratories of the Milwaukee Gas Light Company. During the past two years the laboratory investigations have been carried on at Philadelphia by Mr. Maurice S. White under the immediate direction of Mr. Klumpp, and in Madison under the direction of Mr. Kowalke by Mr. J. N. Lawrence. Mr. Lawrence has been studying the calorimeter problems for two years as a thesis investigation and his work has been accepted for the degree of Doctor of Philosophy.

During the progress of this investigation many tests were necessary to determine the facts in any one point. At the laboratories of The United Gas Improvement Company about 200 individual test runs were made by Mr. White, while Mr. Lawrence, at the University of Wisconsin, made nearly 1,000 individual tests. In addition to the test runs on the individual calorimeters, many tests of calibration of thermometers, meters, and other accessories were made.

The reports of this committee on investigations for 1908 and 1909 were based on 800 individual tests. So that in all there have been made about 2,000 tests.

Since this work was carried on under the supervision of one of the members of this committee and through the assistance of the Committee on Calorimetry it is deemed proper to embody this thesis entitled "Efficiency of Gas Calorimeters" in this report. In this thesis prepared by Mr. Lawrence, the investigation has been carried along the lines that the committee has deemed necessary to determine the problems that were encountered in our previous tests; to determine the effect of certain atmospheric conditions upon the instrument, and to outline methods of operation that make the results obtained more precise. The results obtained by him have been accepted by the committee, and the details of the investigation are expressed in full in Mr. Lawrence's thesis which is herewith submitted.

Respectfully submitted,

R. B. Brown,
C. F. Burgess,
R. C. Cornish,
O. L. Kowalke,
J. B. Klumpp, Chairman.

EFFICIENCY OF GAS CALORIMETERS.

I. Introduction.

(1) *Preliminary.*—During the past few years the subject of gas calorimetry has been given increased attention. In many states municipal gas must now fulfill certain definite specifications as to heating value, candle-power, and sulphur content.[1] The present tendency seems to be to attach much more importance to heating value than to candle-power, especially so in Europe. As a result the use of gas calorimeters has greatly increased and several new forms of such apparatus have appeared.

A gas calorimeter will give various results dependent upon the conditions of operation, and it is essential that the proper working conditions of each type of calorimeter be known. Unless the calorimeter is operated under proper conditions, the heating values determined will be unreliable. The principal factors affecting the efficiency of gas calorimeters of the flow type are (a) the specific heat of the water heated, (b) the relation of the temperature of the inlet water and the temperature of the products of combustion to the temperature of the surrounding atmosphere, (c) the rate of burning of the gas, (d) radiation, (e) humidity of the gas, and (f) humidity of the air supply.

The error due to the specific heat of the water being other than unity is slight and can usually be disregarded, particularly when the heated water is weighed. The proper relation between the temperature of the inlet water and room temperature, and the proper rate of burning of the gas—both of which affect the radiation—can be determined experimentally as will be described hereafter.

It is customary to state the heating value of a gas in British thermal units per cubic foot, measured at 60 degrees F. and 30 inches of mercury, making the correction for partial pressure of the gas on the assumption that the gas is saturated with water vapor. If the gas is not saturated with water vapor the apparent heating value of the gas will be higher than the actual value. The error from this source is so small, that it may be disregarded in commercial practice, but for scientific investigations the error can be eliminated by saturating the gas before it enters the meter.

A calculation shows that the volume of exhaust gases from coal, water or oil gas is slightly smaller than the combined volumes of gas and air supplied per unit of gas burned if the combustible gas, products of combustion and air supply are at the same temperature. Hence, if both air and gas are saturated with water vapor, all of the water formed by the combustion of the gas, and some of the water vapor brought in by the air and gas must condense, thus giving up its latent heat of condensation to the calorimeter. The observed heating value of the gas will then be too high by an amount equal to the heat of condensation of the water vapor deposited due to the contraction in volume of the air and gas admitted. If the air supply is only partly saturated with moisture then some of the moisture formed by the combustion of the gas will be taken up and pass out with the exhaust gases. The latent heat of condensation of this moisture will be lost to the calorimeter and the observed heating value of the gas will be too low.

By assuming certain conditions as to quantity and humidity of air supply, and the volume of the exhaust gases, some investigators have calculated the effect of such humidity of the air supply.[2 and 3] The results are based upon assumed conditions and do not agree very closely among themselves.

It was the primary object of this investigation (a) to redetermine the proper relations between the temperature of the inlet water and room temperature—the reliability of the previous determination having been questioned[3]—(b) to make a direct measurement of the effect of the humidity of the air supply upon the efficiency of the Junkers calorimeter, (c) to apply, so far as possible, the knowledge thus gained to determine the proper working conditions under which several types of calorimeters should be operated, and (d) to determine the relative efficiencies of these calorimeters.

(2) *Previous Investigations.*—Investigations of the Junkers calorimeter have been carried out by (a) Immenkötter[5] at the technical Hochschule of Aschen, (b) by Kowalke[4] at the University of Wisconsin, and (c) by Parr[3] at the University of Illinois.

Immenkötter's investigation was exhaustive and included: (I) A Research on the Characteristics and Sources of Error, and (II Determination of the Calorific Value of Hydrogen by Means of the Junkers Calorimeter. The results of his work may be summarized as follows:

(a) The mechanical construction of the calorimeter is satisfactory.
(b) Radiation errors are not serious.
(c) The meter for measuring the gas needs to be verified.
(d) The Junkers calorimeter has an efficiency of 99.7 per cent.

Complete reports of the work carried out for the American Gas Institute by and under the direction of Kowalke of the

Chemical Engineering Department of the University of Wisconsin, will be found in the PROCEEDINGS of the American Gas Institute for 1908 and for 1909 as previously noted. Among many conclusions drawn from these investigations the following are especially important.

(a) The efficiency of the Junkers Calorimeter is 99.5 per cent. when operating conditions are as follows:

(1) Temperature of inlet water and exhaust gases the same as that of the room, when applying electrical energy.

(2) Rate of combustion of the gas from 7½ to 8½ cubic feet per hour.

(3) Difference in temperature between inlet and outlet water from 15 to 16 degrees F.

(b) The most extreme variations in humidity of gas and air supply may cause variations in heating value of from —5.90 B. t. u. per cubic foot to +0.858 B. t. u. per cubic foot. (All gas volumes measured at 60 degrees F. and 30 inches of mercury.)

(c) The Junkers calorimeter is the most desirable calorimeter for the determination of the heating value of municipal gas.

(d) The meter should be frequently calibrated.

(e) High grade thermometers should be used.

Parr prepared pure hydrogen and determined its heating value by means of the Junkers calorimeter which was operated according to the directions of the American Gas Institute. Thomsen's value of 325 B. t. u. per cubic foot (60 degrees F. and 30 inches of mercury) was assumed as the real heating value of the hydrogen. Under these conditions the values determined in the Junkers calorimeter were approximately 4.5 per cent. lower than Thomsen's value. When the calorimeter was operated with exhaust gases leaving at 5.5 degrees F. below room temperature the indicated heating value came up to 325 B. t. u. per cubic foot. Parr concludes:—"From this data it would appear that under the conditions prescribed by the committee of the American Gas Institute the Junkers calorimeter is in error, aside from errors of the meter, from 13 to 15 units in 325, or approximately 4¼ per cent. Doubtless the entire explanation for this does not reside in the matter of relative humidity of the air but involves also, as already indicated, a loss due to radiation."

"Further experiments with a new form of calorimeter in which the heating value of the gas in question is compared with that of pure hydrogen, assuming Thomsen's value for the heating value of the hydrogen, confirmed the results previously noted."

The three series of investigations just reviewed comprise the only published accounts of serious research work on this subject.

In connection with gas engine research it has been found that the heating values of both producer gas and illuminating gas, as determined with the Junkers calorimeter, do not agree with values obtained by determination with the Witz bomb, or by calculation from the gas analysis. In one case,[6] when the Junkers values for producer gas were compared with the values for producer gas were compared with the values determined with the Witz bomb, the Junkers' values are found to be the lower. In some other instances,[7] when the Junkers' values for producer gas and illuminating gas were compared with values calculated from the gas analysis, the Junkers values for the producer gas were lower than the calculated values, and the reverse was true of the illuminating gas.

A suggested cause for the lower Junkers' values in the case of the producer gas is the incomplete combustion of the methane which is present in small amounts. The higher Junkers' values in the case of illuminating gas are probably due to lack of knowledge concerning the exact composition of the "illuminants."

In still other cases[8] the computed value checks the calorimeter value fairly closely The non-conformity in results of this nature may be due to varying conditions of operation and the composition of the gas.

(3) *Acknowledgements.*—This investigation was carried out under the supervision of Prof. O. L. Kowalke, of the University of Wisconsin, to whom the writer is deeply indebted for advice and counsel. Grateful acknowledgement is also made to Prof. C. F. Burgess for the use of the Chemical Engineering Laboratories, and to the following firms for their courtesy in providing calorimeters for test purposes:—

The United Gas Improvement Co., Philadelphia.
Improved Equipment Co., New York City.
Standard Calorimeter Co., East Moline, Ill.
American Meter Co., New York City.
Sarco Engineering Co, New York City.

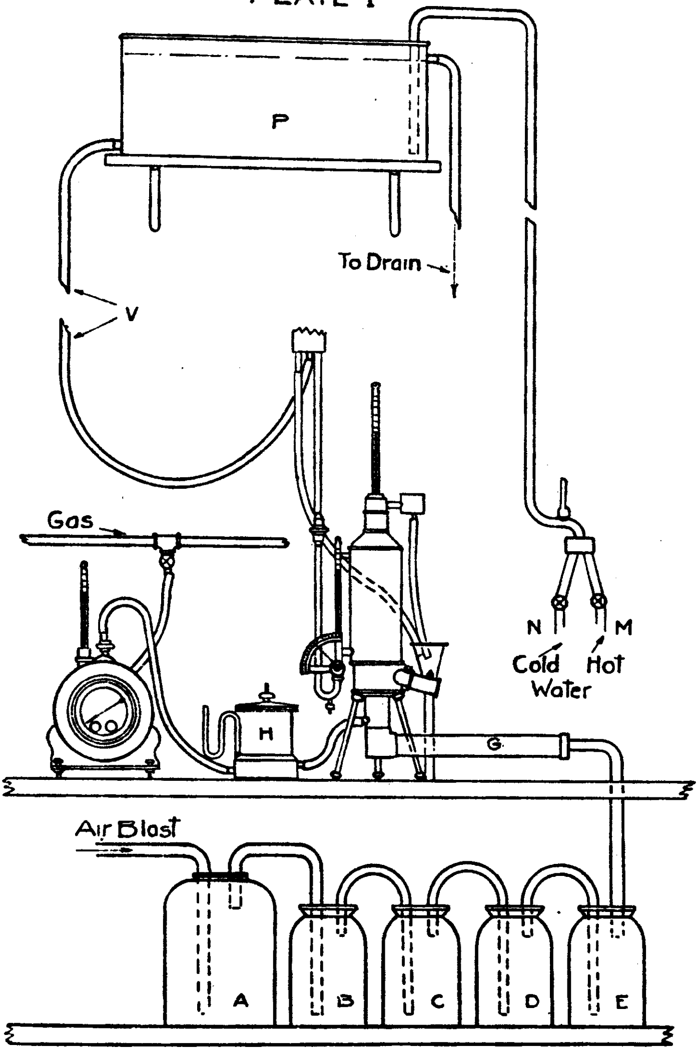
II. APPARATUS AND METHODS OF INVESTIGATION.

The general arrangement of the apparatus and the facilities of the laboratory are shown in Plate I. Hot and cold water were supplied through the pipes (M) and (N) respectively. The hot and cold water mixed with each other at (O) and the desired temperature was controlled by a thermometer (T). Thus the tank (P) could be filled with water of any desired temperature. The outlet to the tank connected directly with the calorimeter. Several other cocks were connected with another outlet arm (not shown in the cut) so that other calorimeters could be conveniently operated at the same time.

During a test the main water supply was always cut off and the water drawn from the tank. The inlet water was thus maintained at a very constant temperature.

Two gas mains were provided. One was connected directly with the city gas supply, and the other connected with a gas holder of sixty cubic feet capacity. The holder was provided with a spraying apparatus so that the sample of gas could be sprayed with water and thus quickly saturated with moisture. Whenever possible the samples of gas used in these tests were stored for at least twenty-four hours before being used, and during this time were frequently sprayed. To guard against any changes in saturation during

PLATE I



the passage of the gas from the holder to the calorimeter, a "saturation" bottle was always inserted in the main just before the gas entered the meter. The device consisted of a four liter bottle loosely filled with excelsior. The excelsior was kept moist with water saturated with illuminating gas, and the bottom of the bottle was covered with such water to a depth of from two (2) to three (3) inches. The gas was led into the bottle through a tube leading down to about one-half inch of the surface of the water. The gas was thus forced to pass up through a considerable mass of wet excelsior and was fully saturated with moisture.

The gas used in these investigations was "carburetted water gas." So many samples of gas were consumed in this work that it was impracticable to analyze all of them. However, the gas was of fairly constant composition and was analyzed from time to time. Two specimen analyses are given below.

Constituent	Sample No. 1 (6/24/11) per cent.	Sample No. 2 (4/17/12) per cent.
CO_2	2.2	3.8
Illum	11.4	11.2
O_2	1.1	1.0
CO	31.3	28.4
*H_2	36.3	37.1
CH_4	12.8	9.3
C_2H_6	1.6	4.4
N_2	3.3	4.8

* Hydrogen determined by palladium black in each case.

The gas was measured by means of a wet test meter manufactured by the American Meter Company. The usual pressure regulator (H) was inserted between the meter and the calorimeter.

The meter was always calibrated before and after each test or series of tests, and the necessary corrections applied to the gas volume. The calibration outfit consisted of a half cubic foot bottle, the volume of which was accurately determined at 75 degrees F. The pressure on the gas in the meter was measured by the usual manometer. In all tabulations of data the values under the heading "Barometer" are made up of the actual barometric pressure plus the pressure in the meter.

In the case of all calorimeters of the flow type the heated water was weighed upon a balance sensitive to one one-thousandth (1/1000) of a pound with a load of ten (10) pounds on each pan. The weights were calibrated and found to be correct to within one one-thousandth (1/1000) of a pound.

All thermometers used were calibrated against a high-grade thermometer certified by the Bureau of Standards, and all corrections applied. The thermometers were calibrated with stem emergent. After six months' use the thermometers were recalibrated and showed no appreciable change. Fahrenheit thermometers were used exclusively in this investigation.

During the investigation of the effect of the humidity of the air supply upon the efficiency of the Junkers calorimeter, the air supply was controlled as follows: Compressed air was supplied by a Westinghouse pump. The compressed air was passed through a series of bottles, A, B, C, D, E. The first bottle, A, was about half filled with water and the air passed directly through about three inches of water. The agitation of the water was sufficiently vigorous to fill the upper part of the bottle with a fine mist through which the air passed on its way to the next bottle. The succeeding bottles were all loosely filled with excelsior. The excelsior was wet and the air was forced to pass through about one inch of water at the bottom of each bottle. After passing out of (E) the air was led into a pipe (G) of galvanized iron where the velocity of air was checked considerably. From the pipe (G) the air passed directly into the calorimeter. The relative humidity of the air, taken at the entrance to (G) would range from 93 per cent. to 98 per cent. The relative humidity was determined with a dew point apparatus for each series of tests, so that in all of the tests to be described the calorimeters were operated upon air of a known humidity.

When it was desired to supply very dry air to the calorimeter the air was passed through the following train. First, through a heavy tin box packed in melting ice, a large amount of the moisture being deposited out because of the lowering of the temperature of the air. Then the air was led through a series of four bottles containing a little concentrated sulphuric acid and filled with broken pumice stone saturated with concentrated sulphuric acid. The air was forced to bubble through the acid at the bottom of each bottle and then pass up through the pumice stone. At the end of this train the air passed through a bottle filled with solid potassium hydroxide which served to remove any sulphuric acid vapors entrained by the air. Of course the temperature of the air was considerably reduced while passing through the tin box packed in melting ice, but the removal of the remaining water by the concentrated sulphuric acid served to bring the temperature of the air back to room temperature. In no case did the temperature of the air supplied from this system vary more than two degrees F. from that of the room. It was usually about one degree higher than room temperature.

Air thus supplied to the calorimeter was practically anhydrous. The actual dew point of the air thus supplied was never determined, because of the difficulty of securing a sufficiently low temperature with the dew point apparatus.

III. EXPERIMENTAL DATA.

(1) *The Junkers Calorimeter.*

The Junkers calorimeter used in these tests was instrument No. 872 owned by the University of Wisconsin. This is the instrument which was used as a standard in previous investigations[4] carried out for the American Gas Institute.

(a) *Effect of Temperature of Inlet Water.*—As has been previously stated the temperature of the inlet water has a marked influence upon the heating values obtained with calorimeters of the flow type. Inasmuch as the directions of the American Gas Institute for the regulation of the temperature of the inlet water with respect to room temperature have been seriously questioned, it was fundamental that this question should be definitely settled before further investigations involving this factor were carried out.

SERIES A.

Conditions of the Tests.

The rate of flow of gas was seven (7) cubic feet per hour; the difference in temperature between the inlet and outlet water was from 15 to 16 degrees; room temperature was 75 degrees. In this and all subsequent tests with the Junkers No. 872, the damper in the exhaust outlet was closed, because it had been found in previous investigations that for this particular instrument higher results could be obtained with the damper closed than with it open which indicated that combustion was perfect with the minimum excess of air.

Gas was drawn from holder.

The results obtained are as follows:

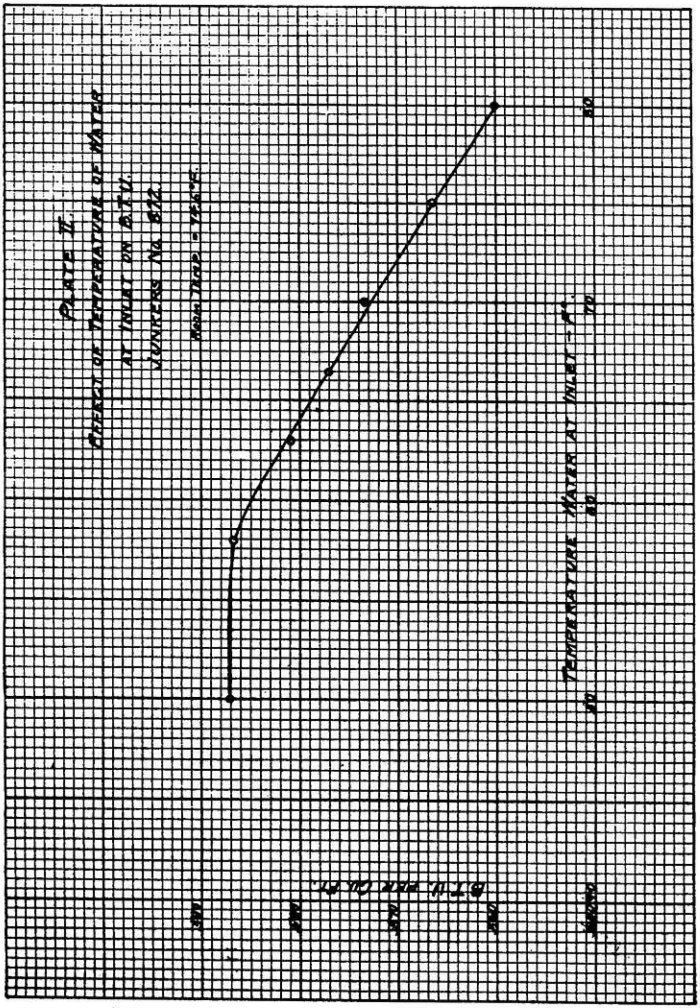
Tem. of inlet water deg.	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
50.0	587.1	586.8	586.5	586.7	586.8
58.0	586.3	585.6	586.7	587.2	586.5
63.0	581.6	581.7	581.6	581.2	581.5
66.5	576.7	577.6	576.5	577.4	577.1
70.0	572.8	573.7	573.1	572.6	573.1
75.0	566.8	565.5	566.4	567.0	566.4
80.0	559.9	560.1	560.0	559.4	559.9

Discussion of Results.

Using the above data a curve was plotted having B. t. u. per cubic foot as ordinates and temperatures of inlet water as abscissae. The curve is shown in Plate II. It is of particular interest that the values obtained for inlet temperatures of 50 degrees and 58 degrees are identical. Therefore, the curve runs parallel with the horizontal axis for a temperature interval of a little more than eight degrees and then falls off regularly for the remainder of the temperature interval.

In previous determinations[4] the inlet temperature curve had shown a flat, or nearly flat, portion when the inlet temperature was about room temperature, indicating apparently a thermal balance at that temperature. It is desirable to operate the calorimeter with inlet water at such a temperature that the observed gross value shall approximate the total heating value of the gas. To obtain this result, the temperature of the products of combustion must be reduced to a point low enough, so that the condensed water should equal the water formed by the combustion of the gas.

From the form of the curve as shown in Plate II it would seem that the point referred to above is reached when the temperature of the inlet water is from 15 to 25 degrees below that of the room.



In order to determine the form of the "Inlet Temperature

Curve" at temperatures more than twenty degrees below that of the room, and also to check the results of Series A, a second series of determinations, Series B, was made starting with water at 40 degrees.

SERIES B.

Conditions of the Tests.

General operating conditions the same as in tests of Series A. Four consecutive determinations were made at each of the following temperatures of inlet water, viz., 40 degrees, 50 degrees, 60 degrees, 70 degrees and 80 degrees.

The results obtained are as follows:

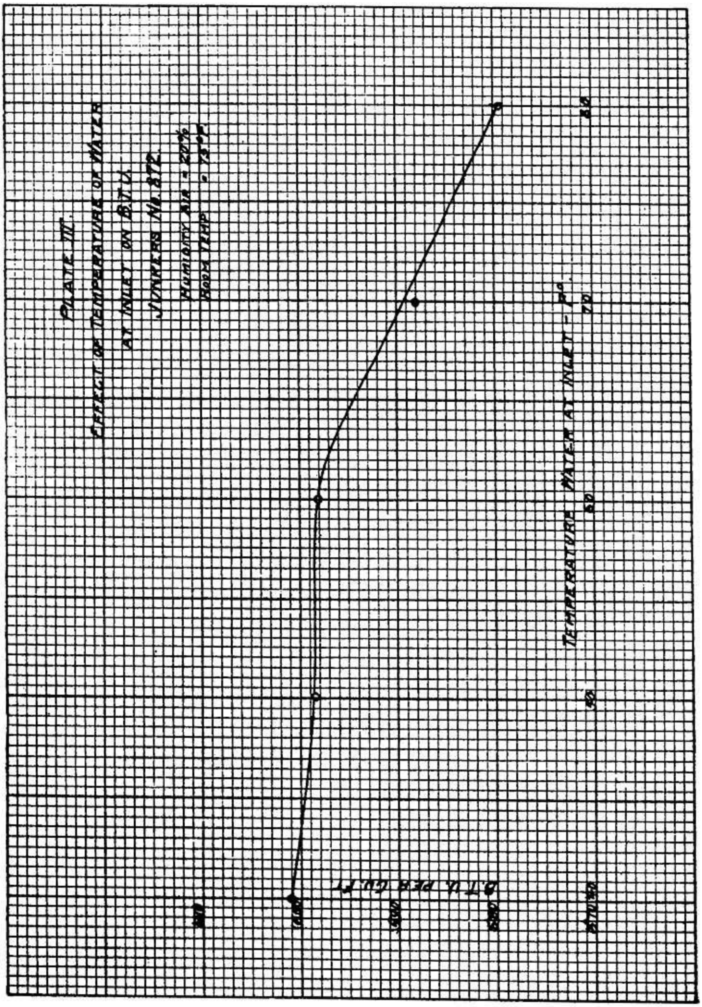
Tem. of inlet water deg.	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
40	601.0	601.9	600.0	601.7	601.2
50	598.5	599.1	597.8	598.7	598.5
60	597.5	597.9	598.6	598.0	598.0
70	587.9	587.3	587.7	589.0	588.0
80	579.9	581.0	581.0	578.9	579.7

Discussion of Results.

Plate III shows a curve plotted from the above data using B. t. u. per cubic foot as ordinates and temperatures of inlet water as abscissae. It is to be noted that as the temperature of the inlet water is progressively raised the heating values registered by the calorimeter at first decrease slightly, then remain nearly constant for a temperature range of ten degrees, and then fall off regularly through the remainder of the temperature interval.

These results are in entire accord with those of Series A, and show that if the Junkers calorimeter is operated on water which enters the calorimeter at temperatures varying from 15 degrees to 25 degrees below room temperature a similar thermal balance is obtained. This indicates that the products of combustion have been cooled to that point where the quantity of water vapor condensed in the heat absorbing part of the calorimeter is equal in amount to that required to be condensed so as to give the maximum heating value obtainable by this instrument operating under the given conditions.

Among other things, the operation of the calorimeter at the above specified conditions for the temperature of the inlet water, compensates the loss of heat suffered by the removal of water vapor, due to mechanical entrainment, in the products of combustion passing too rapidly through the effective absorbing space of the calorimeter.



It must be remembered that in the Junkers calorimeter there is a relatively large annular space below the outlet of the effective condensing tubes in which the velocity of the products of combustion is reduced and where there may be a settling out of water vapor whose latent heat of condensation is not made available for record of the gross heating value of the gas in the calorimeter.

At this point it is of interest to note a statement of Professor Parr[3] in connection with his investigations of the Junkers calorimeter. Commenting upon some of his results he says, "From these results it would seem that for a gas averaging 650 B. t. u. the Junkers apparatus would need to be operated in a manner to deliver the exhaust gases at from 10 to 12 degrees lower than room temperature."

In the present investigation the temperature of the exhaust gases was 9.9 degrees below room temperature when the temperature of inlet water was 60 degrees, and 17.2 degrees below room temperature when the temperature of inlet water was 50 degrees. Professor Parr's method of investigation did not show the total range of admissible inlet temperatures, but the close agreement of the two investigations carried out at different places and by entirely different methods is striking.

The complete data from which the above mentioned results were calculated are tabulated in order to show the exact conditions governing these tests.

SERIES B.

Temperature of Inlet Water 40°.

	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	20.0 throughout			
Barometer	29.38 throughout			
Gas tem	75.6	75.6	75.4	75.4
Cor. factor	0.9388 throughout			
State of meter %	1.92 fast throughout			
Cor. gas vol	0.1842 throughout			
Room tem	73.1	72.8	72.7	72.6
Exhaust tem	49.3	48.6	48.9	48.6
Inlet tem	40.05	40.12	40.17	40.10
Outlet tem	55.13	55.12	55.53	55.13
Rise	15.08	15.00	15.40	15.03
Wt. water	7.341	7.391	7.177	7.374
B. t. u	601.0	601.9	600.0	601.7
Av. B. t. u		601.2		

TEMPERATURE OF INLET WATER.

	50 degrees				60 degrees			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	20.0 throughout							
Barometer	29.38 throughout							
Gas tem	75.1	75.1	75.2	75.2	75.0	75.0	75.1	75.0
Cor. factor	0.9400 throughout							
State of meter %	1.82 fast throughout							
Cor. gas vol	0.1846 throughout							
Room tem	73.1	73.5	73.9	74.0	74.2	74.0	75.0	74.5
Exhaust tem	56.2	56.4	56.5	56.6	64.3	64.3	64.6	64.7
Inlet tem	49.75	49.76	49.87	49.97	59.69	59.74	59.81	59.89
Outlet tem	65.44	65.52	65.62	65.67	75.41	75.47	75.44	75.51
Rise	15.69	15.76	15.75	15.70	15.72	15.73	15.63	15.62
Wt. water	7.042	7.017	7.007	7.040	7.017	7.017	7.070	7.067
B. t. u	598.5	599.1	597.8	598.7	597.5	597.9	598.6	598.0
Av. B. t. u	598.5				598.0			

	70 degrees				80 degrees			
Humidity (air) %	20.0 throughout							
Barometer	29.38 throughout							
Gas tem	75.0	75.0	75.0	75.0	75.0	74.9	74.9	74.8
Cor. factor	0.9400 throughout							
State of meter %	1.82 fast throughout							
Cor. gas vol	0.1846 throughout							
Room. tem	74.9	74.9	74.9	75.0	75.5	75.2	75.2	75.1
Exhaust tem	72.7	72.8	72.8	72.8	80.4	80.5	80.5	80.5
Inlet tem	69.97	69.99	70.00	70.02	79.92	79.76	79.72	79.63
Outlet tem	85.40	85.46	85.49	85.52	95.60	95.26	95.44	95.32
Rise	15.43	15.47	15.49	15.50	15.68	15.50	15.72	15.69
Wt. water	7.033	7.010	7.004	7.015	6.827	6.920	6.797	6.812
B. t. u	587.9	587.3	587.7	589.0	579.9	581.0	578.8	578.9
Av. B. t. u	588.0				579.7			

(b) *Effect of Rate of Flow of Gas.*—According to the directions of the American Gas Institute the proper rate of flow of gas in the Junkers calorimeter should be from six to eight cubic feet per hour. Although this assertion has never been questioned, it was deemed advisable to check the previous work, this time holding the temperature of the inlet water between the limits of 15 to 25 degrees below room temperature, instead of having it near room temperature as was the case in the previous investigation on this point.

SERIES C.

Conditions of the Tests.

The temperature of the inlet water was approximately 20 degrees below room temperature. The temperature difference between the inlet and outlet water was from 15 to 16 degrees. Room temperature was 70.2 degrees. Four consecutive determinations were made with each of the following "Rates of Flow," viz., 4, 6, 7, 8, 9 and 10 cubic feet per hour. The results are tabulated as follows:

Rate of flow in cu. ft. per hr.	B. t. u. per cubic foot				
	No. 1	No. 2	No.3	No.4	Ave.
4	579.2	580.8	580.1	578.9	579.8
6	580.0	579.3	579.8	579.4	579.6
7	581.6	582.3	581.0	580.6	581.4
8	579.9	579.0	580.0	578.9	579.5
8	580.2	580.2	579.5	579.1	579.8
10	579.6	578.5	580.4	578.5	579.3

Discussion of Results.

The results show that when operating conditions are as defined, the Junkers calorimeter gives practically the same efficiency with all of the "Rates of Flow" from 4 cubic feet per hour to 10 cubic feet per hour. The results obtained when burning 7 cubic feet per hour are only slightly higher than the others, but this slight difference is shown consistently in all four of the check determinations. Therefore it would seem that the former directions of the American Gas Institute with respect to the proper rate of combustion of the gas in the Junkers calorimeter are correct, and in all subsequent work the "Rate of Flow" of the gas was regulated to 7 cubic feet per hour.

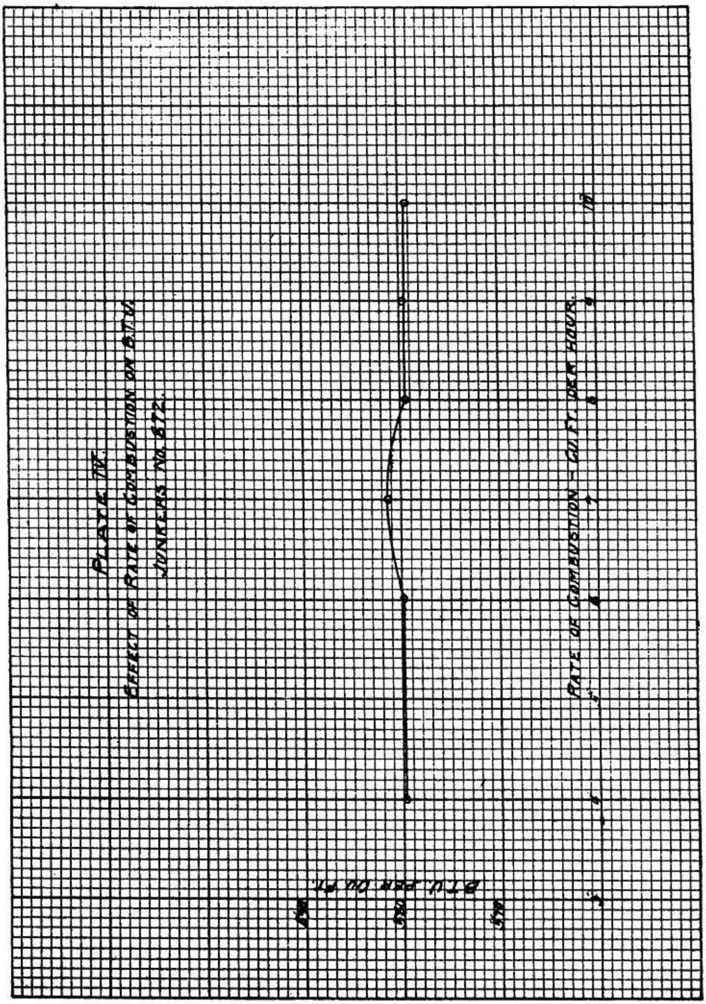


Plate IV shows the "Rate of Flow" curve for the Junkers calorimeter No. 872. B. t. u. per cubic foot are used as ordinates and cubic feet per hour as abscissae. Having established the proper working conditions for the Junkers calorimeter, attention was next turned to a direct measurement of the effect of the humidity of the air supply.

(c) *Effect of Humidity of Air Supply.*—The method of controlling the humidity of the air supply has been discussed under the heading "Apparatus and Methods of Investigation." It was desired to determine the effect of the humidity of the air supply at various temperatures of inlet water, and to note its effect, if any, upon the "thermal balance" of the calorimeter. Hence the range of inlet temperatures used was the same as in Series B.

At first a few attempts were made to work out the "Inlet Temperature Curve" twice during the same day and while drawing from the same sample of gas, using nearly saturated air in one case and anhydrous air in the other case. However, as both time and gas supply were necessarily limited, it was found that, to work out both curves in this manner only two determinations could be made for each point. In many cases two determinations are sufficient, but it was found that, when operating the calorimeter continuously for a period of several hours, unavoidable disturbances would sometimes occur, and if two determinations failed to agree closely there remained no satisfactory basis for definitely fixing that point. As a result the following procedure was adopted: First, the "Inlet Temperature Curve" was worked out using nearly saturated air and making four determinations for each point. This series of determinations occupied the major portion of one day, and no further work was attempted on that day. On another day, using another sample of gas, the same curve was again worked out while anhydrous air was supplied to the calorimeter. After completing the determinations for this curve, saturated air was again supplied to the calorimeter and two points determined using the saturated air. The temperature of the inlet water at these two points was 55 and 80 degrees F., respectively. Four determinations were made for each point.

In order to show the relationship of the two "Inlet Temperature Curves" thus determined, the curve worked out using nearly saturated air was placed over the curve determined with anhydrous air so that it would pass through the two points determined with saturated air. The relationship of all the points was thus determined and both curves drawn on the same coördinate paper.

Plate V shows the curve obtained with nearly saturated air, and Plate VI shows both curves drawn as above described. The data which defines these curves follows:

SERIES D.

Using nearly saturated air. Room temp. 75°.

Tem. of inlet water deg. F.	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
40	604.2	604.3	604.1	602.3	603.7
50	597.7	597.7	598.5	598.5	598.1
60	596.7	597.8	596.9	595.8	596.8
70	584.8	588.1	584.9	586.0	586.0
80	*				

* An unavoidable interruption made it necessary to discontinue this series of determinations before the tests at 80° were made. However, the four points determined by the above data fix the important portion of the curve. The point at 80° used in drawing the curve was calculated by assuming the same percentage drop between 70° and 80° as had occurred in previous determinations.

SERIES E.

Using anhydrous air. Room tem. 75°.

Tem. of inlet water deg.	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
40	595.3	596.8	596.5	596.9	596.4
50	593.3	593.7	593.1	593.8	593.5
60 *	587.5	588.3	598.0	587.3	590.2
70	576.6	577.4	577.4	577.4	577.2
80	576.1	570.0	566.4	568.6	568.0

* For some unaccountable reason the calorimeter was working unsteadily during these determinations. The average value for the point, however, is in accordance with previous results.

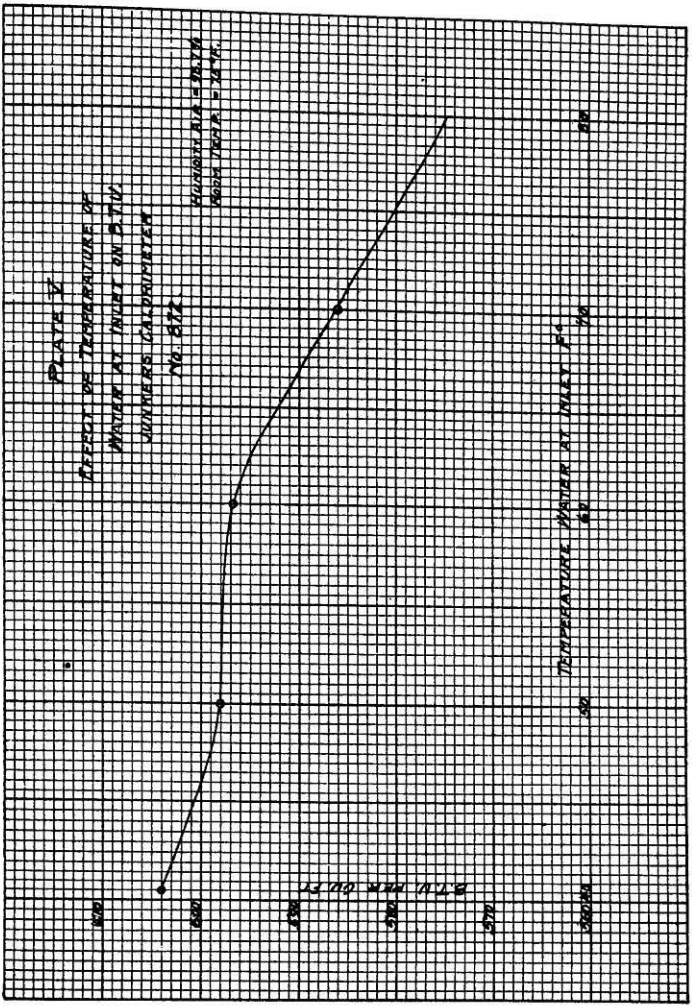
Nearly Saturated Air.

Tem. of inlet water deg.	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
55	600.4	601.6	601.2	599.1	600.6
80	577.3	576.2	577.6	576.8	577.0

The complete data from which the results of Series D and Series E were calculated are tabulated at the close of the "Discussion of Results."

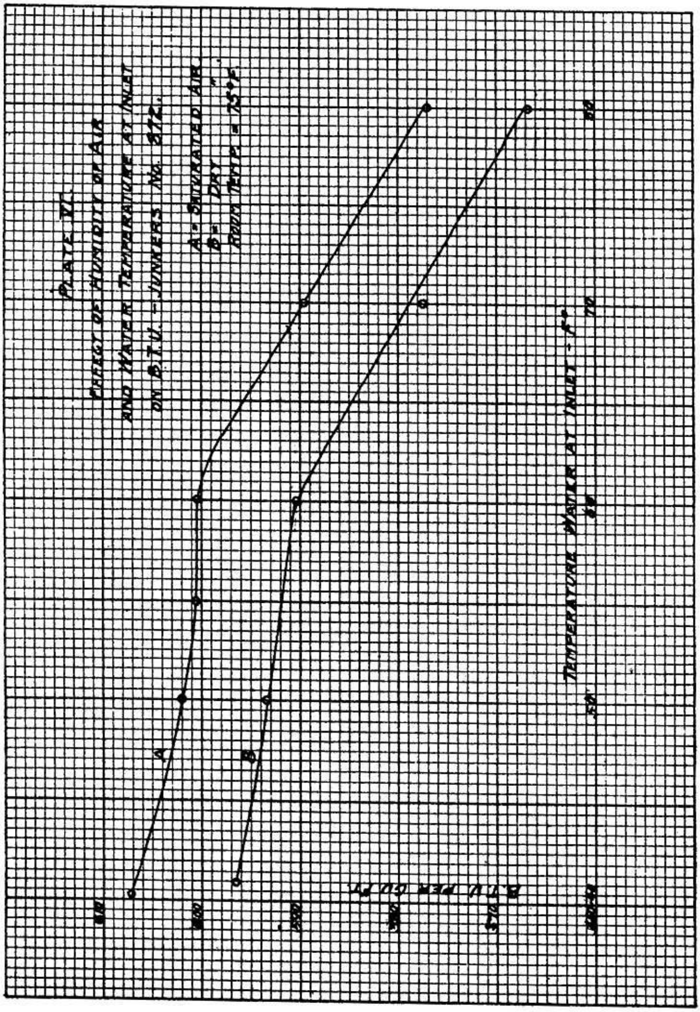
Discussion of Results.

The curves shown in Plates V and VI are interesting from two distinct points of view. First, considered simply as "Inlet Temperature Curves" they show that the form of such a curve is the same no matter what the relative humidity of the atmosphere may be. Both curves confirm the results of Series A and B in that they show the "thermal balance" of



the calorimeter occurs when the temperature of the inlet water is from 15 to 25 degrees below that of the room.

The two curves run nearly parallel throughout their entire length, the saturated air curve lying above the one determined with anhydrous air. It is seen that the difference in heating value of a gas averaging 600 B. t. u. per cubic foot, caused by a difference in humidity of the air supplied to the



calorimeter of about 97 per cent. is 10 B. t. u. Also that this difference is practically constant with the temperature of the inlet water varying from 40 degrees to 80 degrees when room temperature is 75 degrees.

COMPLETE DATA.

Series D. Nearly saturated air.

	Temperature of inlet water							
	40 degrees				50 degrees			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	98.7 throughout.							
Barometer	29.42 throughout.							
Gas tem.	76.4	76.4	76.4	76.4	76.4	76.4	76.4	76.4
Cor. factor	0.9376 throughout.							
State of meter %	2.30 fast throughout.							
Cor. gas vol.	0.1832 throughout.							
Room tem.	74.6	74.6	74.7	74.7	74.7	74.9	75.0	75.1
Exhaust tem.	50.4	50.2	50.2	50.4	57.4	57.6	57.8	57.9
Inlet tem.	40.62	40.54	40.53	40.68	49.92	50.21	50.32	50.41
Outlet tem.	55.68	55.61	55.52	55.54	65.18	65.46	65.69	65.79
Rise	15.06	15.07	14.99	14.86	15.26	15.25	15.37	15.38
Wt. Water	7.350	7.346	7.383	7.426	7.176	7.180	7.134	7.129
B. t. u.	604.2	604.3	604.1	602.3	597.7	597.7	598.5	598.5
Av. B. t. u.	603.7				598.1			

Series D.—Continued.

	Temperature of inlet water.							
	60 degrees				70 degrees			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	98.7 throughout.							
Barometer	29.42 throughout.							
Gas tem.	76.4	76.4	76.4	76.4	76.3	76.2	76.2	76.2
Cor. factor	0.9376 throughout.							
State of meter %	2.30 fast throughout.							
Cor. gas vol.	0.1832 throughout.							
Room tem.	75.4	75.6	75.6	75.6	75.6	75.6	75.6	75.7
Exhaust tem.	65.3	65.4	65.4	65.5	73.2	73.3	73.3	73.3
Inlet tem.	59.86	59.83	59.89	59.97	69.78	69.73	69.80	69.82
Outlet tem.	75.09	75.05	75.08	75.15	85.17	85.20	85.25	85.27
Rise	15.23	15.22	15.19	15.18	15.39	15.47	15.45	15.45
Wt. Water	7.178	7.195	7.199	7.191	6.961	6.964	6.935	6.948
B. t. u.	596.7	597.8	596.9	595.8	584.8	588.1	584.9	586.0
Av. B. t. u.	596.8				586.0			

SERIES E. Anhydrous Air.

	Temperature of inlet water							
	40 degrees				50 degrees			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	Anhydrous throughout							
Barometer	29.42 throughout							
Gas tem	77.5	77.5	77.5	77.4	77.3	77.3	77.3	77.3
Cor. factor	0.9348 throughout							
State of meter %	2.70 fast throughout							
Cor. gas vol	0.1819 throughout							
Room tem	74.3	74.4	74.4	74.6	75.1	75.1	75.2	75.3
Exhaust tem	50.0	50.2	50.2	50.6	57.3	57.5	57.4	57.5
Inlet tem	40.91	40.89	40.96	41.47	50.17	50.21	50.26	50.32
Outlet tem	56.07	55.83	55.63	56.69	65.39	65.61	65.49	65.61
Rise	15.16	14.94	14.67	15.22	15.22	15.40	15.23	15.29
Wt. water	7.143	7.266	7.396	7.134	7.091	7.013	7.084	7.065
B. t. u	595.3	596.8	596.5	596.9	593.3	593.7	593.1	593.8
Av. B. t. u	596.4				593 5			

SERIES E.—(Continued.)

	Temperature of inlet water							
	60 degrees				70 degrees			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	Anhydrous throughout							
Barometer	29.42 throughout							
Gas tem	77.3	77.1	77.0	77.0	76.8	76.8	76.7	76.7
Cor. factor	0.9364 throughout							
State of meter %	2.50 fast throughout							
Cor. gas vol	0.1826 throughout							
Room tem	75.2	74.1	73.9	73.9	74.4	74.3	74.1	74.4
Exhaust tem	65.0	65.0	65.0	65.0	73.2	73.4	73.5	73.5
Inlet tem	59.81	59.80	59.84	59.92	70.22	70.13	70.16	70.18
Outlet tem	75.80	75.85	75.86	75.96	84.84	85.72	85.85	85.88
Rise	15.99	16.05	16.02	16.04	15.62	15 59	15.69	15.70
Wt. water	6.707	6.693	6.822	6.686	6.741	6.763	6.720	6.716
B. t. u	587.3	588.3	598.0	587.3	576.6	577.4	577.4	577.4
Av. B. t. u	590.2				577.2			

Series E.—(Continued). Anhydrous air.

	Temperature of inlet water. 80 degrees			
	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	Anhydrous throughout.			
Barometer	29.42 throughout.			
Gas tem.	77.0	76.8	76.7	76.7
Cor. factor	0.9364 throughout.			
State of meter %	2.50 fast throughout.			
Cor. gas vol.	0.1826 throughout.			
Room tem.	76.2	75.5	75.4	75.4
Exhaust tem.	81.9	82.0	81.9	82.0
Inlet tem.	80.16	80.34	80.12	80.08
Outlet tem.	95.71	95.89	95.48	95.49
Rise	15.55	15.55	15.36	15.41
Wt. Water	6.659	6.625	6.733	6.738
B. t. u.	567.1	564.2	566.4	568.6
Av. B. t. u.		566.6		

NEARLY SATURATED AIR	55 degrees			
Humidity (air) %	96.7			
Barometer	29.42 throughout.			
Gas tem.	76.0	76.2	76.1	76.0
Cor. factor	0.9384 throughout.			
State of meter %	2.24 fast throughout.			
Cor. gas vol.	0.1835			
Room tem.	74.1	75.5	73.9	73.3
Exhaust tem.	61.5	61.7	61.6	61.7
Inlet tem.	55.03	55.09	55.14	55.21
Outlet tem.	70.40	70.49	70.53	70.58
Rise	15.37	15.40	15.39	15.37
Wt. water	7.169	7.168	7.168	7.152
B. t. u.	600.4	601.6	601.2	599.1
Av. B. t. u.		600.6		

	80 degrees			
Humidity (air) %	96.7			
Barometer	29.42 throughout			
Gas tem.	76.7	76.5	76.4	76.5
Cor. factor	0.9384 throughout			
State of meter %	2.24 fast throughout			
Cor. gas vol.	0.1835			
Room tem.	75.1	75.2	75.2	75.2
Exhaust tem.	81.3	81.7	81.6	81.5
Inlet tem.	79.84	79.81	79.76	79.71
Outlet tem.	95.71	95.75	95.67	95.67
Rise	15.87	15.94	15.91	15.96
Wt. water	6.668	6.626	6.654	6.625
B. t. u.	577.3	576.2	577.6	576.8
Av. B. t. u.		577.0		

Subsequent Determinations of the Effect of Humidity.

In order to have further checks upon the work just reviewed other measurements were made at different times during the investigations which followed. Each one of these determinations was made with the temperature of the inlet water approximately twenty (20) degrees below room temperature. The results are summarized below.

SUBSEQUENT TESTS NO. 1.

Ave. B. t. u. per cubic foot with nearly saturated air	595.5
Ave. B. t. u. per cubic foot with nearly anhydrous air	584.2
Difference	11.3

SUBSEQUENT TEST NO. 2.

Ave. B. t. u. per cubic foot with nearly saturated air	604.1
Ave. B. t. u. per cubic foot with nearly anhydrous air	594.2
Difference	9.9
Mean of the two average differences	10.6

The difference of 10 B. t. u. in the heating value of the gas as determined by the calorimeter operating upon saturated and unsaturated air is due to the absorption, by the products of combustion, of water vapor equal in amount to the quantity brought in by the combined volumes of gas and air.

This quantity of moisture brought in by gas and air is dependent upon several things: (1) The temperature of the air, (2) the humidity, and (3) the per cent. excess of air.

The calorimeter should be operated with inlet water at a temperature such that the products of combustion carry off entrained water vapor equal in amount to that introduced by the entering gas and air.

With a high humidity and normal excess of air, and the temperature of the products of combustion lower than room temperature, a considerable quantity of water vapor brought in by the air will be condensed in the calorimeter and make the observed heating value too high. On the other hand, with a similar air supply of low humidity, a quantity of water vapor sufficient to saturate this amount of air will be removed from the calorimeter and the observed heating value will be too low.

Since the variation in heating value as determined by the calorimeter is 10 B. t. u. which is the most extreme variation possible in the humidity of the air supply with normal excess. and since the humidity of the air rarely falls below 20 per cent., the variation in heating value as experienced in practice will not be more than 6 to 8 B. t. u.

It appears from tests of the products of combustion from the Junkers calorimeter operating with the damper closed that the percentage excess of air will lie between twenty and fifty per cent. In view of these conditions commonly experienced in commercial practice, it seems reasonable to say that the error under different conditions of humidity and normal excess of air supply may be 8 B. t. u. within the extreme limits. This error may be fully compensated if the humidity and excess of air supply be known. A knowledge of these conditions will enable the operator so to regulate the temperature of the inlet water, or the products of combustion leaving the calorimeter, that the determination obtainable will be accurate within very narrow limits.

Theoretically, to correct for this condition in an ideal instrument, under extreme humidity conditions, the temperature of the products of combustion should approximate the temperature of the gas and air entering the calorimeter. In an extremely dry atmosphere, this temperature may be from fifteen to twenty degrees lower than the temperature of the room.

Effect of Baffle Plates on Burner.

Dr. Immenkötter[5] made an attempt to determine the effect of baffle plates placed around the stem of the burner used in the Junkers calorimeter, and, from two sets of data which show exactly opposite effects, concluded that the effect of much baffle plates was negligible.

Recent investigations[9] of the Bureau of Standards showed a beneficial effect from the use of such baffle plates.

Inasmuch as the data upon this subject was meager it was thought best to carry out a series of tests in order to obtain concordant data from which a definite conclusion could be drawn. Three series of determinations were made.

Conditions of Tests.

The Junkers calorimeter No. 872 was operated under the proper conditions as previously determined, using natural draft of room air. Baffle plates consisting of nickel-plated metal were placed around the burner steam as follows: (1) A flat disk about 1¼ inches from the burner support. This disk was 1⅜ inches in diameter and was perforated with four large and four small holes. (2) A smaller cone shaped disk about 1 inch above the first. This disk had four fairly large openings through it. (3) A still smaller cone shaped disk, similar to the second and 1 inch above the second disk.

First, a series of determinations was made with the baffle plates in position, then the plates were removed and a similar series of determinations made using the same sample of gas. The data obtained in three such series of tests is summarized below. Inasmuch as a rather poor, dull deposit of nickel was obtained when the disks were first plated, after the first two series of tests were made, the old plate was removed and a more satisfactory, bright deposit was obtained. This fact probably accounts for the greater effect obtained in the third series of tests. Hence the third series of tests is considered the most authoritative.

SERIES F.—(1).

	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
With baffles	582.3	583.9	583.8	584.3	583.6
Without baffles	584.7	582.6	581.9	581.0	581.8*
Av. difference					1.8

*** Average computed using values No. 2, No. 3, No. 4 only.**

SERIES F.—(2).

	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
With baffles	583.7	583.6	583.0	582.6	583.2
Without baffles	581.4	580.0	579.4	—	580.3
Ave. difference					2.9

The above tests having established the fact that the calorimeter gives slightly higher results when the baffle plates are used on the burner, especial precautions were taken in the third test. All of the old nickel was removed from the baffle plates, and then they were replated and well polished so as to give a good reflecting surface.

SERIES F.—(3).

	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
With baffles	599.7	599.3	601.1	599.9	600.0
Without baffles	597.0	595.7	597.1	595.9	596.4
Difference					3.6

Discussion of Results.

The above determinations show that there is an appreciable leakage of heat from the base of the combustion chamber of the Junkers calorimeter when the calorimeter is operated without baffle plates on the stem of the burner. When baffle plates are employed on the stem of the burner the efficiency of the calorimeter is increased by three parts in six hundred, or 0.5 per cent.

General Summary of the Investigations of the Junkers Calorimeter No. 872.

The results of the investigations of the Junkers calorimeter may be summarized as follows:

1. The calorimeter should be operated with water which enters the instrument at a temperature of from 10 to 25 degrees below that of the room, depending upon humidity conditions.

2. The most advantageous rate of combustion of the gas is seven (7) cubic feet per hour, but variations between quite wide limits will cause only a slight error.

3. When operated under the conditions enumerated in (1) and (2) the humidity of the air supplied to the calorimeter has a marked effect upon the efficiency of the instrument. Taking saturated air as the standard, and assuming gas having a heating value of 600 B. t. u. per cubic foot, the error

caused by the use of unsaturated air is —1 B. t. u. for each range of 10 per cent. relative humidity below the standard. This error is practically constant with water entering the calorimeter at temperatures from 40 degrees to 80 degrees when room temperature is 75 degrees.

4. When operating on a gas having a heating value of 600 B. t. u. per cubic foat, the efficiency of the Junkers calorimeter may be increased 0.5 per cent. by the use of baffle plates on the stem of the burner.

(2) *The Improved Junkers Calorimeter.*

The improved Junkers Calorimeter No. 2007 used in this investigation was loaned by The United Gas Improvement Company, of Philadelphia. The fundamental principles of the instrument are the same as in the older type, but some minor changes have been made.

The principal changes are as follows: (1) The thermometers are at the same level. (2) The cross section of the instrument is slightly larger than that of the old instrument, the combustion chamber being slightly enlarged and some of the piping formerly outside of the main body of the instrument being enclosed within the outer shell. (3) The weirs on the calorimeter are permanently connected to several feet of metal piping, so that only a small amount of rubber tubing is necessary for the incoming and outgoing water. (4) The delivery pipe for the outflowing water may be swung through an arc, thus simplifying the operation of switching the water from the drain to the receiving bucket and *vice versa.*

The feature mentioned under (4) did not prove entirely satisfactory. It is evident that when the water is led into the receiving bucket by means of a rubber tube, the tube usually extends from one to two inches down into the bucket, and the greater part of the water will flow down the side of the bucket, thus reducing the tendency toward spattering. If the device mentioned above is used alone, the water must fall from a somewhat greater height and it is not easy to direct its flow down the side of the bucket. Spattering occurred to a greater extent than when the old method was used, and therefore a short length of rubber tubing was connected to the end of the delivery pipe and the water switched into and out of the bucket in the usual way.

The investigations of the Improved Junkers No. 2007 can be divided into three main divisions, viz.: (a) Preliminary tests; (b) Determination of the proper rate of combustion of the gas; (c) Determination of the proper relation between the temperature of the inlet water and room temperature; (d) Determination of the absolute efficiency of the calorimeter by checking it against the Junkers No. 872.

(a) *Preliminary Tests.*

During some preliminary tests it was found that consecutive determinations using the same sample of gas did not check very closely at times, and it was noticed that, if the rate of flow of the gas was high when the burner was inserted in the combustion chamber and the damper was closed, luminous tips of considerable size appeared in the Bunsen flame. If the damper was then opened the luminous tips disappeared. It was evident that when the damper was closed, the draft through the combustion chamber was not sufficiently strong for proper combustion. In order to establish this fact definitely the calorimeter was operated under the proper conditions as determined for the old style of calorimeter, first with the damper closed and then with the damper open. Samples of the exhaust gases were taken in both cases and later analyzed. The analyses follow:

	Damper closed per cent.	Damper open per cent.
CO_2	13.2	10.2
O_2	0.0	6.4
CO	2.6	0.0
N_2	82.6	83.4

The analyses show conclusively that when the damper is closed the combustion is imperfect, and undoubtedly the discordant results above referred to were due, in a large measure, to this cause. When the damper is open the combustion is perfect. Therefore in all subsequent work with this instrument the damper was kept wide open.

Another undesirable feature noted during the preliminary tests was the dripping of water from the combustion chamber. This persisted throughout all subsequent work with the Improved Junkers No. 2007. Evidently some water vapor was condensed out of the products of combustion in the combustion chamber itself.

(b) *Proper Rate of Combustion of Gas.*

Conditions of Tests.

The gas was drawn from the holder used in the previous work on the Junkers No. 872, and other conditions of operation, except the rate of flow of the gas and the position of the damper, were maintained the same as for the Junkers No. 872. Room temperature averaged 81.0 degrees. Damper wide open; natural draft. Maintaining other conditions constant determinations were made with the following rates of flow of gas, viz., 3, 4, 6, 7, 8, 9 and 10 cubic feet per hour. Two determinations were made with each "Rate of Flow." The summarized data follows:

SERIES G.

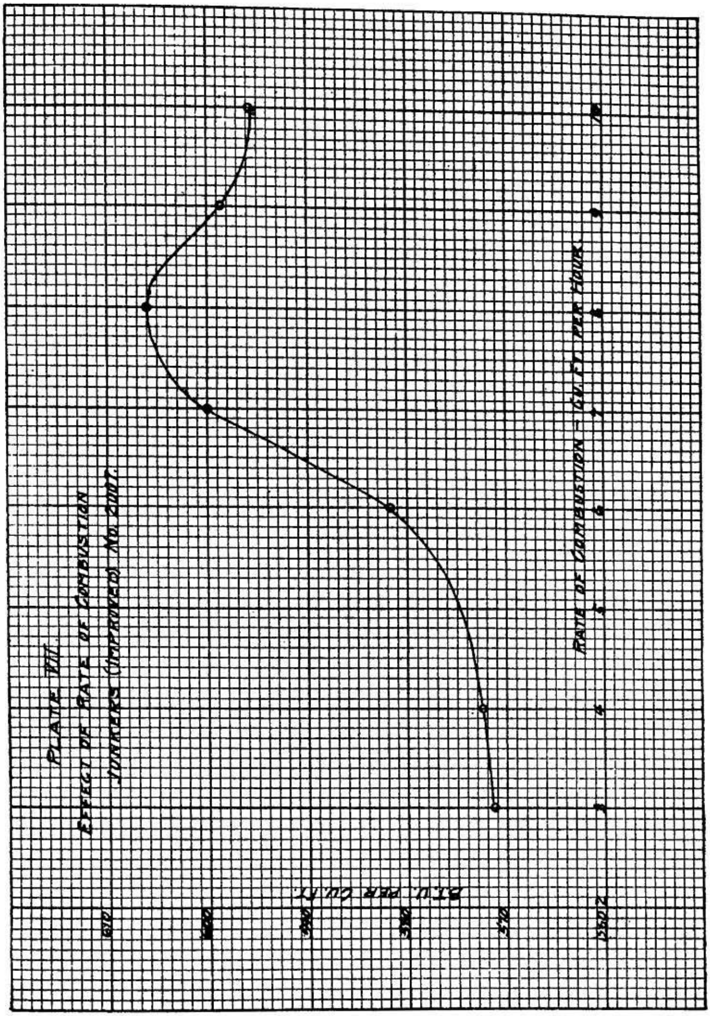
Rate of flow in cu. ft. per hr.	B. t. u. per cubic foot		
	No. 1	No. 2	Ave.
3	571.0	571.6	571.3
4	569.6	575.1	572.4
6	583.7	579.4	581.6
7	601.0	599.2	600.1
8	605.1	607.2	606.1
9	598.2	598.8	598.5
10	595.7	595.7	595.7

Plate VII shows a curve obtained by plotting the average values of B. t. u. per cubic foot as abscissae against corresponding "Rates of Flow" as ordinates.

Discussion of Results.

The "Rate of Flow" curve shows a definite maximum when the gas was burned at the rate of 8 cubic feet per hour. The curve falls off quite rapidly on either side of the maximum.

This is in striking contrast to the corresponding curve for the Junkers No. 872. The explanation of the sharp maximum probably lies in the better draft obtained with this particular rate of combustion of the gas.



In all subsequent work with the Improved Junkers No. 2007 the rate of flow of the gas was always carefully regulated to 8 cubic feet per hour.

(c) *Effect of Temperature of Inlet Water.*

Inasmuch as the main features of the Improved Junkers calorimeter are the same as those of the older type, it was thought to be entirely probable that the same relation between the temperature of the inlet water and room temperature would hold with the new instrument as did with the old. However, in order to leave no room for doubt as to the proper working conditions, the inlet temperature curve was worked out for this instrument also.

Conditions of Tests.

Average room temperature 74.5 degrees; natural draft; humidity of air 33 per cent.; temperature of inlet water used 40, 50, 60, 70 and 80 degrees; difference in temperature of incoming and outgoing water 15-16 degrees. The summarized data follows:

SERIES H.

Temp. of inlet water deg.	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
40	590.8	589.0	587.2	587.6	588.7
50	575.1	574.7	574.7	578.1	575.7
60	566.5	567.3	568.8	566.5	567.3
70	551.7	548.8	554.2	554.3	552.3
80	529.9	530.7	532.2	529.9	530.7

Plate VIII shows a curve obtained by plotting the average B. t. u. per cubic foot as abscissae against the corresponding temperatures of inlet water as ordinates.

Discussion of Results.

As the "Inlet Temperature Curve" for the Improved Junkers is of the same type as the corresponding curve for the older form of the Junkers calorimeter, no particular discussion is needed at this point. As was predicted, the "heat balance" of the calorimeter occurs at the same place as with the Junkers No. 872, viz., when the temperature of the inlet water is from 15 to 25 degrees below room temperature. However, the slope of the curve between the 50 degrees point and the 60 degrees point is a little sharper than with the old style Junkers and hence the average temperature—that of 20 degrees below room temperature—would appear to be the most desirable temperature of inlet water.

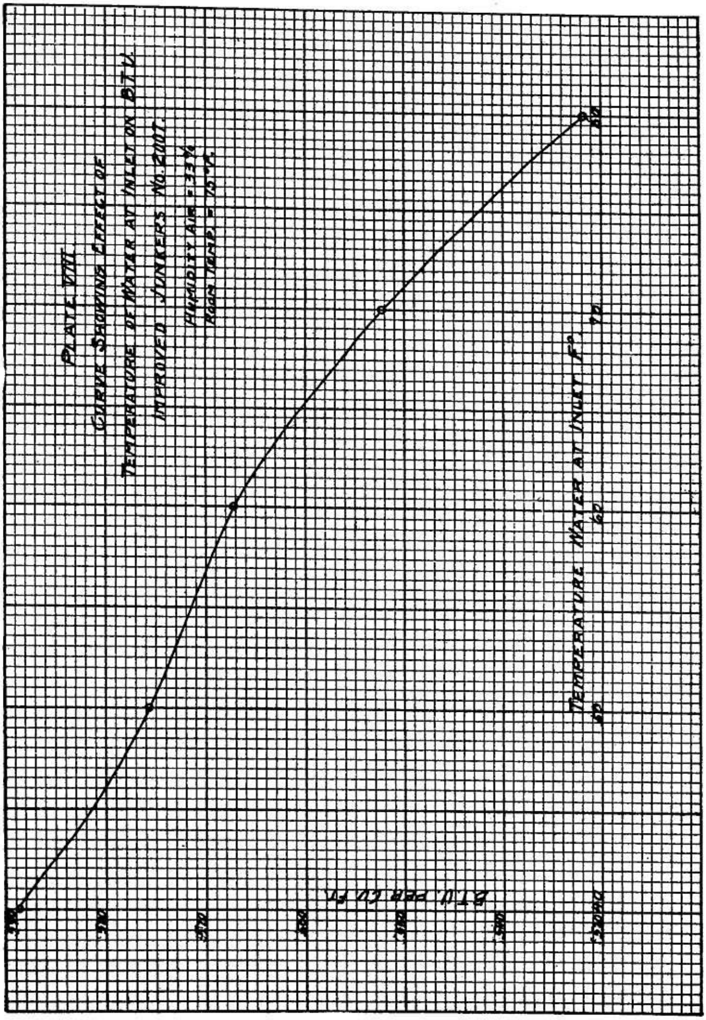


PLATE VIII

CURVE SHOWING EFFECT OF TEMPERATURE OF WATER AT INLET ON B.T.U.

IMPROVED JUNKERS No. 2007.

HUMIDITY AIR = 33%

ROOM TEMP. = 75° F.

It may be stated that, in general, that the check determinations with the Improved Junkers No. 2007 agreed fairly satisfactorily, but the agreement was not quite so close as was the case with the Junkers No. 872. Also, with the improved instrument, variations in the temperature of the inlet water were not noted as quickly by the outlet thermometer as with the old type.

(d) *Efficiency of the Improved Junkers No. 2007.*

The efficiency of the Improved Junkers No. 2007 was determined by checking it against the Junkers No. 872. Each calorimeter was operated under its proper working conditions as previously determined. Both instruments were operating simultaneously and continuously from the beginning to the end of each series of tests. Alternate tests with each instrument were made. Natural draft used with both instruments; baffle plates omitted. The proper working conditions for both types of Junkers calorimeters are summarized as follows:

	Calorimeter	
	Junkers No. 872	Im. Junkers No. 2,007
Rate of flow of gas	7 cu. ft. per hr.	8 cu. ft. per hr.
Tem. inlet water*	15° below room tem.	15° below room tem.
Damper	Closed	Open
Rise in tem. of water in calorimeter	15–16°	15–16°

* Water 20° below room temperature could not be used because of lack of graduations below 60° on one set of thermometers.

The summarized data follows. The complete data is tabulated after the "General Summary."

Series I—(1)

	B. t. u. per cubic foot			
Calorimeter	No. 1	No. 2	No. 3	Ave.
Imp. Junkers No. 2007	581.1	578.0	—	579.6
Junkers No. 872	581.4	580.0	579.4	580.3

Series I—(2)

	B. t. u. per cubic foot				
Calorimeter	No. 1	No. 2	No. 3	No. 4	Ave.
Imp. Junkers No. 2007	580.6	583.4	578.5	581.1	580.9
Junkers No. 872	584.7	582.6	581.9	581.0	582.5
Ave. of Nos. 2, 3, and 4					581.8

Discussion of Results.

The results given above are practically self explanatory. The Improved Junkers No. 2,007 gave results slightly lower than the Junkers No. 872, but the difference is small, being practically within the limits of experimental error.

Subsequent Tests.

An auxiliary series of tests was made to determine the effect of baffle plates upon the stem of the burner of the Improved Junkers No. 2,007. The tests were carried out in the same manner as for the Junkers No. 872. The data follows:

	B. t. u. per cubic foot				
	No. 1	No. 2	No. 3	No. 4	Ave.
With baffles..............	579.5	563.3	577.0	573.0	578.2
Without baffles	574.5	573.2	576.1	573.5	574.3

From these results it is seen that the use of baffle plates on the stem of the burner of the Improved Junkers No. 2,007 increases the efficiency of the instrument by four parts in 578 or nearly 0.7 per cent. In the case of the Junkers No. 872 baffle plates increased the efficiency by 0.5 per cent. Hence, if, in the above comparative tests both calorimeters had been operated with baffle plates on the burner stems, the average heating values would have been practically the same.

General Summary of the Investigations of the Improved Junkers Calorimeter No. 2,007.

The results of the investigations of the Improved Junkers calorimeter No. 2,007 may be summarized as follows:

(1) The proper "Rate of Flow" of the gas is eight (8) cubic feet per hour. Any considerable variation from this rate of combustion will cause the instrument to register low heating values.

(2) The calorimeter should be operated with water which enters the calorimeter at a temperature of from 10 to 25 degrees below room temperature, depending upon humidity conditions.

(3) When the calorimeter is operated with the damper wide open the combustion is perfect; when the damper is closed incomplete combustion results. Therefore the calorimeter damper should always be wide open.

COMPLETE DATA.

SERIES I—(1).

	Junkers No. 872				Improved Junkers No. 2,007			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	25.0 throughout							
Barometer	29.43 throughout							
Gas tem	7.44	74.4	74.4	—	76.4	76.4	—	—
Cor. factor	0.9432 for No. 872				0.9379 for No. 2,007			
State of meter %	0.6 fast for No. 272				0.56 slow for No. 2,007			
Cor. gas vol.	0.1874 for No. 872				0.1886 for No. 2.007			
Room tem	75.1	74.8	74.7	—	75.1	74.9	—	—
Exhaust tem	65.0	65.0	65.0	—	64.0	64.0	—	—
Inlet tem	60.37	60.37	60.60	—	60.44	60.53	—	—
Outlet tem	75.26	75.28	75.46	—	75.38	75.35	—	—
Rise	14.89	14.85	14.80	—	14.94	14.82	—	—
Wt. water	7.317	7.319	7.337	—	7.336	7.365	—	—
B. t. u	581.4	580.0	579.4	—	581.1	578.0	—	—
Av. B. t. u		580.3			579.6			

SERIES I—(2).

	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	38.8 throughout							
Barometer	29.42 throughout							
Gas tem	73.1	73.0	73.0	73.0	75.2	75.2	73.6	75.8
Cor factor	0.9468 for No. 872				0.9403 for No. 2,006			
State of meter %	0.20 fast for No. 872				1.12 slow for No. 2,007			
Cor. gas vol.	0.1890 for No. 871				0.1903 for No. 2,007			
Room tem	74.6	73.6	73.5	74.0	73.6	73.6	73.7	75.0
Exhaust tem	64.6	64.2	64.2	64.6	63.3	63.2	63.3	64.0
Inlet tem	59.81	59.79	59.90	60.31	59.96	60.02	60.21	60.96
Outlet tem	75.18	75.20	75.60	75.42	75.42	75.39	75.33	75.43
Rise	15.47	15.41	15.30	15.29	15.46	15.37	15.12	14.47
Wt. water	7.143	7.145	7.188	7.182	7.147	7.223	7.281	7.642
B. t. u.	584.7	582.6	581.9	581.0	580.6	583.4	578.5	581.1
Av. B. t. u		582.5				580.9		

(4) The presence of baffle plates on the stem of the burner increases the efficiency of the instrument by 0.7 per cent.

(5) When operated under proper conditions the efficiency of the instrument for determining gross heating values is the same as that of the Junkers No. 872.

(6) The device for switching the outflowing water into and out of the receiving bucket is not entirely satisfactory because of the spattering of the water which occurs.

(7) Some water is condensed out of the products of combustion within the combustion chamber. This water drips from the base of the calorimeter. and renders the volume of the measured water of condensation too small.

(8) Variations in the temperature of the inlet water are not noted as quickly by the outlet thermometer as is the case with the Junkers No. 872.

(9) Both thermometers being on the same level, readings can be taken with less inconvenience than when using the Junkers No. 872.

(3) *The American Meter Co.'s Calorimeter.*

The American Meter Co.'s calorimeter No. 122 used in this investigation was loaned by the American Meter Co. of New York City. In all fundamental principles this calorimeter is a Junkers calorimeter. However, a considerable number of minor changes have been made which facilitate the operation of the instrument. These changes may be summarized as follows:

(1) Both thermometers are on the same level.

(2) Special gaskets are provided for securing the thermometers in place.

(3) The absorption chamber can be removed from the outer shell of the instrument, thus facilitating cleaning operations.

(4) Baffle plates are provided for the burner.

(5) The burner has a flat, circular base so that the burner will remain in an upright position when unsupported.

(6) The burner top screws on to the stem.

(7) An adjustable mirror enables the operator to note the gas flame.

(8) A small plumb bob is provided for leveling the instrument.

(9) The position of the damper is indicated by a pointer and scale.

(10) A three-way cock provides a means of directing the outflowing water either to the receiving bucket or to the drain.

(11) A vent is provided to obviate the trapping of air around the three-way cock.

Inasmuch as the basic principles of the instrument are the same as both forms of the Junkers calorimeter, it was not deemed necessary to work out the proper rate of combustion of the gas or the proper relation between the temperature of inlet water and room temperature before making comparative tests.

The only work done with this instrument was to make two series of comparative tests between it and the Junkers No. 872.

Conditions of Tests.

Both calorimeters were operated under identical conditions, these being the standard conditions for the operation of the old form of the Junkers calorimeter, as previously determined in this investigation. Both calorimeters were operating continuously and simultaneously throughout each series of tests. Baffle plates were placed upon the stems of both calorimeter burners. Natural draft used. The summarized data follows and the complete data is tabulated after the "Summary of Results."

SERIES J—(1)

	B. t. u. per cubic foot					
Calorimeter	No. 1	No. 2	No. 3	No. 4	No. 5	Ave.
American Meter Co.'s No. 122	571.5	569.4	570.2	569.6	570.6	570.3
Junkers No. 872	571.9	571.5	570.0	570.9	571.5	571.2

SERIES J—(2)

	B. t. u. per cubic foot					
Calorimeter	No. 1	No. 2	No. 3	No. 4	No. 5	Ave.
American Meter Co.'s No. 122	586.7	585.9	583.8	581.2	581.4	583.8
Junkers No. 872	587.1	586.5	583.5	582.2	580.0	583.9

Summary of Results.

From the above series of tests the following conclusions can be drawn:

(1) When operated under the standard conditions for the old type of the Junkers calorimeter the American Meter Co.'s calorimeter gives the same efficiency as the Junkers calorimeter.

(2) All of the changes enumerated at the beginning of heading (3) appear to be advantageous, and can truly be termed "improvements."

COMPLETE DATA.

SERIES J—(1).

Junkers No. 872

	No. 1	No. 2	No. 3	No. 4	No. 5
Humidity (air) %	46.1 throughout.				
Barometer	29.60 throughout.				
Gas tem.	76.0	76.0	76.1	76.2	76.2
Cor. factor ...	0.9444 throughout.				
State of meter %	2.12 fast throughout.				
Cor. gas. vol. ..	0.1849 throughout.				
Room tem.	77.3	77.2	77.1	77.3	77.3
Exhaust tem. ..	65.1	65.0	64.9	64.9	65.0
Inlet tem.	60.03	60.07	59.86	59.93	59.98
Outlet tem. ...	75.29	75.35	75.38	75.32	75.34
Rise	15.26	15.28	15.52	15.40	15.36
Wt. water	6.929	6.915	6.791	6.854	6.879
B. t. u.	571.9	571.5	570.0	570.9	571.5
Av. B. t. u.			571.2		

American Meter Co., No. 122

Humidity (air) %	46.1 throughout.				
Barometer	29.60 throughout.				
Gas tem.	77.6	77.6	77.6	77.6	77.7
Cor. factor	0.9401 throughout.				
State of meter %	1.28 fast throughout.				
Cor. gas vol. ..	0.1856 throughout.				
Room tem.	77.2	77.2	77.0	77.4	77.4
Exhaust tem. .	66.2	66.3	66.2	66.3	66.4
Inlet tem.	59.97	60.07	59.79	59.96	59.92
Outlet tem. ...	75.41	75.71	75.43	75.73	75.32
Rise	15.44	15.64	15.64	15.77	15.40
Wt. water	6.870	6.757	6.766	6.704	6.877
B. t. u.	571.5	569.4	570.2	569.6	570.6
Av. B. t. u. ...			570.3		

SERIES J—(2).

	Junkers No. 872				
	No. 1	No. 2	No. 3	No. 4	No. 5
Humidity(air)%	46.1 throughout.				
Barometer	29.62 throughout.				
Gas tem.......	79.0	79.4	80.5	80.8	81.4
Cor. factor	0.9336 throughout.				
State of meter %	0.82 fast throughout.				
Cor. gas vol. ..	0.1852 throughout.				
Room tem. ...	79.8	80.2	81.0	80.2	80.6
Exhaust tem. .	65.6	65.6	65.6	65.3	65.4
Inlet tem.	60.22	60.33	59.94	60.03	60.02
Outlet tem. ...	75.53	75.58	75.37	75.13	75.22
Rise	15.31	15.25	15.43	15.10	15.20
Wt. water.....	7.102	7.123	7.003	7.141	7.067
B. t. u.........	587.1	586.5	583.5	682.2	580.0
Av. B. t. u....			583.9		

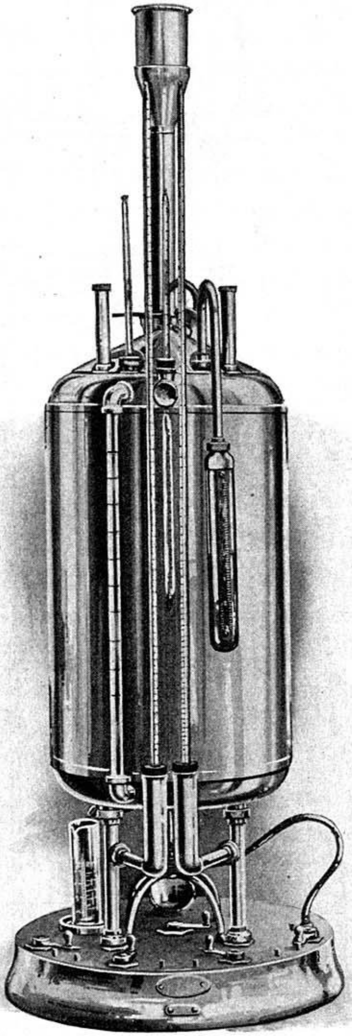
	American Meter Co., No. 122				
Humidity(air)%	46.1 throughout.				
Barometer	29.62 throughout.				
Gas tem.......	79.6	79.7	80.0	80.0	80.1
Cor. factor	0.9343 throughout.				
State of meter %	1.54 fast throughout.				
Cor. gas vol. ..	0.1840 throughout.				
Room tem.....	79.5	79.4	78.5	78.5	78.9
Exhaust tem..	66.1	66.0	65.8	65.5	65.8
Inlet tem......	60.16	60.44	59.82	60.02	59.94
Outlet tem.....	75.64	75.48	75.31	75.38	75.53
Rise	15.48	15.04	15.49	15.36	15.59
Wt. water.....	6.974	7.167	6.935	6.962	6.862
B. t. u.........	586.7	585.9	583.8	581.2	581.4
Av. B. t. u....			583.8		

(4) *The Doherty Calorimeter.*

The Doherty calorimeter used in this investigation was loaned by the Improved Equipment Company of New York City. A front view of the calorimeter is shown on the following page, and Plate IX shows the relation of all the parts. Inasmuch as the Doherty calorimeter is radically different in construction and operation from any other calorimeters on the market, a detailed description of the instrument will be given.

Description of Calorimeter.

The fundamental principle of the Doherty calorimeter is the direct displacement of the gas under test by the water which is heated by the combustion of the gas, thus maintaining absolutely constant the ratio of volumes. The pressure is



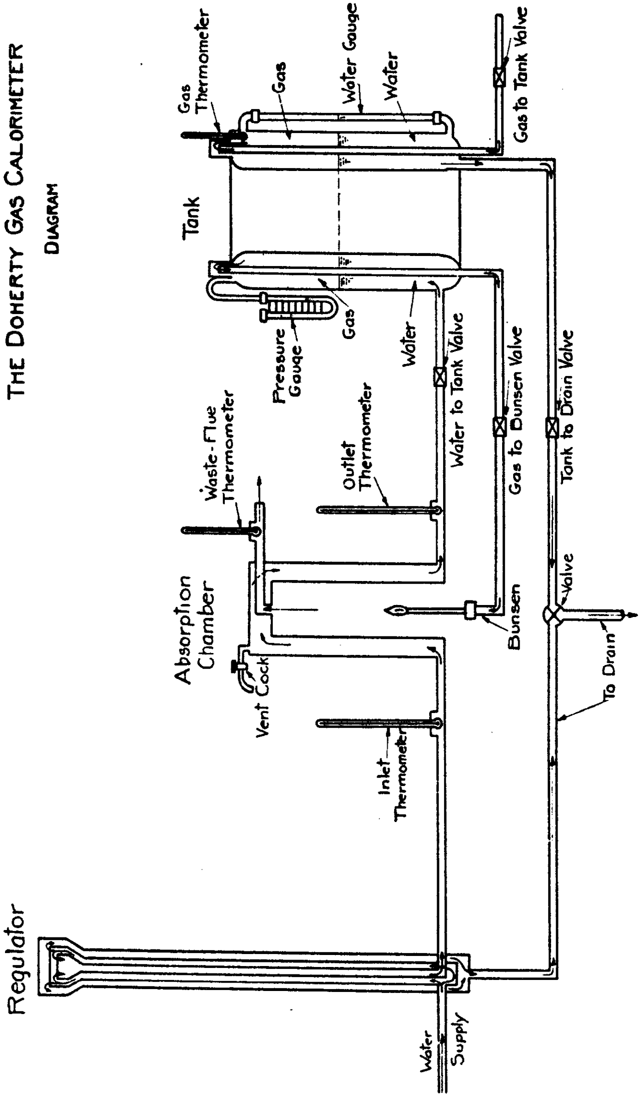
The Doherty gas calorimeter.

imparted to the gas by the displacing water; and this water secures its constant pressure from a constant static "head" in the regulator of the calorimeter.

PLATE IX

THE DOHERTY GAS CALORIMETER

DIAGRAM



Every cubic inch of water passing through the heat absorbing chamber is heated by the burning of a cubic inch of gas displaced by this water. This being the case, determination of the heating value in British thermal units per cubic foot becomes a question of measuring temperatures, with suitable corrections for existing conditions of temperature of the gas and the pressure upon the gas. The observed heating value of the gas is obtained by multiplying the rise in temperature by the weight of a cubic foot of water at the temperature at which it entered the gas tank. To obtain the corrected heating value the observed heating value is divided by the usual correction factor which reduces the gas volume to standard conditions, viz., 60 degrees F. and 30 inches of mercury. Thus measurement of gas and weighing of water are necessary with this instrument.

The Doherty calorimeter has two essential parts—the absorption chamber and the tank. Both of these are cylinders of annular section, the former being placed within the latter. A layer of felt guards against interchange of heat through the walls.

The regulator is simply a stand-pipe in which a constant head or pressure is maintained by means of a supply of flowing water, part of which escapes to the drain, the remainder keeping the stand-pipe full as displacement occurs in the tank.

The exhaust gases are expelled through a vent located near the top and on the front of the instrument. No damper is provided in the vent.

The tank has a gauge glass for indicating the water level inside, and a U-gauge showing the pressure on the gas in inches of water. The gauge glass is divided into nine equal divisions, the volume between the extremes being exactly one-third of a cubic foot. . A thermometer extends into the top of the tank and indicates the temperature of the gas.

The water passes from the stand pipe through the absorption chamber and into the tank. An arrangement of adjustable baffles within the absorption chamber makes it possible to adjust the absorption surface so that the products of combustion can be delivered to the atmosphere at varying temperatures without changing the temperature of the inlet water. The gas and water supplies are controlled by suitable valves.

All thermometers can be seen in the front view of the calorimeter. The two large thermometers are the inlet and outlet thermometers, the outlet being on the left and the inlet on the right.

Operation of the Calorimeter.

The method of making a determination may be outlined as follows: The tank is filled with gas to be tested and the supply shut off. In order to fill the tank with gas it must first be filled with water. The gas supply valve is then opened and the water allowed to run out, gas being drawn into the tank. Water is admitted from the stand-pipe, imparting regulator pressure of the gas. The pressure can be varied to some extent by a manipulation of valves. The Bunsen is lighted, and set in position in the combustion chamber. When the water level in the gauge glass has risen to the first graduation the temperatures of both inlet and outlet water are read, and such readings are repeated as the water level passes each graduation on the gauge glass, thus giving ten readings in all. The average of the ten readings on each thermometer is taken as the basis of the test. After applying the corrections to the average readings on each thermometer, the difference between the corrected average readings gives the temperature interval through which the water was heated. The method of calculation of the heating value of the gas has been indicated in a previous paragraph but will be shown in detail at this point.

We will assume that the average outlet temperature was 65.00 degrees. Now the outlet temperature indicates the temperature at which the water entered the tank, for the gas is displaced by the water heated. Therefore in this computation we must use the weight of a cubic foot of water at 65.00 degrees which is 62.34 pounds.

Then

$$\text{B. t. u. of gas} = \frac{62.34 \times d}{V}.$$

And

$$V = \frac{17.64 \times [(h + h') - a]}{460 + t}.$$

Where

V = volume of gas corrected to 60° and 30 inches of mercury.
h = barometric pressure in inches of mercury.
h' = U-gauge pressure in inches of mercury.
a = vapor tension pressure in inches of mercury.
t = temperature of gas in tank.
d = difference in temperature of water before and after heating.

This process gives the gross heating value of the gas. A drip is provided around the lower end of the absorption chamber, which collects the water of condensation, discharging it into a glass graduate marked both in cubic centimeters and in British thermal units. A means of determining "net" heating values is thus provided in the same manner as in other types of calorimeters.

The investigation of the Doherty calorimeter may be divided into four main divisions, viz.: (a) Determination of the proper rate of combustion of the gas; (b) Determination of the proper relation between the temperature of the inlet water and room temperature; (c) Determination of the efficiency of the Doherty calorimeter No. 16 by checking it against the Junkers calorimeter No. 872; (d) subsequent investigations.

(a) *Determination of the Proper Rate of Combustion of Gas.*

By proper manipulation of the valves, somewhat varying pressures on the gas in the tank may be produced. Of course, the greater the pressure the faster will be the rate of flow of the gas to the Bunsen burner. It was found possible to produce "rates of flow" varying from 0.5 cubic foot per hour to 2.5 cubic feet per hour.

Conditions of Tests.

While holding all other operating conditions constant the Doherty No. 16 was operated upon the same sample of gas employing the following different "rates of flow" in the order named, viz., 0.327, 0.590, 1,115, 1.726 and 2.428 cubic feet per hour. Two determinations were made with each "rate of flow." The summarized data follows:

SERIES K.

Rate of flow in cu. ft. per hr.	B. t. u. per cubic foot No. 1	No. 2	Ave.
0.327	576.0	572.8	574.4
0.590	601.3	607.2	604.3
1.115	600.6	598.6	599.6
1.726	601.2	599.8	600.5
2.428	594.5	599.5	597.0

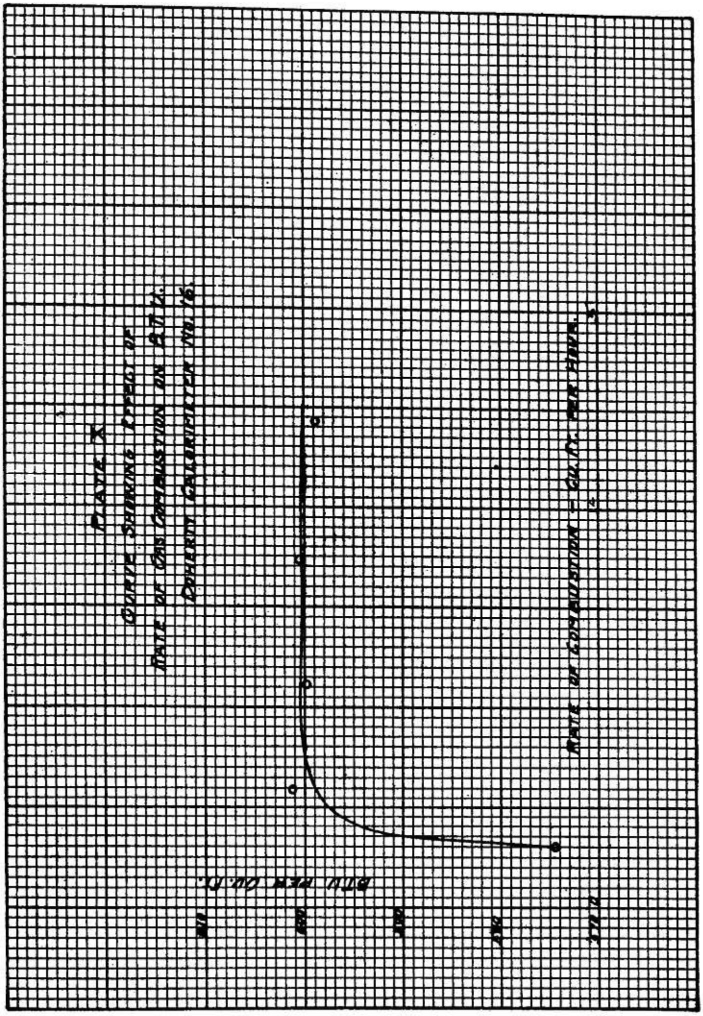
Discussion of Results.

It is noticeable that the results at the first two "rates of flow" are rather discordant. Considerable effort and time was expended to get concordant results with slow "rates of flow," but the calorimeter refused to operate steadily under these conditions. The calorimeter seemed to give practically uniform results with all of the higher "rates of flow" obtainable. However, it was found that a pressure of two inches of water was the most constant pressure obtainable with this instrument, and as this pressure gave a "rate of flow" of about 1.7 cubic feet per hour this "rate of flow" was adopted as the standard for the Doherty No. 16. Plate X shows the "rate of flow" curve obtained by plotting cubic feet per hour as abscissae against B. t. u. per cubic foot as ordinates.

(b) *Effect of Temperature of Inlet Water.*

Conditions of Tests.

Two series of tests were made. The first series of tests was of a preliminary nature, and was particularly designed to note the effect of changing the surface exposed in the absorption chamber by manipulation of the pointer at the top of the instrument. As has been previously mentioned this pointer is connected wtih adjustable baffles within the absorption chamber, by means of which the absorbing surface may be increased or diminished, thus lowering or raising the temperature of the exhaust gases.



The first series of tests was made with water ranging in temperature from 55 degrees to 85 degrees with room temperature averaging 76 degrees. Two consecutive tests were made at each of the following temperatures, viz.: 55, 60, 65, 70, 75, 80 and 85 degrees. The summarized data follows:

Series L—(1).

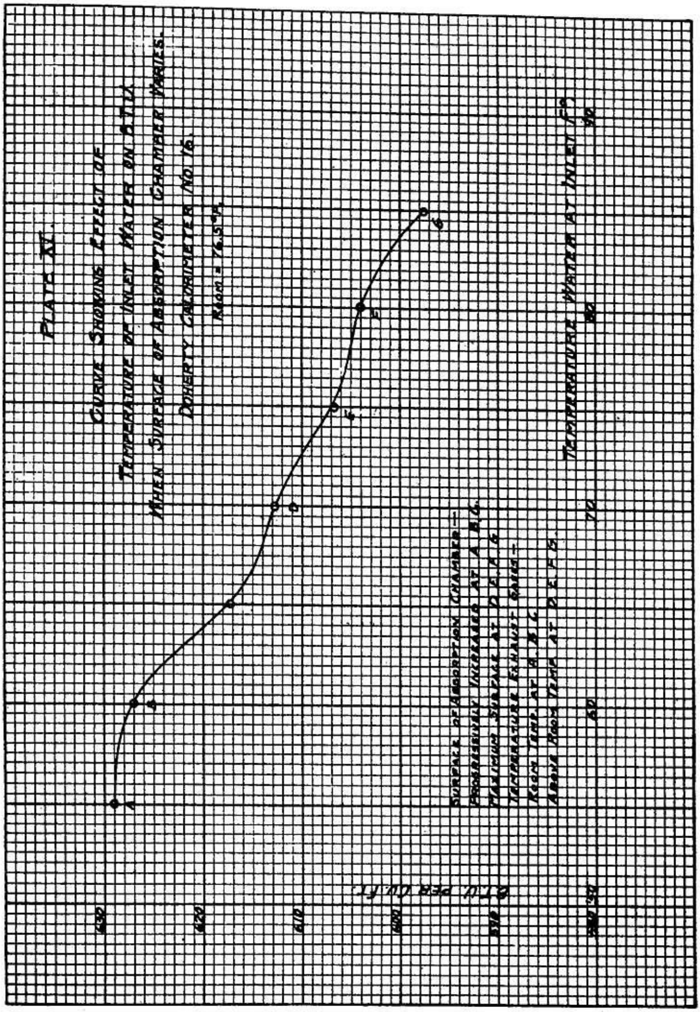
Tem. of inlet water deg.	B. t. u. per cubic foot			Room tem.	Exhaust tem.
	No. 1	No. 2	No. 3		
55	628.2	630.2	629.2	77.3	77.0
60	926.2	627.6	626.9	76.1	76.1
65	617.3	616.6	617.0	76.1	76.1
70	613.1	612.5	612.8	77.3	79.2
75	606.7	606.7	606.7	77.8	82.7
80	604.0	603.4	604.1	78.1	87.2
85	597.6	——	597.6	78.6	93.0

Discussion of Results.

It is of interest to note that for the first three inlet water temperatures the temperatures of the exhaust gases and of the room are identical, yet the heating value of the gas was successively lowered as the temperature of the inlet water was raised. It is not easy to explain this phenomena from the work recorded up to this point, but a subsequent investigation, which will be referred to later, offered a partial explanation. The decrease in heating value of the gas with the other temperatures of inlet water is fairly regular.

Plate XI shows a curve plotted from the data just recorded. The abscissae are temperatures of inlet water, and the ordinates are B. t. u. per cubic foot. About the only conclusion of any value that can be drawn from these results is that the Doherty calorimeter does not give the same heating value of a gas with different temperatures of inlet water, even though the exhaust gases are at the same temperature in all cases. In all subsequent tests the pointer at the top of the calorimeter was so adjusted that the maximum surface in the absorption chamber was exposed.

In order to check the results just reviewed two other tests were made at a later date, after the inlet temperature curve for the Doherty No. 16 had been established. These tests were conducted as follows: With the maximum surface of the absorption chamber exposed, a series of tests was made with the temperature of the inlet water about 20 degrees below room temperature. Then the temperature of the inlet water was lowered about 8 degrees, and the surface of the absorption chamber decreased, by moving the pointer, so that the exhaust gases left the calorimeter at the same temperature as in the first case. Then a second series of determinations was made. The results follow.



FIRST TEST.

Temp. of inlet water deg.	B. t. u. per cubic foot				Room temp.	Exhaust temp.
	No. 1	No. 2	No. 3	Ave.		
54.8	626.6	625.2	623.3	625.0	75.0	66.5
48.5	634.4	633.1	634.4	634.0	75.0	66.5
			SECOND TEST.			
58.4	591.4	592.1	592.1	594.1	71.3	69.0
52.4	600.1	594.9	598.8	598.8	71.5	69.0

Discussion of Results.

The results of these two series confirm the conclusions drawn from the results of Series L—(1). The heating values registered by the Doherty calorimeter increase as the temperature of the inlet water decreases even though the temperature of the exhaust gases remains constant.

The only explanation of the results obtained in this connection seemed to be as follows: Inasmuch as the gas is displaced by water, and is in contact with the water for about 20 minutes, it is reasonable to suppose that there may be some absorption of carbon dioxide from the gas during a test, for carbon dioxide is the most soluble in water of any of the constituents of ordinary illuminating gas. It is also a well known fact that the solubility of carbon dioxide in water is greater the lower the temperature of the water. Therefore it was thought that the higher values obtained with the colder water might be explained in part by an increased absorption of carbon dioxide from the gas during the test. In order actually to determine the extent to which the carbon dioxide was absorbed from the gas during the performance of a test, a special series of experiments was carried out.

Carbon Dioxide Absorption Tests.

The tests were carried out as follows: The calorimeter tank was filled with gas in the usual way and then the gas expelled in the same manner as when making a test. The gas was burned in the regular burner outside of the combustion chamber. At three different periods the flame was extinguished and the gas sampled as it flowed out of the end of the tube which connected the instrument proper to the burner. The first sample was taken when the water level in the gauge glass reached the first graduation, the second sample was taken when the water level was midway between the first and last graduations, and the third sample was taken when the water level reached the last graduation. The samples were then immediately analyzed for carbon dioxide by the use of potassium hydroxide solution in a Hempel gas pipette. Such tests as just described were carried out with the water displacing the gas at the following temperatures, viz., 45.3, 55.7, 64.0 and 79.9 degrees. Before making any tests the gas was drawn directly through the calorimeter and sampled at the end of the burner tube. Three such samples were taken and analyzed. At the close of the tests another sample was taken in the same way and analyzed for carbon dioxide. The gas used was drawn from the holder previously mentioned. The results follow.

GAS DRAWN DIRECTLY THROUGH CALORIMETER PREVIOUS TO MAKING ABSORPTION TESTS.

Sample number	Carbon dioxide Per cent.
1	3.4
2	3.3
3	3.3

GAS DRAWN DIRECTLY THROUGH CALORIMETER AFTER MAKING ABSORPTION TESTS.

Sample number	Carbon dioxide Per cent.
1	3.1

Per cent.

Average before and after 3.2

Absorption test	Tem. water degrees	Carbon dioxide Sample			
		No. 1 Per cent.	No. 2 Per cent.	No. 3 Per cent.	Ave. Per cent.
No. 1	45.3	3.1	2.9	2.7	2.9
No. 2	55.7	3.1	2.7	2.5	2.8
No. 3	64.0	2.7	2.5	2.6	2.6
No. 4	79.9	2.7	2.5	2.6	2.6

Discussion of Results.

Before discussing these results it should be stated that the gas analyses were performed with a burette which could be read accurately no closer than to 0.1 cubic centimeter. Hence the above analyses can be considered accurate to 0.1 per cent. as 100 cubic centimeters of gas was taken for each analysis. Precautions were taken to prevent errors caused by drafts, incomplete drainage of burette, etc.

The average of the carbon dioxide content of the gas passing directly through the calorimeter before and after the absorption tests was 3.2 per cent. of the total volume of the gas. The percentages of carbon dioxide obtained in the various samples analyzed were all a little lower than the original percentage in the gas. In absorption tests No. 1 and No. 2 a progressive absorption is shown as the gas remains in contact with the water for the more extended periods. This progressive absorption is not shown in tests No. 3 and No. 4. The average percentage of carbon dioxide absorbed is nearly the same in all cases, the results indicating a slightly greater absorption at the higher temperatures. However, as the gas analyses showed that the gas at the close of the experiments contained 0.2 per cent. less carbon dioxide than at the beginning, it is reasonable to suppose that the absorption was constant throughout the range of the tests.

It is seen that the explanation of higher heating values obtained when colder water is used and the exhaust gases held at a constant temperature does not lie in increased carbon dioxide absorption with the colder water. In general it may be said that, considering a gas having a carbon dioxide content of 3.2 per cent., the absorption taking place while making a test will reduce the percentage to 2.7 per cent. That is, the percentage of combustible in the gas is increased by the same amount (0.5 per cent.). Reference to this fact will be made later in the discussion of the efficiency of the Doherty calorimeter.

In the light of the experiments just reviewed it would seem that variations of the surface exposed in the combustion chamber made to neutralize the effect of different temperatures of inlet water introduce a factor which cannot be satisfactorily explained from the present data.

The second series of tests made with different temperatures of inlet water was conducted in the following manner. The pointer at the top of the absorption chamber was set so as to expose the maximum absorption surface in the chamber. The gas was burned at the rate of 1.7 cubic feet per hour. Two determinations were made with each of the following temperatures of inlet water, viz., 40, 50, 60, 70 and 80 degrees. Natural draft was used. Relative humidity of the atmosphere was 25 per cent. The summarized data follows. Complete data given at the close of "Discussion of Results."

SERIES L—(2).

Tem. of inlet water deg.	B. t. u. per cubic foot		
	No. 1	No. 2	Ave.
40	623.2	625.1	624.2
50	609.2	611.2	610.2
60	604.3	601.6	603.0
70	589.8	589.8	589.8
80	576.1	574.7	575.4

Plate XII shows a curve obtained by plotting "temperatures of inlet water" as abscissae against "B. t. u. per cubic foot" as ordinates.

Discussion of Results.

The curve plotted from the results of Series L—(2) and shown in Plate XII is similar to corresponding curves obtained for the Junkers type of calorimeter. The lower the temperature of the inlet water, the higher are the heating values registered by the calorimeter. The curve changes slope slightly over the temperature range of from 50 to 60 degrees, thus indicating a "thermal balance" with this range of temperatures. The change in slope of the curve between the temperatures of 50 degrees and 60 degrees is not so definite as that obtained with the Junkers No. 872.

In view of these facts it would seem that the Doherty calorimeter should be operated with inlet water from 0 degree to 20 degrees below room temperature, depending upon humidity conditions.

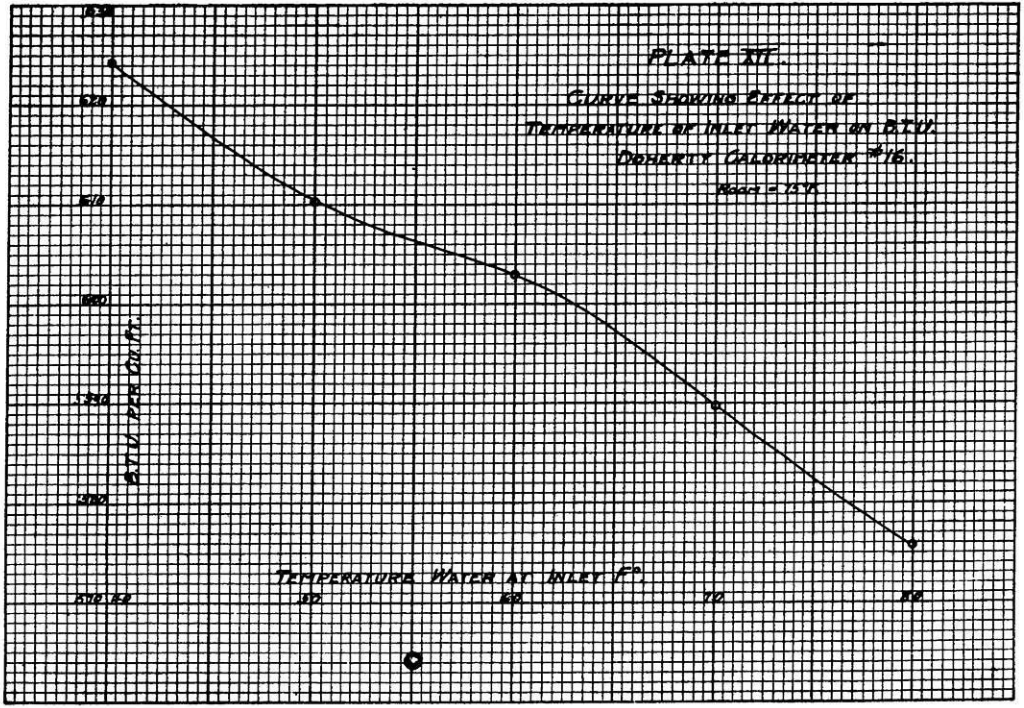


PLATE XII.

CURVE SHOWING EFFECT OF
TEMPERATURE OF INLET WATER ON B.T.U.
DOHERTY CALORIMETER #16.

Room = 75°F.

COMPLETE DATA.

SERIES L—(2).

	Tem. of inlet water			
	40 degrees		50 degrees	
	No. 1	No. 2	No. 1	No. 2
Humidity (air) %	25.0 throughout			
Barometer plus gauge	29.07 throughont			
Gas tem	58.9	59.2	63.9	64.6
Cor factor	0.9714	0.9714	0.9582	0.9582
Room tem	75.1	75.0	75.4	75.1
Exhaust tem	55.9	55.9	62.8	63.2
Inlet tem	40.79	40.85	49.94	50.30
Outlet tem	50.49	50.58	59.30	59.69
Rise	9.70	9.73	9.36	9.39
B. t. u.	623.2	625.1	609.2	611.2
Av. B. t. u.	624.2		610.2	
	60 degrees		70 degrees	
Humidity (air) %	25.0 throughout			
Barometer plus gauge	29.07 throughout			
Gas tem	69.7	70.6	76.6	77.4
Cor factor	0.9426	0.9426	0.9244	0.9244
Room tem	75.5	74.2	75.4	75.5
Exhaust tem	70.4	70.7	78.3	78.4
Inlet tem	60.13	60.22	70.04	69.72
Outlet tem	69.27	69.32	78.80	78.48
Rise	9.14	9.10	8.76	8.76
B. t. u.	604.3	601.6	589.8	589.8
Av. B. t. u.	603.0		589.8	
	80 degrees			
Humidity (air) %	25.0	25.0	—	—
Barometer plus gauge	29.07	29.07	—	—
Gas tem	83.9	85.5	—	—
Cor factor	0.9028	0.9028	—	—
Room tem	74.9	75.0	—	—
Exhaust tem	86.3	86.4	—	—
Inlet tem	80.34	80.27	—	—
Outlet tem	88.71	88.62	—	—
Rise	8.37	8.35	—	—
B. t. u.	576.1	574.7	—	—
Av. B. t. u.	575.4			

(c) EFFICIENCY OF THE DOHERTY CALORIMETER No. 16.

The efficiency of the Doherty Calorimeter was determined by checking it against the Junkers No. 872.

Conditions of Tests.

Both calorimeters were operated with the inlet water ranging from 15 degrees to 20 degrees below room temperature. The rate of flow of gas in the Doherty calorimeter was 1.7 cubic feet per hour, in the Junkers calorimeter 7 cubic feet per hour. The Doherty was operated with natural draft, the air supplied having a humidity of about 26 per cent. The Junkers calorimeter was operated with forced draft, the air supplied having a relative humidity of about 93 per cent. Alternate tests were made with each instrument. The summarized data follows. The complete data is given at the close of the "Discussion of Results."

SERIES M—(1).

	B. t. u. per cubic foot				
Calorimeter	**No. 1**	**No. 2**	**No. 3**	**No. 4**	**Ave.**
Junkers No. 872 ...	594.2	595.6	593.8	594.3	595.4
Doherty No. 16....	590.1	596.2	597.8	594.5	594.7

SERIES M—(2).

Junkers No. 872 ...	599.9	600.8	600.3	601.1	600.5
Doherty No. 16....	600.0	600.0	600.0	596.8	600.0*

*Average No. 1, No. 2 and No. 3.

SERIES M—(3).

Junkers No. 872 ...	606.5	605.8	605.9	—	606.1
Doherty No. 16....	607.1	606.6	605 8	—	606.5

Discussion of Results.

It is seen that, when operated as above stated, the Doherty No. 16 gives the same results as the Junkers No. 872. It must also be remembered that the Junkers calorimeter was operated on air having a relative humidity of a little over 90 per cent. while the Doherty calorimeter was operated on air having a relative humidity of only about 26 per cent.

The results obtained with the Doherty Calorimeter No. 16 seem to indicate that the condensing and absorbing surface was of sufficient capacity to condense all of the water vapor resulting from the combustion of the gas, and that practically no water vapor left the instrument by mechanical entrainment. When operating this instrument with a gas consumption of

1.7 cubic feet per hour, and with the inlet water temperature 20 degrees F. below room temperature, and with an air supply of 26 per cent. humidity, readings were obtained which were of the same magnitude as those obtained with the Junkers No. 872 operated with air which approximated saturation.

If the condensing surface in the Doherty had been similar in capacity to that of the Junkers, it would seem that the temperature of the inlet water in the Doherty would have to be 10 degrees to 15 degrees F. lower than that of the Junkers for the respective humidity conditions named above, to obtain concordant results.

In case the air entering the Doherty calorimeter were practically saturated as it was in the Junkers, it appears that concordant results would be obtained when the temperature of the inlet water to the Doherty approximated that of the room. If the temperature of the inlet water and humidity of the air were the same as in the Junkers, the reading of the Doherty would be from 5 to 6 B. t. u. higher than the Junkers.

Inasmuch as the percentage of carbon dioxide in illuminating gas is moderately constant, the positive error produced by this factor will be fairly constant, being about 0.5 per cent. From the curve shown Plate XII, it is seen that the drop in heating value registered between the inlet temperatures 55 degrees and 60 degrees is six B. t. u.. The average relative humidity of the air in the building where these tests were performed was about 24 per cent. during the winter months, and from 80 per cent. to 90 per cent. during the summer months. Thus, changes in humidity occurring at different periods of the year would cause a maximum variation in the heating values of about 6 B. t. u. Assuming a gas having a heating value of 600 B. t. u. per cubic foot, it is seen that the change in the heating value caused by resultant effect of humidity and carbon dioxide absorption will vary from about —4 B. t. u. in the winter to approximately +2 B. t. u. in the summer. Therefore, the temperature of the inlet water should be varied at different seasons of the year so as to counteract

COMPLETE DATA.

SERIES M—(1).

	Junkers No. 872				Doherty No. 16			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	93.0	93.0	93.0	93.0	27.9	27.9	27.9	27.9
Barometer	29.43	29.43	29.43	29.43	29.47	29.47	29.47	29.47
Gas tem	75.2	75.2	75.2	75.3	70.1	68.3	67.5	67.8
Cor. factor.....	0.9413 for Junkers				0.9626 for Doherty			
State of meter %	1.68 fast throughout				—	—	—	—
Cor. gas vol....	0.1851 throughout				—	—	—	—
Room tem.....	74.6	74.7	75.3	75.4	75.5	75.3	75.3	75.2
Exhaust tem...	61.5	61.3	61.4	61.5	68.0	67.0	67.0	66.8
Inlet tem	55.06	55.08	55.15	55.23	55.56	55.35	55.53	55.59
Outlet tem.....	70.29	70.36	70.38	70.48	64.67	64.57	64.87	64.28
Rise	15.23	15.28	15.23	15.25	9.11	9.22	9.23	9.18
Wt. water......	7.222	7.215	7.217	7.213	—	—	—	—
B. t. u.	594.2	595.6	593.8	594.3	590.1	596.2	597.8	594.5
Av. B. t. u.....	594.5				594.7			

SERIES M—(2).

	Junkers No. 872				Doherty No. 16			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	93.6	93.6	93.6	93.6	26.9	26.9	26.9	26.9
Barometer	29.31	29.32	29.31	29.31	29.28	29.28	29.28	29.28
Gas tem........	75.6	75.4	75.2	75.1	73.8	71.1	71.1	70.5
Cor. factor.....	0.9368 throughout				0.9472 throughout			
State of meter %	1.44 fast throughout				—	—	—	—
Cor. gas vol....	0.1847 throughout				—	—	—	—
Room tem......	74.5	75.0	75.5	76.0	75.6	75.0	76.0	75.2
Exhaust tem...	65.7	65.5	65.5	65.4	71.9	70.6	71.0	70.4
Inlet tem	59.87	59.81	59.83	59.78	60.06	59.52	59.95	59.69
Outlet tem.....	75.40	75.38	75.34	75.27	69.18	68.64	69.07	68.76
Rise	15.53	15.57	15.51	15.49	9.12	9.12	9.12	9.07
Wt. water......	7.135	7.127	7.149	7.168	—	—	—	—
B. t. u.	599.9	600.8	600.3	601.1	600.0	600.0	600.0	596.8
Av. B. t. u.....	600.5				599.2			

SERIES M—(3).

	Junkers No. 872				Doherty No. 16			
	No. 1	No. 2	No. 3	No. 4	No. 1	No. 2	No. 3	No. 4
Humidity (air) %	90.4	90.4	90.4	—	25.3	25.3	25.3	—
Barometer	29.26	29.26	29.26	—	29.23	29.23	29.23	—
Gas tem.......	73.7	73.7	73.7	—	72.1	70.7	70.2	—
Cor. factor.....	0.9397 throughout				0.9454 throughout			
State of meter %	0.74 fast throughout				—	—	—	—
Cor. gas vol....	0.1865 throughout				—	—	—	—
Room tem	75.0	75.1	75.3	—	76.0	75.6	75.2	—
Exhaust tem...	66.1	66.2	66.2	—	70.6	70.3	70.0	—
Inlet tem.......	59.91	60.01	60.26	—	59.77	60.08	59.36	—
Outlet tem.....	75.44	75.59	75.49	—	68.98	69.28	68.55	—
Rise...........	15.53	15.52	15.50	—	9.21	9.20	9.19	—
Wt. water	7.274	7.280	7.290	—	—	—	—	—
B. t. u.........	606.5	605.8	605.9	—	607.1	606.6	605.8	—
Av. B. t. u.....	606.1				606.5			

this influence, bearing in mind that each decrease of 10 per cent. in relative humidity decreases the heating value of a gas averaging 600 B. t. u. per cubic foot by 1 B. t. u.

A series of comparative determinations between the Doherty No. 16 and the Parr No. 4 will be found at the close of the discussion of the Parr calorimeter.

Further Observations.

Occasionally, when operating the Doherty calorimeter, air would be trapped in the system of pipes so that the pressure would be irregular. Whenever the pressure on the gas in the instrument is not constant, the readings of the outlet thermometer are subject to serious fluctuations. These fluctuations may be sufficiently serious to vitiate the results of the determination, and whenever such conditions prevail no determination should be recorded until the air is dislodged and constant pressure obtained. With constant pressure the results obtained with the Doherty calorimeter agreed among themselves and with those of the Junkers No. 872 in a very satisfactory manner. Air trapped in the instrument can many times be liberated by means of the vent cock provided for such an emergency. This cock is located at the top and towards the back of the instrument. In some cases, however, it was necessary to drain the instrument and then refill it before constant pressure was obtained.

The trouble just mentioned was not encountered very often, and in general the operation of the Doherty calorimeter was satisfactory. The results of a series of comparative determinations which were vitiated by the trouble just discussed are tabulated below.

	B. t. u. per cubic foot		
Calorimeter	No. 1	No. 2	No. 3
Junkers No. 872..........	611.4	611.4	611.1
Doherty No. 16..........	619.6	616.3	603.1

The results need no discussion. The constant Junkers values show that the trouble did not lie in a gas of uneven heating value.

Another point may be mentioned here. On two occasions after allowing the Doherty calorimeter to stand idle for a few weeks, it was found that the passage of gas from the main to the tank was extremely slow in one instance and completely obstructed in another. Evidently the passageway had become clogged from deposition of material from the gas. The obstruction was easily removed by applying suction from a vacuum pump to the small pipe provided for delivery of the gas to the burner. If it was necessary to operate the calorimeter on a very dirty gas this trouble would, in all probability, be aggravated.

The combustion of the gas in the Doherty calorimeter was found to be perfect. A typical analysis of the exhaust gases is as follows:

Constituent	Per cent.
CO_2	8.0
O_2	9.0
CO	0.0
N_2	83.0

The effect of baffle plates on the burner stem was found to be inappreciable.

The time required for the performance of a complete test is twenty minutes. The instrument can be purged by allowing the gas to be tested to pass directly through the instrument—having the tank nearly full of water—and allowing the gas to burn outside of the calorimeter. The purging operation can thus be accomplished while the operator is engaged with other work.

The screen through which the water passes as it enters the "regulator" is rather coarse, and is soldered in position. It would be desirable to use a finer screen, and make the screen removable, thus permitting the meshes to be freed from solid matter.

A hook is provided on the front of the instrument from which the thermometer used to register room temperature is supposed to be hung. If such a thermometer is hung as designated, it will be affected somewhat by the bodily warmth of the operator. Therefore it is desirable to hang this thermometer at a short distance from the calorimeter.

The glass U-tube of the pressure gauge is cemented to the metal cap by means of plaster of Paris. When new, this joint holds satisfactorily, but if moistened a few times by accident or otherwise, it leaks gas and causes low heating values to be registered by the calorimeter. The use of a water-proof cement and the elimination of one or two joints would be advisable.

General Summary of the Investigations of the Doherty Calorimeter No. 16.

The results of the investigations of the Doherty calorimeter No. 16 may be summarized as follows:

(1) The gas burned does not have to be metered, hence errors resulting from improper measurement of the gas volume are avoided.

(2) The heated water is neither weighed or measured, hence errors arising from either of these conditions are obviated.

(3) The proper pressure to be maintained on the gas in the tank is two inches of water. This gives a rate of flow of gas of 1.7 cubic feet per hour.

(4) The calorimeter should be operated with water, the temperature of which should be from 0 to 20 degrees below that of the room, depending upon humidity conditions. For a detailed discussion of this point the reader is referred to the "Discussion of Results" under the heading "Efficiency of the Doherty Calorimeter."

(5) The efficiency of the instrument, when operated as indicated in (3) and (4) is the same as that of the Junkers No. 872. For detailed statement see "Efficiency of the Doherty Calorimeter."

(6) There is sufficient condensing and absorbing surface so that no water vapor is carried out of the calorimeter by mechanical entrainment in the products of combustion when

the temperature of the inlet water is regulated to suit the conditions of humidity.

(7) Unsteady operation is sometimes caused by the trapping of air in the system of pipes within the calorimeter. When such conditions prevail, no determinations should be attempted until the trouble has been removed.

(8) Occasionally the passage of the gas into the tank is obstructed by an accumulation of solid matter. This is particularly the case if the instrument is allowed to stand idle for a time after having been in use for several weeks.

(9) Variations in the temperature of the inlet water are noted fairly quickly by the outlet thermometer, but not quite as quickly as is the case with the old style Junkers.

(10) The time required for making a determination is twenty minutes.

(11) Baffle plates used on the stem of the Bunsen burner exerted no appreciable effect.

(12) Changes in the amount of surface exposed in the absorption chamber introduce complications which are not easily explainable. It is recommended that the calorimeter be always operated with the maximum surface of the absorption chamber exposed to the products of combustion.

(13) Check determinations agree satisfactorily.

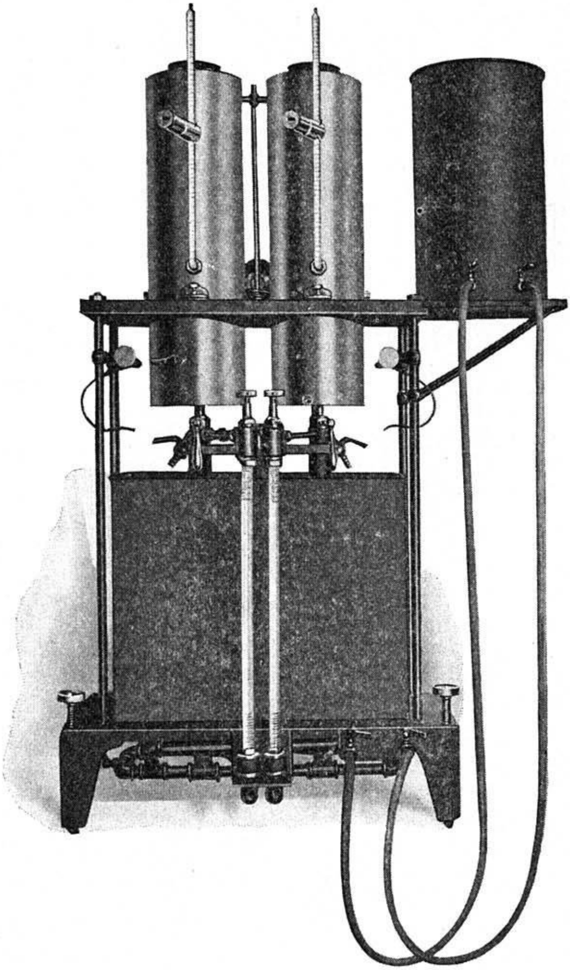
(14) The rise in temperature of the water as it passes through the calorimeter is about 9.5 degrees F. Therefore any error in reading the temperatures will cause a somewhat greater percentage error in the results than is the case with the Junkers calorimeter, in which the water is heated through a temperature interval of from 15 to 16 degrees F.

(15) When operating on average illuminating gas, an absorption of 0.5 per cent. of carbon dioxide occurs during the progress of a test.

(16) A calorimeter case is provided for the instrument, and the calorimeter can be operated while in position within the cabinet. Thus the instrument is easily protected from dust and fumes.

(17) The calorimeter is easily portable, and does not have to be taken apart for shipment.

(18) The mechanical construction of the pressure gauge should be improved.

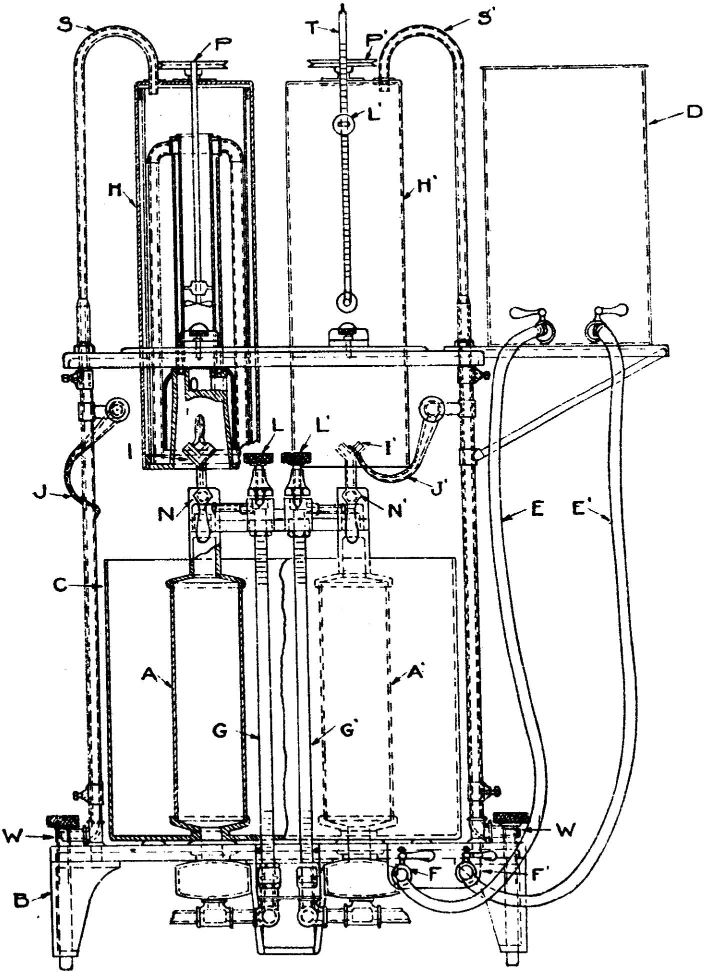


Parr gas calorimeter.

(5) THE PARR CALORIMETER.

The Parr gas calorimeter used in this investigation was loaned by the Standard Calorimeter Company of East Moline, Illinois. A front view of the instrument is shown on the preceding page, and Plate XIII shows the cross section. As

PLATE XIII



SECTION OF PARR CALORIMETER

the calorimeter differs from all others in almost every respect, a detailed description will be given.

Description of the Calorimeter.

The cross section of the instrument shown in Plate XIII was copied from a similar view given in a pamphlet issued by The Standard Calorimeter Co. The description of the instrument is taken largely from a description given by Professor Parr in the *Journal of Industrial Engineering Chemistry,* Volume 2, Number 8, Page 357.

In the Parr calorimeter two parallel systems are so arranged that equal volumes of gases may be taken and placed under equivalent conditions of temperature and pressure, being submerged in the same vessel of water, (C) The pressure is obtained from water in the gravity tank (D) which is connected by rubber tubing (E) and (E′) and iron piping to the gas tanks (A) and (A′) The heater tanks (H) and (H′) containing equal amounts of water, are arranged with burners, conduits and stirrers devised to extract the heat. The rise in temperature is indicated on Fahrenheit thermometers (T) and (T′) which pass into the heater through gaskets. It will be seen that the rise in temperature of the two systems will be in proportion to the heat liberated in each. If, therefore in one of the systems a standard gas, such as hydrogen, be employed, and its heating value be taken as standard at 60 degrees F. and 30 inches of mercury, then the heating value of the hydrogen will be to the heating value of the unknown gas, at the same condition as to temperature and pressure, as the ratio of the indicated rise in temperature of the two thermometers. The details of the apparatus are carried out with reference to this principle. The stirring of the water is effected by a small motor, located just behind the heaters (H) and (H′) and on a level with the gravity tank (D). A common belt actuates the two pulleys (P) and (P′), with turbines arranged on the interior of the heaters. The heaters are connected with automatic overflows at the rear, which can be adjusted to measure equal amounts of water.

Provision is made for measuring the volumes of the gases with accuracy by reducing the area of the containing vessels above and below so that the starting and stopping points may be accurately indicated on the glass gauges (G) and (G′) on the front of the instrument.

Swinging pilot lights (J) and (J′) are provided at the left and right for simultaneous ignition of the burners.

The gas holders (A) and (A′) are cylinders, 7.5 cm. x 255 cm.,! reducing above and below to a neck of 2.5 cm. in diameter and holding approximately 1½ liters. They are submerged in the large square tank (C) which rests on the base (B) of the instrument.

Seven to nine minutes are required for burning out the contents of the gas cylinders. The needle valves (N) and (N′) are finely adjusted so that the water levels on the glass gauges (G) and (G′) may be made to stop at any desired graduation. Corresponding graduations on the two gauges represent exact equivalents of gases. Before beginning a test the water levels in the gauges are brought to corresponding marks by means of the needle valves (L) and (L′). It is not necessary to know the exact volumes in some definite unit, since it is only essential to have equivalent quantities. Since these quantities are subjected to the same temperature and pressure, the operation is independent of barometric conditions and room temperature. The operation is also independent of the relative humidity of the atmosphere, provided the same amount of water is generated by the combustion of each gas. The only condition, therefore, not covered by the above provisions is the matter of radiation. For this element in the case, advantage is taken of the fact that the heating value of hydrogen—325 B. t. u. per cubic foot at 60 degrees F. and 30 inches of mercury—is about half the heating value of ordinary municipal gas. Hence, by installing a double cylinder, or rather a third cylinder, not shown in the cut, with exactly equal volume with the other two gas containers and cross-connecting the same in such a way as to make it possible to burn two volumes on one side against one volume on the other, almost exactly equivalent quantities of heat are discharged under each heater. Thus the radiation will be practically the same in both systems.

It will be evident also, that, for some types of gas, having approximately 300 to 350 B. t. u. per cubic foot with hydrogen as the standard of comparison, equal volumes of each would be taken, while for lower grades of material of say 100 to 150 heat units, the reverse of the first condition would be called for and two volumes of the unknown gas would be burned against one volume of hydrogen.

The hydrogen used with the Parr calorimeter is generated from an alloy of sodium and lead sold under the name of "Hydrone." The gas is generated in a simple generator operating on the Kipp principle. When the "Hydrone" is brought into contact with water a copious evolution of hydrogen occurs, and the quality of the gas is high.

Operation of the Calorimeter.

See that the gravity tank is nearly full of water which should be saturated with gas of the same kind as is to be tested. Admit water to the gas holder, release the air in the cylinders through the inlet cocks on either side. These cocks are set at an angle slightly to the rear and downwardly, on either side, connecting directly with each of the front cylinders. Fill completely with water until the same flows from the inlet cocks. By a rubber hose the right hand cock is connected with the gas supply and the left hand cock with the hydrogen generator.

The cylinders are filled with gas by lowering the gravity tank and opening the inlet cocks. The gas is allowed to flow in until the level as shown on the glass gauges disappears at the bottom. A little more gas is then allowed to run in, then the inlet cocks are closed and the gravity tank elevated to its place. A sufficient surplus of gas is thus admitted so the level will not yet appear on the gauges. The water levels are then brought into the glasses and adjusted to the same level by opening the vents at the top of the gauges. The heaters are filled with tap water to the point of overflow and allowed to drain by means of the automatic siphon discharges.

The motor is now started, the belt being so placed as to turn the pulleys to the right or as the hands of a watch, thus causing the central column of water to rise.

When equalization of temperature has been obtained the reading of each thermometer is taken and the gas at the burners lighted. This is accomplished by having a small flame adjusted at the tip of each of the swinging pilot lights, turning each to place and at once turning open the needle valves to the burners. The relative rates of flow should be kept approximately the same, and the rate of combustion so gauged that the complete discharge of the gas is accomplished in from 7 to 9 minutes.

At the close of the test one is allowed to complete the discharge at little ahead of the other. The needle valve is closed when the water level reaches any desired mark, the other system slowed down as it approaches the end and finally shut off at the same gauge mark as the first system.

After permitting an equalization of temperatures the thermometers are read as at first. If ordinary municipal gas of 600 to 700 B. t. u. is being tested, the rise in temperature on the right hand side will be from 4 to 6 degrees. The rise in temperature for one tank of hydrogen will be from 2.00 to 2.75 degrees. Hence two measures of hydrogen should be taken. This is accomplished by having the cross-connecting cocks open above and beneath the base.

It is well to have the temperatures in the two heaters somewhat near together at the start and 3 to 4 degrees lower than that of the room. In this way the equalization of the temperature in each heater after turning off the gas is not materially affected by external radiation.

Calculations.

The calculation is based on the fact that if equal volumes of gas at the same temperature and pressure be made to burn under equal volumes of water, the rise in temperature of the two volumes will be proportional to their heating values.

$$\text{That is, } \frac{(\text{Rise})}{(\text{Rise})}, = \frac{(\text{B t. u.})}{(\text{B. t. u.})}.$$

It is only necessary, therefore, to insert in the above proportion the accepted value for the B. t. u. of hydrogen, and take one-half the indicated rise in temperature for that system where two volumes are employed. For example, the indicated readings for a test are as follows:

ROOM TEMPERATURE, 75° F.

	Hydrogen two volumes	Municipal gas one volume
Initial tem.	70.45	71.20
Final tem.	74.81	75.36
Rise	4.36	4.16
Rise, 1 volume	2.18	

$$X = \frac{4.16 \times 325}{2.18} = 620 \text{ B. t. u. per cubic foot.}$$

In this calculation, the value of Thomsen for hydrogen at 60 degrees F. and 30 inches of mercury is taken as the basis to which the calculation of the municipal gas is made, namely, 325 B. t. u. per cubic foot.

Calibration of the Parr Calorimeter No. 4.

The Parr calorimeter may be calibrated in two ways.

Method I.—The capacity of the gas holders was determined as follows. The holders were filled with distilled water to the same mark on each gauge glass. The lower water cocks were then closed and the rubber tubing removed. Then the water from each tank was drawn off and weighed. The flow of water was stopped so that the water levels on the lower graduations of the gauge glasses were at the same marks. The weights of water obtained from the three tanks were found to be practically equal. The differences in the weights of water obtained were within the limits of experimental error.

The capacity of the heaters was determined as follows. Each heater was filled to the point of overflow with distilled water, and the siphon discharges allowed to drain their limits.

Then the water was drawn off and weighed. The weights were equal to within the limits of experimental error.

Method II.—This method includes the water equivalent of the heaters and was employed several times during the investigation of the Parr calorimeter. Equal volumes of water gas were burned simultaneously under each heater, filled as above described, and the rise in temperature noted on each thermometer. The rise in temperature on each thermometer was practically the same. Representative data follows.

Left hand heater			Right hand heater		
Initial tem.	**Final tem.**	**Rise**	**Initial tem.**	**Final tem.**	**Rise**
72.67	76.91	4.24	72.58	76.81	4.23
72.57	76.82	4.25	72.79	77.03	4.24

In the above case, when equal volumes of the same gas were burned in each system, the heat absorbed was the same and hence radiation is equal in both systems. Hence no particular difficulties were encountered. However, when it was desired to calibrate the instrument by this method so as to take into consideration the volumes of both gas holders of the left hand system, the heat absorbed in the left hand heater was twice as great as that absorbed in the right hand heater, and hence the radiation was greater if the water in both heaters was at the same temperature. In order to overcome this difficulty as far as possible the initial temperature of the water in each heater was so adjusted that it would be as far below room temperature as the final temperature would be above room temperature. Thus the radiation of heat should be just balanced by the absorption of heat. When such conditions prevail, however, the reading of the final temperature is more difficult, as the final temperature is sufficiently far above room temperature to have appreciable radiation effects come in. However, this method seemed the most acceptable and was adopted. A large number of observations were made and the mean of all observations used from which to draw conclusions. A series of observations taken just before the comparative tests (discussed later) were made are tabulated below. One-half the rise obtained in the left hand heater under these conditions should be equal to the rise obtained in the right hand heater.

Left hand heater				Right hand heater		
Initial tem.	Final tem.	½ Rise	Date	Initial tem.	Final tem	Rise
72.10	80.48	4.19	2/14/12	73.75	77.93	4.18
72.10	80.49	4.195	2/14/12	74.14	78.32	4.18
71.82	80.23	4.205	2/14/12	74.00	78.19	4.19
71.67	80.09	4.21	2/14/12	73.85	78.03	4.18
72.26	80.62	4.18	2/15/12	74.11	78.26	4.15
71.94	80.32	4.185	2/15/12	73.72	77.91	4.19
71.78	80.15	4.185	2/15/12	73.86	78.07	4.21
71.82	80.27	4.225	2/15/12	73.97	78.23	4.26
72.05	80.38	4.16	2/15/12	74.04	78.24	4.20
72.27	80.85	4.29	2/20/12	73.94	78.18	4.24
71.81	80.44	4.315	2/20/12	73.79	78.08	4.29
71.83	80.44	3.305	2/20/12	73.88	78.14	4.26
72.11	80.65	4.27	2/20/12	74.05	78.31	4.26
	Ave.	4.22				4.21

It is thus seen that the difference between the two average elevations of temperature is only 0.01 degree F. when the same elevations in each system are compared. When an actual determination is being made the rise in each system is approximately the same, and only one half rise of the left hand system is compared with that of the right hand system. Therefore when an actual determination is being made, the value for the left hand system which is used in the calculation is only 0.005 degree F. too high. As this value is within experimental error in reading the thermometers, both systems were considered to be equivalent.

Radiation Tests.

In order to determine the rapidity with which heat is radiated from or absorbed by the heaters several radiation tests were made. The data from two characteristic tests are tabulated below.

Radiation Test No. 1.

The heaters were filled with water about four degrees below room temperature, the motors started, equalization of temperatures in the heaters allowed to take place, and then the temperatures registered by both thermometers were read. The stirrers were allowed to run continuously and at the end of a half hour the temperatures were again read. The data follow.

Room tem. { Beginning.. 77.0
End ...... 76.0 Ave. 76.5

Left hand heater			Right hand heater		
Initial tem.	Final tem.	Rise	Initial tem.	Final tem.	Rise
72.60	72.87	0.27	72.58	72.89	0.31

Radiation Test No. 2.

The water heaters were filled with water about four degrees above room temperature, the motors started, and after equalization of temperatures had occurred the thermometers were read. After a period of 40 minutes had elapsed the temperatures were again read. The data follow.

Room tem. { Beginning.. 77.0
End .... 76.0 Ave. 76.5

Left hand heater			Right hand heater		
Initial tem.	Final tem.	Fall	Initial tem.	Final tem.	Fall
79.51	78.86	0.65	79.53	78.90	0.63

It is thus seen that heat interchange between the room atmosphere and the water in the heaters is fairly rapid. Therefore, when operating the Parr calorimeter it is very essential that the instrument be carefully guarded from drafts, and that very nearly the same amounts of heat be absorbed during the same time interval in each heater.

Purity of the Standard Gas.

Several samples of hydrogen were prepared and used for preliminary tests before any comparative determinations were made with the Parr No. 4 and other calorimeters. A number of these samples were analyzed.

After freshly charging the generator with "hydrone" it is necessary to allow considerable of the hydrogen gas to escape in order to purge the generator from all foreign gas. Inasmuch as illuminating gas is used to displace the air in the generator—in order to avoid an explosive mixture of hydrogen and air—the hydrogen was first tested for the ordinary constituents of illuminating gas. The first test made gave the following results.

Test No. 1.

Constituent	Per cent.
CO_2	0.0
Ill.	1.1
O_2	0.8
CO	0.6

A moderate amount of hydrogen—(2 to 2½ liters)—was allowed to escape before this analysis was made. It is very evident that a considerable residue of illuminating gas remained unexpelled.

A second partial analysis was made after the generator had been freshly charged at another time. Before making this analysis a large amount of the hydrogen—(5 to 6 liters)—was allowed to go to waste so as to be certain that all of the illuminating gas had ben displaced. The tests for ordinary constituents of illuminating gas gave the following results:

Test No. 2.

Constituent	Per cent.
CO_2	0.0
Ill.	0.0
C_2	0.0
CO	0.0

It would seem therefore that 5 or 6 liters of the hydrogen should be allowed to escape before the illuminating gas is fully displaced.

Having determined about how much gas must be wasted before it is free from illuminating gas impurities, a direct determination of the hydrogen was carried out. The hydrogen was determined by the "palladium black" method. Tests No. 3 and No. 4 are typical of the character of the hydrogen used in the work which will be discussed later. Hydrogen alone was determined in Test No. 3.

Test No. 3.

Constituent	Per cent.
H_2	100.0

Test No. 4.

Constituent	Per cent.
CO_2	0.0
Ill.	0.0
O_2	0.0
CO	0.0
H_2	100.0

From the tests recorded above it would seem that, if a sufficiently large quantity of the newly prepared hydrogen is allowed to escape, the quality of the gas is entirely satisfactory.

Observations from Preliminary Tests.

A large number of preliminary tests were made with the Parr calorimeter before it was checked against the Junkers No. 872. This was thought to be necessary in order to acquire skill in the operation of the Parr instrument. The operation of this calorimeter is so radically different from other types that it would hardly be fair to compare results obtained with it, after operating it only a few times, with the results obtained with a calorimeter with which the operator had made a large number of determinations.

Several points of manipulation were noted during these preliminary tests which may well be mentioned at this place.

It is highly desirable to follow the directions explicitly with regard to the relation between the final temperature of the water in the heaters and room temperature. These temperatures should be the same. This is necessary for it sometimes takes over a minute for a complete equalization of temperatures to take place within the heaters. The final temperature cannot be read with certainty unless there is practically no exchange of heat between the water in the heaters and the atmosphere of the room.

At the end of a test it was found desirable to stop the water levels in the gauge glasses at the first graduation at the top of the glasses. If the meniscus is allowed to go past the first graduation it quickly enters the constricted portion of the gas tank, and hence its speed is greatly increased, and consequently it is much more difficult to stop the meniscus at the desired point. If the gas is shut off when the water levels reach the first graduation at the top of the gauge glasses no difficulty is experienced in properly controlling the gas volumes. If the water level is allowed to pass slightly beyond the first graduation, say one-fifth of a division, no serious error is introduced, because the volumes of the gas tanks are considerably diminished at this point.

At the beginning of a determination, and after the water levels in the gauge glasses have been brought into view it is desirable to wait a few moments before making the final adjustment of the water levels. Otherwise conditions of pressure may not have become entirely constant.

The graduations on the thermometers furnished with the instrument are so coarse, that it is difficult to get a close reading if the head of the mercury column happens to be directly back of a graduation line.

Considerable hydrogen is wasted by the generator. The storage chamber of the generator is not sufficiently large to hold all of the hydrogen generated at times, even if care is exercised in allowing the water to come in contact with the "hydrone" gradually. A somewhat larger storage chamber would seem to be desirable. However, this trouble could be partially remedied in the case of this particular generator, by employing a spring sufficiently strong to hold the charge of "hydrone" well up into the top of the storage chamber. The spring in the generator used in these investigations was so weak that the charge of "hydrone" would settle down into the lower part of the storage chamber. Hence the available storage capacity for the generated gas was limited, and the amount of hydrogen which must be wasted in order to displace the illuminating gas was increased.

The use of two generators would eliminate one rather annoying feature accompanying the continued operation of this instrument. It is impossible to tell just when the supply of hydrogen will be exhausted, and it sometimes occurs that, when it is desired to make a test one finds no hydrogen or else an insufficient supply. Then before a test can be made, it is necessary to clean out the generator and charge it anew. Then hydrogen must be allowed to escape for a time until all the illuminating gas is displaced. All of this recharging operation takes time, and such delays are at times very annoying. If two generators were furnished with the instrument, one could always be kept in condition for use. Both generators could be kept in connection with the calorimeter, and by means of a three-way cock it would be very easy to switch over to a freshly charged generator when one becomes depleted. The exhausted generator could then be recharged at leisure and no delay would be caused in the determination.

Comparative Tests. Junkers No. 872 and Parr No. 4.

Observing the proper conditions of operation as determined in the work previously described three series of comparative determinations were made between the Junkers No. 872 and the Parr No. 4. The exact conditions of operation for the Junkers instrument are indicated in the tabulated data given at the close of this discussion. Alternate tests were made with each instrument. Let it be remembered, however, that air having a relative humidity of over 90 per cent. was supplied to the Junkers instrument, while the Parr calorimeter operated on air having a relative humidity of about 25 per cent. The summarized data follow; the complete data are given at the close of the "Discussion of Results."

SERIES N—(1).

Calorimeter	B. t. u. per cubic foot No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	Ave.
Junkers No. 872	608.6	602.0	599.9	601.4	—	—	603.0
Ave. of Nos. 2, 3, and 4							601.1
Parr No. 4	599.2	598.3	601.5	604.2	—	—	600.8
SERIES N—(2).							
Junkers No. 872	596.0	594.9	594.6	594.8	593.4	592.6	594.4
Parr No. 4	597.4	598.8	597.1	594.2	590.3	591.2	594.8
SERIES N—(3).							
Junkers No. 872	607.2	606.6	604.2	601.3	603.0	—	604.5
Parr No. 4	612.7	607.2	597.4	597.3	597.7	—	602.5

Discussion of Results.

The results just tabulated show very conclusively that under the proper working conditions for each instrument, the efficiency of both calorimeters is the same. To obtain this efficiency with the Junkers calorimeter it must be borne in mind that the air supplied to this instrument must be practically saturated with moisture. If the moisture produced by the combustion of both gases burned is nearly the same conditions of relative humidity of the atmosphere do not affect the results of the Parr calorimeter.

COMPLETE DATA.

SERIES N.—(1).

	Junkers No. 872					
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Humidity (air) %	90.9 throughout					
Barometer	29.18	29.14	29.14	29.14	—	—
Gas tem	77.7	76.9	76.8	76.8	—	—
Cor. factor	0.9261	0.9273	0.9273	0.9273	—	—
State of meter %	2.44 F.	1.98 F.	1.98 F.	1.98 F.	—	
Cor. gas vol	0.1807	0.1818	0.1818	0.1818	—	—
Room tem	75.4	75.8	74.7	75.2	—	—
Exhaust tem	64.7	64.6	64.5	64.6	—	—
Inlet tem	55.24	55.02	55.00	55.09	—	—
Outlet tem	70.53	70.46	70.41	70.49	—	—
Rise	15.29	15.44	15.41	15.40	—	—
Wt. water	7.193	7.082	7.077	7.100	—	—
B. t. u.	608.6	602.0	599.9	601.4	—	—
Av. B. t. u		603.0				
		Parr No. 4				
Hydrogen heater						
Initial tem.	69.32	73.10	72.83	72.80	—	—
Final tem.	73.93	77.63	77.39	77.34	—	—
½ rise	2.305	2.265	2.28	2.27	—	—
Gas heater						
Initial tem	69.18	73.13	72.83	72.73	—	—
Final tem	73.43	77.30	77.05	76.95	—	—
Rise	4.25	4.17	4.22	4.22	—	—
B. t. u	599.2	598.3	601.5	604.2	—	—
Av. B. t. u		600.8				

SERIES N—(2).

	Junkers No. 872					
Humidity (air) %	93.5 throughout					
Barometer	29.02	29.02	29.02	29.02	28.98	28.98
Gas tem.	77.0	77.0	76.4	76.6	76.7	76.9
Cor factor	0.9234	0.9234	0.9234	0.9234	0.9221	0.9221
State of meter %	2.12 fast throughout					
Cor. gas vol.	0.1808	0.1808	0.1808	0.1808	0.1805	0.1805
Room tem	75.1	75.4	74.4	75.6	74.4	75.0
Exhaust tem	60.0	62.2	62.0	62.0	62.4	61.8
Inlet tem	55.35	55.38	55.26	55.34	55.24	55.27
Outlet tem	70.66	70.72	70.47	70.57	70.36	70.35
Rise	15.31	15.34	15.21	15.23	15.12	15.08
Wt. water	7.038	7.012	7.068	7.061	7.084	7.093
B. t. u.	596.0	594.9	594.6	594.8	593.4	592.6
Av. B. t. u.			594.4			

SERIES N—(2).—(Continued.)

Parr No. 4

Hydrogen heater						
Initial tem.	70.20	70.54	70.31	69.60	70.42	70.54
Final tem.	74.77	75.11	74.86	74.14	74.99	75.07
½ Rise	2.285	2.285	2.275	2.270	2.285	2.265
Gas heater						
Initial tem.	70.14	70.52	70.29	69.62	70.37	70.49
Final tem.	74.34	74.73	74.47	73.77	74.52	74.61
Rise	4.20	4.21	4.18	4.15	4.15	4.12
B. t. u.	597.4	598.8	597.1	594.2	590.3	591.2
Av. B. t. u			594.8			

SERIES N—(3).

Junkers No. 872

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Humidity (air) %	92.9 throughout					
Barometer	29.25 throughout					
Gas tem.	77.1	77.0	77.5	77.2	77.5	—
Cor. factor	0.9294 throughout					
State of meter %	2.2 fast throughout					
Cor. gas vol.	0.1818 throughout					
Room tem.	74.8	74.7	75 9	75.0	75.0	—
Exhaust tem. ...	62.2	62.2	62.4	62.2	62.2	—
Inlet tem.	55.15	55.13	55.48	55.51	55.57	—
Outlet tem.	70.42	70.43	70.64	70.66	70.72	—
Rise	15.27	15.30	15.16	15.15	15.15	—
Wt. water	7.229	7.208	7.246	7.216	7.236	—
B. t. u.	607.2	606.6	604.2	601.3	603.0	—
Av. B. t. u.			604.5			

Parr No. 4

Hydrogen heater						
Initial tem.	70.31	71.21	71.27	71.59	72.32	—
Final tem.	74.84	75.77	75.84	76.15	76.92	—
½ Rise	2.265	2.28	2.285	2.28	2.30	—
Gas heater						
Initial tem.	70.25	71.22	71.32	71.38	71.92	—
Final tem.	74.52	75.48	75.52	75.57	76.15	--
Rise	4.27	4.26	4.20	4.19	4.23	—
B. t. u.	612.7	607.2	597.4	597.3	597.7	—
Av. B. t. u.			602.5			

Comparative Tests—Doherty No. 16 and Parr No. 4.

One series of comparative tests was made between the Doherty No. 16 and the Parr No. 4. Each calorimeter was operated on air of the same humidity, and according to the standard directions previously discussed. The summarized data follow and the complete data governing the determinations follow the "Discussion of Results."

SERIES O.

	B. t. u. per cubic foot					
	No. 1	No. 2	No. 3	No. 4	No. 5	Ave.
Doherty No. 16	609.1	610.4	611.7	608.4	610.3	610.3
Parr No. 4	608.8	610.7	609.7	611.8	609.7	610.1

Discussion of Results.

The results just tabulated need very little comment. They show that the Doherty and Parr calorimeters give identical results when operated under proper conditions. This series of tests furnishes a good cross-check upon previous work.

COMPLETE DATA.

SERIES O.

	Doherty No. 16				
	No. 1	No. 2	No. 3	No. 4	No. 5
Humidity (air) %	26.4 throughout				
Barometer	29.05	29.05	28.99	28.99	28.99
Gas tem.	72.5	70.5	71.8	70.3	70.1
Cor. factor	0.9405	0.9405	0.9385	0.9385	0.9385
Room tem.	75.0	75.0	75.3	75.0	75.0
Exhaust tem	70.7	69.6	70.5	69.8	69.3
Inlet tem	59.26	58.71	59.28	58.88	58.32
Outlet tem	68.45	67.92	68.49	68.04	67.51
Rise	9.19	9.21	9.21	9.16	9.19
B. t. u.	609.1	610.4	611.7	608.4	610.3
Av. B. t. u.			610.0		
			Parr No. 4.		
Hydrogen heater					
Initial tem	72.83	71.21	70.52	70.98	71.32
Final tem	77.41	75.83	75.04	75.08	75.84
½ rise	2.29	2.31	2.26	2.30	2.26
Gas heater					
Initial tem	72.85	71.20	70.59	70.64	71.21
Final tem	77.14	75.54	74.83	74.97	75.45
Rise	4.29	4.34	4.24	4.33	4.24
B. t. u.	608.8	610.7	609.7	611.8	609.7
Av. B. t. u.			610.1		

General Summary of the Investigations of the Parr Calorimeter No. 4.

The results of the investigation of the Parr calorimeter may be summarized as follows:

(1) The use of a gas meter is obviated.

(2) The heated water is neither weighed or measured in making a determination.

(3) The calorimeter is of the "still water" type.

(4) The efficiency of the instrument is the same as that of the old style Junkers, the Doherty and the American Meter Co.

(5) The operation of the calorimeter necessitates the preparation of hydrogen as a standard gas. The quality of the hydrogen is satisfactory. There is a little uncertainty as to the heating value of pure hydrogen, but Thomsen's value is the most dependable, and there seems to be no good reason for bringing this value seriously into question.

(6) The mechanical construction of the hydrogen generator might be somewhat improved.

(7) The use of two generators would avoid annoying delays.

(8) Two methods are available for calibrating the instrument. Both methods are satisfactory.

(9) If the same amount of moisture is formed from the combustion of both gases burned in the calorimeter, the relative humidity of the atmosphere exerts no appreciable effect.

(10) Appreciable transfer of heat occurs between the water in the heaters and the surrounding atmosphere. In order to avoid radiation errors it is necessary to have the same amount of heat generated in each system during corresponding intervals of time. The instrument should not be exposed to drafts.

(11) The time required for a complete test is twenty minutes.

(12) The heat generated by the stirring devices is small and is practically the same in both heaters, hence it introduces no error.

(13) At the close of a test it is desirable to stop the water levels at the first upper graduation of the gauge glasses.

(14) No error is caused by the specific heat of the water being other than unity, for the same water is used for the standard gas as for the gas which is tested.

(15) The instrument is heavy and not easily portable.

(16) The graduation marks on the thermometers are so coarse as to make accurate readings impossible if the head of the mercury column happens to be directly behind a graduation mark.

(17) Considering a gas of 600 B. t. u. per cubic foot, an error of 0.02 degree in reading one of the thermometers will cause an error in the heating value of 5 B. t. u. As the rise in temperature is only a little over four degrees the percentage error caused by any error in reading the thermometers is greater than in the case with the other instruments investigated. Also the rise in temperature is determined by readings taken at the beginning and end of a test, not from the average of a number of readings taken during the progress of a test, as is the case with the other instruments to which reference has been made. This fact makes the observed rise in temperature somewhat more difficult to determine with accuracy.

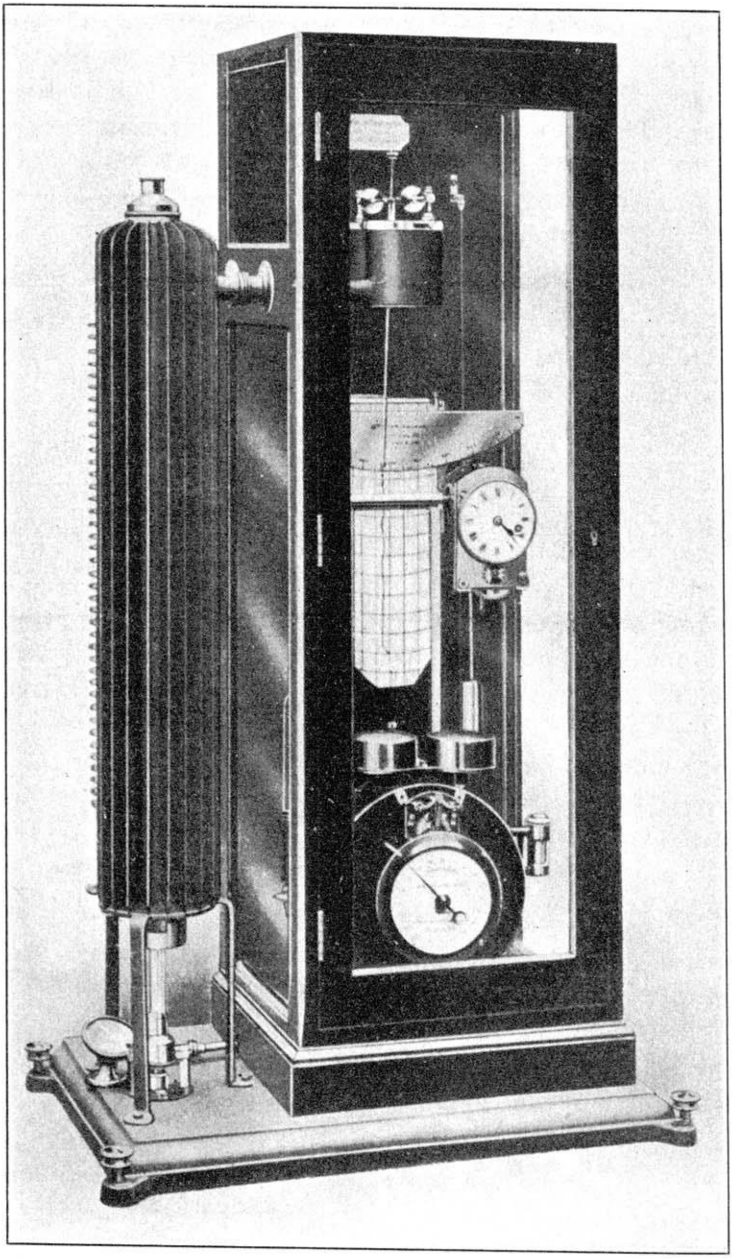
(19) Errors caused by variations in the temperature of inlet water in the case of calorimeters of the flow type are obviated in this instrument. The Parr calorimeter can be satisfactorily operated without the use of an overhead tank for the water supply.

(20) The calorimeter is more complicated in its construction than the other calorimeters investigated, and it appears that it requires some more skill for its proper operation than the other types.

(21) The Parr calorimeter gives "gross" heating values only.

(6) *The "Sarco" or Beasley Recording Calorimeter.*

The Sarco (10) Recording Calorimeter used in this investigation was loaned by the Sarco Engineering Co., of New



"Sarco" recording gas calorimeter.

York City. A view of the instrument is shown on the preceding page. The calorimeter is of the recording type and is entirely different in every particular from the others used in this investigation. It may be well to state in the beginning that the Sarco Calorimeter registers "net" heating values only.

Description of the Calorimeter.

The general form of the calorimeter can be easily seen from the illustration. The gas enters through a cock located on the right hand side and near the base of the calorimeter, passes through the governor which reduces the pressure, then goes to the meter, which is seen at the bottom of the case, and from the meter into the Bunsen burner which can be seen outside and at the left of the case. The burner extends up into what is termed the "hot limb" of the apparatus. This "hot limb" is one arm of a large U-tube, the other arm is almost entirely obscured by the "hot limb," only the edges of its radiation disks being visible. Both ends of the U-tube terminate in float boxes, one of which is seen within and at the top of the case. The other float box is directly back of the one visible.

The principle of the calorimeter may be briefly summarized as follows. The gas is burned within a well radiated chimney, or "hot limb" as it is termed, the products of combustion escaping to the air. Both "limbs" or arms of the U-tube are provided with disks or flanges to promote radiation of heat. The working of the calorimeter depends upon the fact that the average rise in temperature of this chimney is proportional to the heat developed by the flame. This chimney contains an annular chamber, which forms one limb of a U-tube, the other being a simple tube maintained at atmospheric temperature. The U-tube is filled with oil, and as both limbs terminate in tanks, it is possible, by means of floats and suitable pulleys to operate a pointer which records on suitable charts the difference in level between the two limbs of the U-tube caused by the expansion of the oil in the "hot limb." The illustration shows the general design of the instrument, the chimney and the "cold limb" being connected through to tanks which are contained within the case, together with the clock. The clock, by means of suitable gears drives the chart on which the difference in level of the oil in the limbs of the U-tube is recorded. Of course the scale is so arranged and the instrument so calibrated that this difference in level is made to read off B. t. u. (net) per cubic foot.

In a recording gas calorimeter it is obvious that the flow of gas must be automatically maintained at a constant and pre-determined rate if accuracy is to be maintained. To do this, it is first necessary to control the pressure by means of governing apparatus, so that in spite of variations at the inlet of the governor, the pressure at the outlet remains constant. This in itself is not sufficient, if no other method of regulation were provided. The quantity of gas passing is controlled by its pressure and the size of the orifice through which it flows. The rate of flow would consequently vary with the specific gravity of the gas, and render the record of the calorimeter uncertain and misleading. To overcome this difficulty, a special regulating test meter is provided, with the measuring drum geared to a pendulum escapement. The drum of the meter drives this escapement just as the spring of a clock drives the clock, and as the pendulum attached to the clock controls the speed, so the escapement attached to the meter controls the speed of the drum, thus ensuring a constant rate of flow, unaffected by variations in specific gravity, or in fact, any other slight pressure variations in the apparatus.

The pointer operated by the floats indicates on a fixed scale the heating value of the gas and also records the heating value on the chart which is made to fit the scale. The position of the pointer can be adjusted by means of a set screw which secures it to the spindle.

The instrument is calibrated to show the calorific value in British thermal units (net) per cubic foot of gas measured under standard conditions of 60 degrees F. and 30 inches of mercury, and is arranged to burn two (2) cubic feet of gas per hour. The instrument gives its results assuming two (2) cubic feet of gas to be supplied under standard conditions as quoted above and a thermometer is provided on the gas supply, so that the usual corrections may be made for any variation.

No direct determination of heating value is made with this instrument. The proper indication depends entirely upon the proper calibration. It is obvious that the smaller the opening is made through which the products of combustion pass into the air the greater will be the amount of heat absorbed by the oil in the "hot limb." Hence by increasing the size of this opening the calorimeter may be made to read lower, and by decreasing the size of this opening the indications will be higher, and by proper regulation of this factor the instrument may be made to register the proper heating value on the scale and chart. An easy form of adjustment of the size of the opening at the top of the "hot limb" is provided. The necessary alteration may be effected by varying the position of a fairly large screw which extends through the top flange of the "hot limb" and can be made to close the opening partially. The proper position of the screw is indicated by the makers, and this position is marked by filing the threads for a short distance.

Operation of the Calorimeter.

Before operating the calorimeter the pointer should be adjusted to the zero mark, and the water line in the meter adjusted by means of the gauge at the right side of the meter. The gas is then turned on and lighted, and the clock connected to the gear which drives the recording mechanism. The hot limb gradually comes up to a constant temperature, and after twenty to thirty minutes the pointer indicates the heating value of the gas. Of course the indicated heating values must be corrected by reducing the gas volume to standard conditions. The same correction formula may be used as with other instruments.

General Observations.

It was found that when the calorimeter was operated with gas not saturated with moisture, the water line in the meter would change appreciably in the course of three or four days. This was due, of course, to the fact that the unsaturated gas picked up some moisture while passing through the meter. It was found that an error of from 5 to 7 B. t. u. might be introduced from this cause after the calorimeter had been operated for six or seven days, using a gas averaging 550 B. t. u. (net) per cubic foot. It should be noted that these observations were made during cold weather, when the gas as drawn directly from the city mains would have the lowest percentage saturation after entering the building that it would have during any period of the year. This difficulty is largely removed, however, by leading the gas through a "saturation" bottle just before it enters the meter. In all later tests the gas was supplied to the meter in a saturated condition. It was found that the meter underwent no appreciable change during one week of continuous operation. However, it is deemed advisable to check up the water line of the meter and zero reading of the pointer once in seven to ten days, and thus guard against any possible errors resulting from these factors. It was found that the zero reading of the instrument would sometimes change after a period of continued operation so the instrument would give results ranging from 3 to 5 B. t. u. high. If this factor is given attention occasionally no serious error will result.

By means of the glass gauge at the side of the meter it was found that the registrations of the meter could be controlled satisfactorily, but when set according to directions the gas was supplied at the rate of 2.08 cubic feet per hour rather than 2.0 cubic feet per hour as was intended. Therefore slightly more heat was generated in the chimney than was intended, and it would be expected that the screw at the top of the chimney ought to be set so as to make the opening for the escape of the products of combustion a little larger than indicated by the makers. Thus the increased amount of heat generated would be compensated by the increased escape of heat from the chimney. It is well to bear this point in mind during the discussion which follows, as conditions were found to be as above predicted.

Method of Conducting the Tests.

The work on this calorimeter covered a period of time extending from March 1, 1912, to April 26, 1912. During this period the calorimeter was operated under varying conditions and several series of check determinations were made. The instrument was checked against the Junkers No. 872 which was operated upon air having an average relative humidity of 94 per cent., and the water of condensation collected and measured with all necessary precautions.

Before making any check determinations the screw at the top of the "hot limb" or chimney of the "Sarco" calorimeter was adjusted so that the readings of the calorimeter agreed with the net heating values of the Junkers No. 872. The position in which the screw was finally allowed to remain differed from that indicated by the manufacturers by the width of two screw threads, the difference in position being such that the opening was slightly larger than would have been the case if the screw had been in the indicated position. The reason for this slight difference in the adjustment of the screw has already been mentioned.

After making this adjustment the calorimeter was checked against the Junkers No. 872 in the following manner. Each series of tests was begun at about nine o'clock in the morning and extended until about three o'clock in the afternoon. The gas was drawn directly from the city mains, and its heating value (net) determined each hour in the Junkers No. 872. Both the Junkers and the "Sarco" were allowed to operate continuously throughout the series of tests. The readings recorded for the "Sarco" calorimeter were read off from the fixed scale at the time of making the corresponding determination with the Junkers. The graduations on the charts furnished with the instrument did not coincide exactly with those of the fixed scale, hence all readings were taken from the fixed scale.

In checking the "Sarco" calorimeter against such an instrument as the Junkers, the averages of a considerable number of determinations should be compared, for the gas is burned nearly four times as fast in the Junkers as in the "Sarco" and the former will note changes in calorific value of the gas more quickly than will the latter. Hence corresponding readings may vary somewhat, but the average of several determinations should give a reliable basis for comparison.

For the first four weeks the "Sarco" calorimeter was operated each day and was shut down during the night. During the last two weeks the calorimeter was operated continuously day and night.

The summary of the comparative tests between the "Sarco" and the Junkers No. 872 follows.

SERIES P—(1) 3/8/12

Time P. M.	Junkers No. 872	"Sarco"
12:21	554	555
12:28	555	563
12:59	554	557
1:05	555	555
2:05	553	552
2:08	557	552
3:00	548	552
3:05	554	552
Ave.	554	555

SERIES P—(2) 3/9/12

Time A. M.	Junkers No. 872	"Sarco"
9:06	548	560
9:14	550	550
9:59	548	541
10:07	546	541
11:03	538	547
11:10	534	548
P. M.		
12:03	543	550
12:53	548	548
1:52	539	554
1:59	537	555
3:00	552	546
3:08	555	547
3:40	548	548
3:48	554	552
3:54	552	555
4:00	556	554
Ave.	547	549

SERIES P—(3). 3/16/12

Time A. M.	Junkers No. 872	"Sarco"
10:53	528	522
11:04	527	522
11:52	523	518
P. M.		
12:02	522	519
1:01	527	519
1:08	524	519
1:56	525	522
2:04	525	525
2:49	525	529
2:55	525	532
Ave.	525	523

SERIES P—(4). 3/29/12

Time A. M.	Junkers No. 872	"Sarco"
9:08	534	535
9:13	534	535
10:10	531	537
10:16	532	537
P. M.		
12:12	531	533
12:18	533	530
1:10	537	527
1:21	534	526
2:04	538	532
2:15	539	530
2:54	534	529
3:04	535	529
Ave.	534	532

SERIES P—(5). 4/26/12

Time A. M.	Junkers No. 872	"Sarco"
8:50	563	564
8:59	565	565
10:00	566	567
10:08	565	567
P. M.		
12:12	565	561
12:20	566	561
12:53	565	564
1:00	565	563
1:29	560	562
1:37	561	561
2:01	559	566
2:09	558	566
Ave.	563	564

Discussion of Results.

The series of determinations tabulated above show that the agreement between the average values registered by the Junkers No. 872 and the "Sarco" Recording Calorimeter is satisfactory. It is impossible to read the values indicated by the latter instrument closer than two (2) B. t. u. If we consider the Junkers No. 872 as the standard, then the deviations of the average values of the "Sarco" in the five series of tests is as follows, Series P—(1) + 1 B. t. u., Series P—(2) +

2 B. t. u., Series P—(3) — 2 B. t. u., Series P—(4) — 2 B. t. u., Series P—(5) + 1 B. t. u. The average difference for the five series of tests is seen to be zero.

General Summary of the Investigations of the "Sarco" Recording Calorimeter.

The results of the investigations of the "Sarco" Recording Calorimeter may be summarized as follows:

(1) The mechanical construction of the instrument is good.

(2) The instrument is sensitive and will indicate changes in calorific value quickly.

(3) The instrument registers "net" heating values only.

(4) The calorimeter makes a continuous and permanent record of the heating value of the gas.

(5) In order to minimize meter errors, the gas should be saturated with moisture before it enters the instrument.

(6) The calorimeter should be shut down once in every seven to ten days, and the water line of the meter and the zero reading of the pointer checked up.

(7) Inasmuch as no direct measurement of the heating value of the gas is made with this instrument, its values should be checked occassionally by comparison with values obtained by the use of a calorimeter making direct determination.

(8) When the above precautions are observed the instrument gives satisfactory results.

(9) The charts furnished with the instrument did not exactly fit the graduations of the fixed scale. More exact charts should be made.

(10) The oil used in the calorimeter is slowly volatilized. Small additions of oil should be made as needed.

(11) The instrument may be easily made to agree with any desired standard.

(12) The instrument is necessarily rather heavy and is not easily portable.

(13) It is impossible to read the heating value of the gas as indicated on the scale or charts more closely than to within two (2) B. t. u.

(14) The directions for setting up and operating the calorimeter are very meager. The setting up of a new instrument would be much easier if more explicit directions were given. It would seem desirable to furnish a sketch showing the essential parts of the instrument, and to refer to these parts by letter or number in the printed directions.

(7) THE AMERICAN METER CO.'S GAS METER.

Meters manufactured by the American Meter Company were used in the investigations just reviewed. As the meters were carefully calibrated before and after each series of tests, and oftener if any considerable temperature change took place, it was found that the change in calibration of such meters was rather large for even moderate changes in temperature. Therefore it was thought desirable to make a series of tests in order to determine just how much the registrations of such meters are affected by changes in temperature.

Method of Investigation.

A thermometer was inserted in the meter so that the bulb was immersed in the water within the meter. In order to raise the temperature of the water in the meter quickly the following simple apparatus was devised. A box somewhat larger than the meter was lined with asbestos paper. A support was provided for the meter within the box so that when the meter was in place its base was about one third of the distance from the bottom to the top of the box. On the bottom of the box a series of six (6) thirty-two candle-power incandescent lamps was arranged so as to distribute heat evenly over the box. Two holes in the side of the box allowed the passage of tubes which connected the meter to the calibration apparatus. The meter could thus be calibrated without removing it from the box.

The procedure was as follows: The meter was first cooled so that the water it contained was a a little below 60 degrees F. Then the meter was placed in position in the box, and the temperature of the water gradually raised to 60 degrees when the meter was quickly calibrated. Before this and all succeeding calibrations care was exercised to have the entire body of water in the meter at the same temperature.

After determining the calibration at 60 degrees, the temperature was raised to 65 degrees and the calibration repeated. This process was continued for each temperature interval of five (5), degrees up to and including 90 degrees. No water was added to or removed from the meter during this work.

After covering the range of temperatures from 60 degrees to 90 degrees inclusive, the water was again cooled to a little below 60 degrees and the process repeated. The results of the two series of calibrations checked very satisfactorily and are given below.

DATA.

TEST No. 1.

Room tem. —75° F. *Calibration apparatus standardized at 75° F.*

Time	Tem. water in meter Deg. F.	Error		
A. M.				
8:35	60.0	3.22	per cent.	slow
8:52	65.5	1.80	"	"
9:07	70.3	0.46	"	"
9:19	75.2	0.90	"	fast
9:36	80.1	2.42	"	"
9:52	85.4	4.23	"	"
10:06	90.7	6.15	"	"

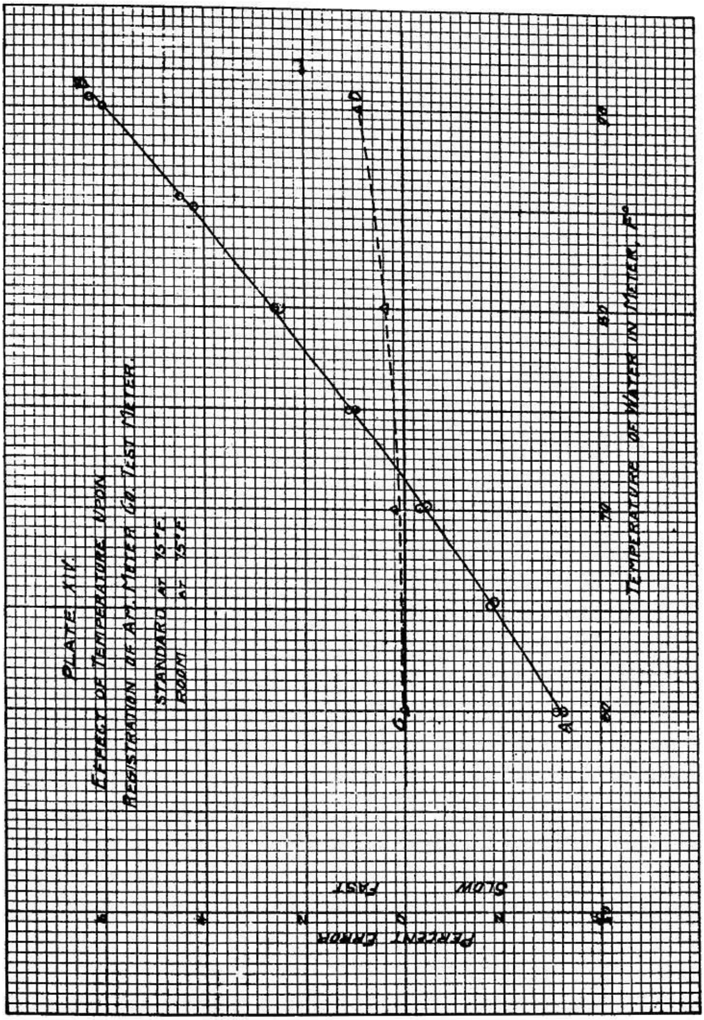
TEST No. 2.

Time	Tem. water in meter Deg. F.	Error		
A. M.				
11:34	60.0	3.10	per cent.	slow
11:45	65.4	1.82	"	"
M.				
12:00	70.4	0.52	"	"
P. M.				
1:07	75.2	1.06	"	fast
1:21	80.1	2.50	"	"
1:36	85.0	4.11	"	"
1:50	90.0	5.99	"	"

The results are shown graphically in Plate XIV. The percentage errors are plotted as ordinates, and the temperatures of the water in the meter as abscissae.

Discussion of Results.

With the calibration apparatus at 75 degrees F. it is seen that the meter changes decidedly as the temperature of the



water within the meter varies. Thus, at 60 degrees the meter is 3.2 per cent. slow and at 90 degrees is 6 per cent. fast.

If now the gas volume measured is to be corrected to standard conditions, namely, 60 degrees F. and 30 inches of mercury, the net error resulting after making these corrections is shown in curve labeled (CD).

The following table will show the correction factor and per cent correction which must be applied to the observed reading of the meter to reduce the gas to standard conditions:

Tem.	Correction factor	Per cent. correction	Per cent. error
90° F.	0 917	8.3	+5.1
80° F.	0.946	5.4	+2.3
70° F.	0.974	2.6	—0.6
60° F.	1.000	0.0	—3.2

Where minus (—) means slow, and plus (+) means fast.

From curve (AB) it will be seen that the registration is 3.2 per cent. slow.

Taking 60 degrees as the basis and subtracting 3.2 per cent. from the values given in the column for per cent. correction the values given in the column of per cent. error are obtained. Subtracting the values of per cent. error in the last column from the percentages of error as shown in curve (AB) at the proper temperatures of water in the meter, the points on the curve (CD) are obtained.

The space lying between the curve (CD) and the line representing zero correction will then indicate the net error. This is on the assumption that the gas or air used in the calibration was saturated with water vapor.

It will be noted that at ordinary room temperature the net error is exceedingly small and seems to be well within the limits that may be expected with this type of meter. For very accurate work it can be seen that extreme care must be exercised in adjusting the temperature of the water in the meter to that of the gas passing through and also to the temperature in the calibration apparatus.

IV. CONCLUSIONS.

The nature of the work is such that conclusions of each individual test have been drawn at the close of each main division in the report.

It is not desired to recommend any particular calorimeter, but to present the facts of each instrument in an entirely impartial manner.

Calorimeters should be operated under predetermined methods and the operating instructions should be strictly followed. The various accessories used in connection with the calorimeter, such as the meter, balance or graduates, and thermometers, should be known to be correct or approximately so, and if in error, a compensating correction should be made. Calorimeters metering the gas by water displacement dispense with the use of a gas meter and thereby eliminate the errors from this source. It is not supposed that any instrument can be perfect, but the designs of some types have approached perfection so that the results obtained are entirely within the limits of personal error.

It is known that the humidity conditions of the atmosphere introduce a discrepancy in the final readings of some water jacket type instruments, but these may be corrected for within close limits. The method of making such corrections is to reduce the temperature of the exhaust products somewhat lower than the entering gas and air. In a perfectly efficient calorimeter, with a very high percentage of atmospheric humidity, the products of combustion should leave the instrument at approximately the temperature of the atmosphere. To produce a corresponding reading of the quality of the gas, the products should leave the instrument at a temperature considerably below that of the atmosphere—where the relative atmospheric humidity is very low. Such a reduction will vary from 0 degree to 15 degrees F., and may be produced by lowering the temperature of the inlet jacket water to temperatures varying from 0 degree to 25 degrees below the atmosphere.

A test of a recording calorimeter not of the water jacket type was made, and the results obtained demonstrated that this instrument gave continuous readings of the net heating value of the gas that could be relied upon for comparative purposes. However, such an instrument must be calibrated from readings made on a calorimeter of the water jacket type.

Your committee feel that the work they have done on testing various instruments has been a means of studying the subject in great detail, and hope that the facts presented in the reports to the Institute will enable the subject to be better understood by individual members and throw some light on the various factors that are included in measuring the heating value of gas.

We have been informed that the National Bureau of Standards, at Washington, is now investigating this subject and examining instruments of various types and makes, and will present the results by publication during the coming year.

Therefore, we conclude our work with the submission of this report.

V. REFERENCES.

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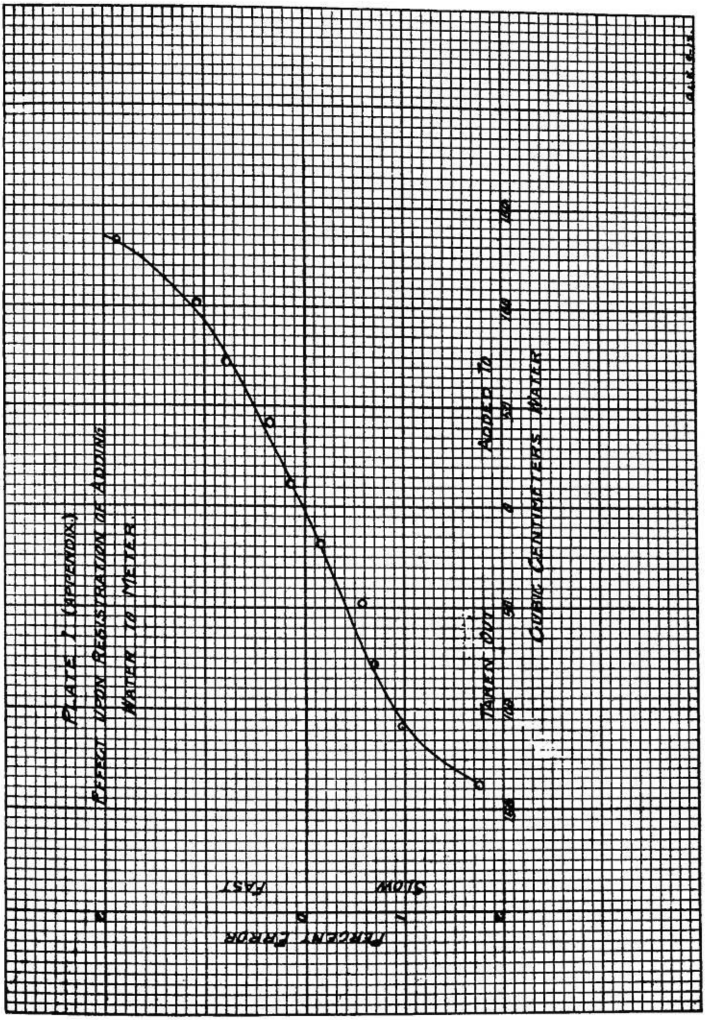
APPENDIX I.

SOME OBSERVATIONS ON THE CALIBRATION AND OPERATION OF AN AMERICAN METER COMPANY WET TEST METER.

During the progress of the investigation which Mr. Lawrence conducted on calorimeters, it became apparent that the discrepancies found in the results of various tests could be attributed to the registration and other vagaries of the wet test meter. Previous to this time it had not been appreciated how great the error could be which the registration of the meter would make in the results from the observations made in conducting a test for heating value. Accordingly a separate investigation was made concerning the various features of the wet meter.

Effect of Changes in the Amount of Water in the Meter.

It seemed desirable to determine how the registration of the



meter would change when successive small quantities of water were added. Accordingly American Meter Company meter

No. 453 was calibrated by means of a half cubic foot bottle and then successive additions of 30 cubic centimeters of water were made. After the addition of each 30 cubic centimeters the meter was recalibrated. In all ten such additions and calibrations were made. The results of these tests are recorded in Table 1, and Plate 1. It will be seen from this tabulation that as the calibration becomes uniform a change in the quantity of water in the meter of 30 cubic centimeters will produce a change in the accuracy of registration of the meter of 0.35 per cent.

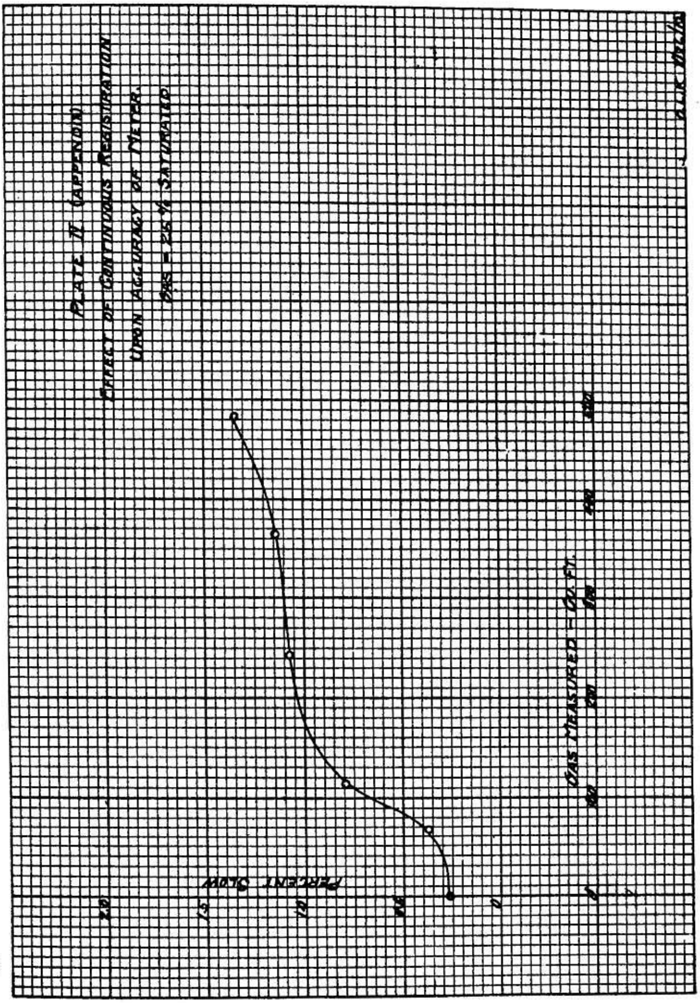
It may be well to state in this connection that it is necessary to have the inlet and outlet ports of the meter open to the atmosphere when any addition of water is made to the meter or any water is removed. It is also desirable to have the meter make several revolutions before the actual calibration is performed when water is put in or taken out of the meter.

Effect of Continuous Run.

The question also arose in this investigation as to how long a meter could be run without there being a serious change in the accuracy of its registration due to a change in the amount of water in the meter. To determine this point, the meter previously mentioned was first calibrated and the accuracy of its registration determined, then gas was passed through it at the rate of about 5 to 6 feet an hour for extended periods of time. At intervals of about one day, the meter was recalibrated. This process was continued for a number of days. The result of this investigation is shown in Table 2 and Plate 2. The gas which pasesd this meter was rather dry, its humidity being about 25 per cent. and it can be seen that this fact produces a considerable change in the registration of the meter. A wet test meter used for calorimeter operation should be checked frequently, as often as two or three times a week in commercial practice and for scientific determinations should be tested before and after each series.

Adjustment of Water Level.

Every company owning a gas calorimeter which requires the use of a meter, is not in possession of a calibration bottle for the purpose of standardizing the meter. In view of this fact it seemed desirable to make some investigation of the



accuracy with which a person could adjust the water level in a meter to a mark which had been set by means of a calibration bottle. The same meter was used in this as in the previous tests. First, the meter was set to register correctly by calibrating it against a one-half cubic foot bottle, then a piece of gummed paper was pasted around the gauge glass on the meter so that the bottom of the meniscus in the gauge glass was on a level with the upper edge of the strip of gummed paper. Then an unknown quantity of water was withdrawn from the meter and to this quantity another unknown quantity of water was added. This water was poured back into the meter until the meniscus in the gauge glass had, in the estimation of the observer, returned to the point where it had been set according to the calibration with the half cubic foot bottle. Upon adjusting the water level in this manner the meter was calibrated in the above mentioned manner. This process was repeated several times and upon several occasions. The results of these tests are shown in Table No. 3. It appears from these results that if the observer has a mark on the gauge glass or near it so that he can sight across two points and so adjust the meniscus without any danger of parallax, it is possible to adjust the meter so that the accuracy of its registration is well within the limits demanded by commercial practice. This method is not to be recommended, however, for scientific investigations.

The committee has been informed that Mr. Walter H. Hinman, of the American Meter Company, had devised a sight which is to be attached to the body of the meter and which is to surround the gauge glass so that the operator upon glancing across the sight posts could observe very closely when the meniscus was at the proper point. If all existing meters could be supplied with a simple sight that could be attached to the stuffing box of the gauge glass, it would provide an effective means of fixing the water level in the calorimeter to the proper point. Perhaps a pin point gauge, such as is frequently used in hydraulic measurements, may be equally as effective as the sight post method of adjusting the water level.

From the work which has been done thus far on calorimeters, it would appear that any scheme that would avoid the use of a metering device would be an improvement, inasmuch, as it removes one serious element from the number which may effect the accuracy of the determination of the heating value.

TABLE 1.

TABLE SHOWING VARIATION OF REGISTRATION OF METER WITH VARYING AMOUNTS OF WATER.

Test	Temp. water °F in meter	Value of standard in cubic feet	Reading of meter cubic feet	Water added cc.	Percent error		Remarks
					Fast	Slow	
1	84.2	0.4993	0.4907			1.76	Initial condition
2	84.0	"	0.4944	30		0.98	
3	83.8	"	0.4958	30		0.70	
4	83.5	"	0.4965	30		0.56	
5	83.5	"	0.4984	30		0.18	
6	83.0	"	0.5000	30	0.14		
7	83.1	"	0.5010	30	0.34		
8	83.2	"	0.5032	30	0.78		
9	83.3	"	0.5047	30	1.08		
10	83.7	"	0.5090	30	1.94		Final condition

TABLE 2.

EFFECT OF CONTINUOUS USE ON REGISTRATION OF METER.

Period	Value of standard	Calibration of meter	Per cent. error—slow corrected to 81° F.	Cu. ft. gas for period	Total gas metered cu. ft.	Temperature of water in meter F°.
0	0 4993	0 4980	0.26	start		81.0
1	0.4993	0.4934	0.37	68.7070	68.7070	78.3
2	0.4993	0.4945	0.78	44.8795	113.5865	80.4
3	0.4993	0.4850	1.15	133.1190	246.7055	75.3
4	0.4993	0.4920	1.28	117.3937	364.0992	80.4
5	0.4993	0.4924	1.68	118.1828	482.2820	82.0

TABLE 3.

CALIBRATION DATA ON SETTING GAS METER BY GAUGE GLASS LEVEL.

Trial	Temp. water in meter °F.	Calibration after setting	Calibration corrected to 72.2° F.	Per cent. error	
				Fast	Slow
1	72.2	0.4980	0.4980	—	0.32
2	72.2	0.4996	0.4996	0.06	—
3	72.2	0.4993	0.4493	O. K.	O. K.
4	84.2	0.5106	0.4993	O. K.	O. K.
5	84.2	0.5100	0.4987	—	0.12
6	84.2	0.5092	0.4979	—	0.28

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Some Present Pickling Methods.

By Oliver W. Storey.

In the hot working of iron, steel and cast iron, the unavoidable formation of a scale makes the subsequent operation of pickling necessary, especially in the various galvanizing, plating and enameling processes. This scale consists essentially of the magnetic oxide of iron, which is resistant to corrosive action.

Ordinary mill scale, as found on hot-worked materials, is present in various thicknesses. On black sheets it is present as a thin coating, while on heavy rolled shapes it is much thicker, often being over 1/32″ in thickness. The coating especially when heavy is usually porous and brittle, while more flexible and continuous when thin.

The resistance of a certain quality of iron oxide to corrosive action is the basis of the protective coatings of the Bauer-Barff and Wells processes. By these methods a thin continuous coating of the magnetic oxide is produced on the surface of the iron and the article is rendered immune to corrosion as long as the continuity of the coating is not broken. Since the magnetic oxide is electronegative to iron by nearly two volts, the damaging of the surface will start a rapid electrochemical corrosion of the iron base.

For ease in removing scale by pickling a continuous coating of the magnetic oxide is undesirable since it is insoluble in the pickling acid and prevents the action on the underlying iron. It is well known that the principal function of the pickling acid is not dissolving the scale but the dissolving of the underlying iron sufficiently to loosen the scale. Scale formed under ordinary hot working conditions is porous and is usually easily removed.

If all the scale found on iron and steel were pure magnetic oxide, the problem of pickling would not be as troublesome as it is at present. Not only does the thickness of the scale vary, but its composition varies owing to impurities. Ordinary black sheets do not always present a smooth surface but often are very rough. It will be found that cinder, slag and scale contained in these rough places cause trouble in pickling. Since a much longer time is required to remove the scale from these rough spots the rest of the surface will be overpickled and the cleaned iron will present an uneven surface. Similar troubles are found in the pickling of iron pipe. Forged material is especially difficult to pickle owing to the cinder and scale that is driven into the iron.

Acids Used for Pickling.

The acids usually used for pickling are sulphuric, hydrochloric and hydrofluoric. The last is frequently used on castings to dissolve any adhering sand that may be in a position where it cannot be easily removed by tumbling or sand blasting. Sulphuric acid is the one almost universally used for pickling purposes. This is owing to its cheapness and ease of transportation in large quantities by tank cars. Sixty deg. and 66 deg. Be. acid is worth from 80c. to 90c. a hundred f.o.b. plant in most industrial districts, this price holding for a brimstone acid containing a minimum of arsenic. The sulphuric acid must have high purity since certain impurities will cut down the pickling power. Arsenic especially is most undesirable as an exceedingly small quantity is harmful.

Prof. C. F. Burgess was among the first to show the quantitative relation between the arsenic content of sulphuric acid to its pickling power and to give an explanation of this phenomenon.[1] It had been known in general for over sixty years that the presence of arsenic in sulphuric acid was detrimental when used for pickling purposes, but no definite work had been done or had any explanation been offered.

Dr. O. P. Watts has elaborated on this work and the influence of various materials on the rate of corrosion of iron has been investigated in the Chemical Engineering Laboratories of the University of Wisconsin and some interesting results obtained.[2] These results show that arsenic is an effective retarder of corrosion and the same is true of tin. Lead, which is soluble to a slight extent in sulphuric acid, is also a retardent. While certain materials are more or less effective in retarding corrosion, others may cause accelerated action.

It would appear that a mixture of acids, such as sulphuric and hydrochloric, ought to cause an accelerated rate of corrosion, but the results show a high rate of retardation.

These experiments indicate that the acids used for pickling purposes must be free from those materials that retard corrosion to be able to secure a maximum pickling efficiency. A small amount of these retarding materials present in the acid will often cut the capacity of the pickling plant in two and perhaps double the acid cost. A study of the action of sulphites and of selenium on the corrosion rate would be of importance, since these are also usually present in varying quantities in commercial acid. In fact, the whole question of the influence of impurities as to their influence on efficiency of pickling is worthy of further investigation.

Where large quantities of the acid are used it is bought in carload lots and stored in large iron containers. If the acid has to be transported and stored in glass carboys it adds materially to the cost, owing to the large amount of handling during transportation, higher freight charges owing to freight classi-

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[1] Tr. A. E. S. 8., 165, (1905).

[2] O. P. Watts, Tr. A. E. S. 21, 337, (1912).

fication, breakage of carboys and the danger in handling glass containers of acid.

The layout of a pickling plant depends on several factors, these being principally the character of the material to be pickled, capacity required, and the relation of the pickling process to the rest of the plant.

The character of material is of utmost importance as the various grades of iron, steel, and cast iron corrode at widely varying rates, the rate depending upon the kind of acid and the purity of the iron.[3] In general, the lower the carbon content of the iron the lower the corrosion rate in materials subjected to the same heat treatment.

Pickling of Black Steel Sheets.

Probably the two materials that are most frequently pickled are black steel sheets and wrought iron and steel pipe, including both water pipe and conduit. Steel sheets are usually covered with a thin scale that can be easily removed, while the scale usually found on pipe is more difficult to remove owing to its weight. The methods used for pickling these materials will be taken up in detail.

To operate a pickling plant successfully requires a large supply of hot and cold water. A large amount of water is needed for washing after pickling to remove all traces of acids and metallic salts.

The pickling of black sheets is usually done with the so-called pickling machines. Such machines are now on the market capable of handling the material rapidly and economically, a typical one in general use being the Mesta pickling machine.[4] It consists essentially of a vertical plunger working in a cylinder, with three arms 120 deg. apart at the top of the plunger which is worked by steam or compressed air. Two vats are required with this type of machine; one acid and the other water. While one crate of sheets on the first arm is pickling in the first vat, the second crate on the second arm is being washed in water, while the third is being unloaded or reloaded. If a third vat is necessary the machine can be built with four arms.

The vats are constructed to the dimensions required by the material to be pickled. The crates are often made of wood but more often of some acid-resisting alloy. Where wood is employed nails or bolts of copper are necessary. The sheets are rested on edge in this crate, which is usually large enough to hold from 1500 to 2000 lb. of the material.

When sulphuric acid is used the strength of the solution usually varies from 3 to 8 per cent, and it is usually kept as near boiling as possible by injecting live steam into the vat. The high temperature has a remarkable effect on the rapidity and efficiency of the action. The sheets are forced apart to secure complete pickling by violently agitating the acid solution. With suitable agitation and separation of the sheets, this

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[3] Burgess and Engle, Tr. A. E. S. 9, 199, (1906).
[4] Metallurgical and Chemical Engineering, Vol. 8, No. 10, p. 598.

process may be completed in six to 10 minutes with a 6 per cent pickle. When a weak pickle, such as a 3 per cent solution and a temperature of about 180 deg. Fahr. is used, the sheets usually require about 30 minutes for complete removal of scale.

After being pickled they are transferred to the washing tank where the acid and ferrous salts are removed as completely as possible by copious supplies of fresh water. If the wash water is hot the sheets will dry quickly when brought into the air with the formation of but a negligible quantity of iron oxide. If the sheets are not for immediate use and are to be stored or shipped they are dipped in a lime or soda solution to kill any acid that may be present and prevent the formation of rust.

This method of pickling will remove all of the scale, but owing to the short period in the acid will not remove any cinder that may have been rolled into the surface of the sheet. If the sheet remains in the acid a greater length of time, the acid may attack enough of the iron to precipitate out a black deposit of carbon or some form of combined carbon that may cause trouble in later processes. Therefore, the sheets stay in the acid the minimum length of time required to remove the ordinary mill scale. About 140 lb. of 66-deg. acid is required per ton of sheets, though this of course varies with the thickness and other characteristics of the material.

Pickling of Pipe.

In the pickling of steel and wrought-iron pipe a different method is in use. For ordinary galvanizing purposes only the exterior of a pipe needs to be entirely free of scale in contrast with pipe for conduit purposes, where both interior and exterior have to be cleaned.

Vats are made the requisite length, 4 ft. to 6 ft. wide, and from 2 ft. to 3 ft. deep. The acid bath, the strength of which varies from 3 to 10 per cent of sulphuric acid, is heated by means of injected steam. The pipes are held in two acid-proof chains and at short intervals of time they are tumbled over each other by working these chains.[5] This operation is repeated several times during the pickling period. The tumbling of the material is necessary for several reasons. It circulates the bath, especially in the interior of the pipe and it helps loosen some of the tougher scale of the exterior by abrasion and it also washes away the detached scale. When the exterior is sufficiently clear of scale the pipes are washed in water, as with sheets, and if they are to be hot galvanized, they are dipped into a hydrochloric acid solution. Upon removal the iron chloride formed is allowed to dry and acts as a flux in the galvanizing bath.

The pickling of pipe for conduit purposes presents a different problem. There are two methods in use for giving conduit a protective coating, enameling and galvanizing. Galvanizing may be hot, wet or electro, and dry or sherardizing. The same general method of pickling with sulphuric acid is used. Conduit pipe is 10 ft. long and must be thoroughly

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[5] Buchert, Stahl und Eisen, **32,** 1487-9.

cleaned on the interior and exterior. Any scale remaining on the inside of conduit pipe will be a sufficient cause for its rejection by the Board of Underwriters, whose requirements are rigid.

Before entering on the description of methods used for pickling conduit pipe it will be necessary to describe the scale found on the interior and exterior of the pipe. This will necessarily require a brief description of the methods of manufacture.

Conduit pipe is butt welded. The skelp is heated in a furnace whose bottom is usually lined with silica. At the temperature of the furnace the acid silica and basic iron oxide unite to form one of the easily fusible silicates of iron. When the skelp is withdrawn from the furnace it is drawn into the forming die so that the bottom of the skelp will come in the inside of the pipe. The silicate slag will therefore be found on the interior of the conduit. This silicate then runs to the bottom of the conduit and solidifies as a strip of hard glassy slag that adheres quite firmly to the iron. It has been suggested that the upper part of the skelp be turned in, but owing to the rapidity with which the silicate slag ruins the dies this is never practiced. This silicate slag is the cause of the trouble that is encountered in pickling pipe.

Since the interior of conduit pipe must be free from scale it presents difficulties that are not present when ordinary pipe is treated. The acid in the interior must be kept in circulation so as to have the rate of pickling as fast on the interior as on the exterior. Various methods have been tried, of which the more successful may be described.

Pickling on end is a natural method to suggest, the material being hung on racks and lowered into the acid vats. The hydrogen liberated on the interior of the pipe and rising to the surface creates a circulation of the acid bath. This method is effectual but it is open to several objections. The hanging of the material on the racks requires an extra operation and the same is true in taking the material down. The racks occupy a large space for a given number of pipe and the space required for the pickling plant is large. Large hoists are required for the lifting of material over a distance of at least 11 ft. Should the drainage sewers be down at the ordinary distance of about 6 ft. and it is required that the waste liquor run into them, it will be seen that the tanks will have to be elevated some distance to procure proper drainage. If any break should occur in the hoisting apparatus, a fall of 11 ft. to 12 ft. of the heavily loaded racks would probably be fatal to the pickling tank. The tanks would not be adapted for the pickling of other classes of materials.

The other methods of pickling consist of treating the conduit in a horizontal position instead of vertical. In this way the layout of the plant will be simpler since the tanks will be from 2 ft. to 3 ft. deep, 4 ft. wide and 11 ft. long. The material is laid in a cradle arrangement, the couplings on the one end of the pipe causing them to be completely separated and allowing the entire surface to be subject to the acid attack. This method allows of large quantities of pipe to be pickled in one vat. The methods used for getting a good circulation of acid in horizontal tanks differ.

The intermittent method is one in which the circulation is secured in the following manner: At certain intervals of about every fifteen or twenty minutes the racks or cradles of pipe are lifted from the tanks so that the pipes are at an angle with the horizontal, allowing them to drain easily. By plunging the rack up and down in the acid several times the loose scale and dirt are removed from the interior and the pickling is again allowed to proceed. This method is especially satisfactory where a weak pickle is used.

Another method of securing circulation is to have the pipe lay in a rocking cradle working in the acid. This secures excellent circulation, but it is open to the objection that it requires machinery to be present in a pickle room and in the bath where deterioration is rapid. By introducing paddle wheels, propellers and plungers, into the vats, circulation has been secured, but none of the methods given seem to give entire satisfaction.

In the treatment of conduit, the time of pickling is judged by the interior appearance. The exterior may become free from scale in a short time, but the interior may still contain a large amount. The conduit must remain in the pickle until all of this scale is removed or until the iron surface or screw threads become visibly corroded. When this happens the pipe must be removed from the pickle to avoid being scrapped and the remaining scale must be sand blasted or otherwise removed from the interior.

Where the pipe contains the hard ridge of iron silicate, ordinary pickling and sand blasting will not entirely remove it, and the remainder is generally left in the interior of the pipe. Such a rigid scale is detrimental since it makes fishing difficult and is liable to cut the insulation of the fished wire.

If the pipe is to be used for cold galvanizing purposes it is washed with cold water after removing from the pickle. It may be dipped in cold dilute hydrochloric acid and then taken directly to the plating tank to prevent any oxide from being formed. If the pipe is to be sherardized, it is dipped into hot water to remove the acid and iron salts, then into a lime water and finally into a hot-water bath. Upon removing from the hot water the pipe dries quickly and a minimum of iron oxide is formed. This small amount of oxide is not detrimental, but, in fact, appears to give a brighter coating. If the pipe is to be enameled it is treated in the same manner as is the sherardized material.

Strength and Temperature of Pickle and Other Details.

The strength of the pickle varies a great deal, running from 3 to 8 per cent sulphuric acid. These various strengths have their advantages and disadvantages. When a 3 per cent solution is used a larger plant is required. This is offset by the various other advantages gained. When a 3 per cent solution, at a temperature of about 170 deg. Fahr., is used the rate of pickling is slow, requiring from three to twenty-four hours to pickle ordinary pipe. With this slow rate pipe will not be easily over-pickled if it should be accidentally left in the pickle too long. The slow rate of hydrogen liberation lessens the amount of finely divided acid thrown into the air and makes it easier upon the workmen and also upon the buildings and machinery. It is also possible to "kill" a low percentage bath until almost free from acid and this prevents any acid being run into the drains. With high-percentage acid baths it is customary to "kill" a bath to a certain percentage and then run it off as waste. The high-percentage bath is also harder upon the workingmen. With a low-percentage pickle the amount of acid used per ton of pipe is much less than with a high-percentage pickle, usually running below 80 lb. per ton.

The temperature of the pickle is also very important, since the higher the temperature of the bath the faster the pickling. For most purposes it is best to have a boiling bath because it not alone produces a bigger tonnage, but it also removes all grease from the article to be pickled. With a boiling pickle, however, large volumes of acidulated steam are given off, with attendant corrosion of machinery, buildings, and the bad effect upon workmen.

The pickle is run until the action becomes too slow, when more acid is added. When a solution becomes concentrated with ferrous sulphate, the pickle is "killed" and then is generally run off as waste. The concentration in ferrous sulphate when "killed" varies a great deal, standing from 12 to 25 per cent, depending upon the practice at the plant.

Few plants attempt to utilize the ferrous salts and sulphuric acid in the waste pickle, since no satisfactory method has been offered. Its utilization has been made subject of a large number of patents. One of the most recent is that of F. F. Farnham, who electrolyzes the solution and obtains iron and sulphuric acid.[6] Where utilization is practiced a common method is to neutralize the free acid by means of iron scrap, evaporating and crystallizing the iron salts, producing the copperas of commerce. This copperas has various uses, such as the making of various shades of red pigments, Indian red and Venetian red. Recent advocacy by agricultural experiment stations of this material as a weed killer has increased the outlet for it, but with all of the uses proposed, a general recovery from all spent liquors would undoubtedly flood the market.

In galvanizing and sherardizing plants, where the zinc sometimes has to be stripped from the iron, owing to defects and other causes, an old pickle is usually used for stripping the zinc and is found to work best. The potential of iron is below that of zinc and naturally the iron in the pickle as ferrous sulphate has a tendency to plate out and remove the zinc, though little acid is present.

Air hoists are generally used in pickling rooms owing to their

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[6] F. F. Farnham, Patent No. 1,006,836, Metallurgical and Chemical Engineering, Vol. 9, No. 12, p. 670.

simplicity, ease of operation and low cost of upkeep. Though compressed air as a source of power is costly, the other advantages gained by the use of compressed air counterbalance this factor.

Large and non-corrosive drains should be provided to take care of large amounts of water and killed acid. The best floors for pickling rooms are made of the iron scale that is deposited in the bottom of pickling tanks. This material is porous, is not attacked by acids, cheap and easily laid. Cement and concrete will quickly disintegrate and are therefore not available.

Another use found for the scale and sludge deposited in the bottom of the pickling vats is for the stopping of leaks in these vats.

By merely plastering this sludge into the leaky part the leak may be easily and effectually stopped.

This paper does not attempt to give all methods in use, but rather to describe what may be considered as general practice in pipe and sheet pickling at the present date. Pickling is a branch in the metallurgy of iron and steel that is open to a large amount of improvement. Mechanical treatment and cleaning of the materials has often been tried, but sulphuric acid treatment seems most satisfactory. Pickling plants are run more or less on hit-and-miss methods and the only improvements that have been made are in the mechanical end. The fault does not lie entirely with the chemical end of the industry for improvements may be made in the hot working of the metal so as to give a product of a kind that can be more easily pickled.

The ideal condition will be where the scale would be entirely soluble in some solvent while the iron would be insoluble. Since this is probably impossible, it would be well to obtain a condition where a minimum of scale is formed and in this way requiring but a short acid attack, resulting in minimum corrosion of the iron base.

Viewing the operation from a scientific standpoint the pickling process seems to be the application of "main force and awkwardness." The object is to present a clean iron surface, and this is done not by dissolving or otherwise eliminating the coating, but by dissolving away the iron surface itself. There is here an economic loss, not only in the mill scale and of the acid, but of the good iron which is taken away. It is difficult to predict in what direction the possibility of improvement lies; it may be in the discovery of some cheap solvent for the scale itself, in some electrolytic or other method of reducing the iron oxide, or perhaps in some mechanical or physical method.

Even though the remedy is not in sight the problem is of sufficient magnitude to warrant extended investigation.

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Iron Pipe Used for Electric Conduit

By

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Iron Pipe Used for Electric Conduit

By Oliver W. Storey

The manufacture of rigid metallic conduit has become an industry of importance to the chemical engineer during the past decade. The competition among the manufacturers of this class of material has become very keen and has helped to develop a variety of methods of treating pipe to make it conform to the requirements of the National Board of Fire Underwriters. As the competition increased, the quality of the finished product increased and now the conduit is of a very high grade.

An electric conduit system may be defined as "a raceway in a building to provide for the ready introduction and removal of electric wires and to provide efficient mechanical protection to them."

This definition requires the following necessary features for such a conduit. It should occupy the least possible space; it should be rugged and mechanically strong, yet be easy to work and install; it should resist corrosive action and it should efficiently protect and preserve the insulation of wires contained in it; and it must be moderate in cost.

Materials possessing all of the qualities mentioned are available but their cost is prohibitive. Ordinary iron or steel pipe is cheap and possesses all of the necessary qualities except resistance to corrosive action, but by treating it to certain processes it becomes available for conduit purposes. It is the purpose of this article to describe these various methods of treatment and their comparative durability.

In the past many substances were used for the manufacture of conduit such as fibre, paper, rubber and moulded pulp. Metal pipe was also lined with paper, wood or compositions but these methods have been practically abandoned for the present practice.

At the present time butt-welded mild steel pipe 10 ft. long is used for conduit. This makes a cheap and excellent base since it is very rugged and can be easily worked.

The present manufacture of unlined conduit may be divided into two general classes, enameled and galvanized. The enameling affords protection to the pipe by a corrosion resisting film of enamel while the galvanizing affords protection by galvanic action.

It is only within the past few years that the sale of galvanized or so-called "white pipe" in contrast to the black enameled or "black pipe" has reached large proportions with a consequent decrease of production of the latter. This condition is caused primarily by the reduction of price of galvanized conduit with increasing competition and also by the general conservation tendency in the iron and steel trade to secure a maximum of protection even with greatly increased cost.

In this article the cleaning of the pipe previous to galvanizing or enameling will not be described. The subject of pickling of conduit pipe is an extensive one and has been discussed in another article.[1] It is assumed that all pipe is clean and in a condition to turn out a good grade of conduit.

Manufacture of Black Enameled or "Black Pipe"

The manufacture of "black pipe" appears as a simple proposition, but the large number of difficulties that appear in carrying out the process of enameling requires a great deal of technical skill to insure success.

The selection or compounding of a suitable enamel is of primary importance. Such an enamel when baked must conform to the specifications of the National Board of Fire Underwriters which are as follows: Section 58, Rule L: "The pipe from which the conduit is made must be thoroughly cleaned to remove all scale and must then be protected against effects of oxidation, by baked enamel, zinc, or other approved coating which will not soften at ordinary temperatures, and of sufficient weight and toughness to successively withstand rough usage likely to be received during shipment and installation; and of sufficient elasticity to prevent flaking when ½-in. conduit is bent in a curve the inner edge of which has a radius of 3½ in. All conduit must have an interior coating of a character and appearance which will readily distinguish it from ordinary commercial pipe commonly used for other than electrical purposes."

Other large users of conduit issue specifications that are usually more rigid. Typical of these are the "Specifications for Conduit and Conduit Fittings" issued by the U. S. Navy Department of May 20, 1912. The sections relating to enameled conduit follow:

a. The enamel shall be of an approved type and be not less than 0.005 in. in thickness.

b. Not to be affected by moisture or at a temperature of 100 deg. C.

c. To be of sufficient elasticity to prevent flaking and to adhere with smooth surface when conduit is bent at normal temperatures in a curve, the inner surface of which has a

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[1] Met. & Chem. Eng., Vol. II, No. 1, p. 45.

radius of seven times the normal I. P. S. for ½ in. and 10 times the normal I. P. S. for all other sizes.

d. Not to be affected by the following after an immersion of 24 hours:

1. A 30 per cent solution of sulphuric acid.
2. A 30 per cent solution of nitric acid.
3. A 30 per cent solution of hydrochloric acid.

The specifications of the Board of Underwriters will allow much cheaper enamels to be used than those of the Navy Department. The latter's requirements are very exacting and only the best of enamels may be used.

The baking enamels used contain linseed oil as a base. The other constituents are tars, asphaltums, pitches, and gums, giving it its black color. The usual thinner is benzine. The enamels are made in many grades depending upon the amount of linseed used. By using a small percentage of linseed oil and a large proportion of asphaltums dissolved in benzine a very cheap enamel baking at a low temperature may be made. By using a high percentage of linseed oil with dissolved gums and asphaltum added an excellent one baking at high temperatures may be made. The addition of small percentages of other materials is practiced to improve certain qualities.

A method of testing for a good enamel is as follows:

Remove a strip of enamel from the pipe with a sharp knife. This strip should approach rubber in its elasticity and yet should be hard enough while on the pipe not to be easily scratched by the finger nail. Even after ageing for several years in a warm dry atmosphere this test should still apply.

The general methods used in conduit pipe enameling are alike and differ merely in details. The pipe is hung on racks and dipped into a tank of enamel, and after withdrawing and dripping is run into an oven and baked.

The clean, dry pipe coming from the pickle room are ready for enameling. The couplings on one end found necessary to secure complete separation of the pipes in the pickling vat are again found necessary to hang them upon the enameling racks.

The racks are usually made of cast iron with a double row of notches into which the pipe will slip easily but upon which the shoulders of the coupling will rest. With small sizes of pipe the notches may be deep enough to support two lengths. The racks are supported by a monorail system. The capacity of each is from 50 to 200 ½-in. pipe and requires a different rack for each size of pipe. Since a large percentage of conduit is ½ in. the number needed for the other sizes is small especially for those above 1 in.

After the pipes have been hung upon the racks they are dipped into the enamel which is usually contained in a riveted iron tank about 11 ft. deep, 2 ft. wide and long enough to accommodate the dipping rack. The tanks often contain 1000 gallons of enamel. With an enamel worth 65 cents per gallon the value of the contents is a considerable sum and precautions must be taken to prevent its becoming ignited, to prevent any deleterious foreign matter entering it or to prevent adding a poorer quality of enamel which necessitates testing of all new lots of enamel.

The danger of fire is increased by heating the enamel by steam coils in the bottom of the tank. The heating is necessary to maintain a constant temperature and to thin the enamel. This method is safer, cheaper and gives better results than thinning with benzine. If a volatile solvent is added the enamel continually changes in consistency with corresponding variation in the finished product. Warm enamel also coats the pipe more evenly by eliminating any air bubbles clinging to the pipe surface.

The rack of pipe is lowered into the enamel and allowed to remain until it has reached the same temperature. It is then hoisted out of the tank and the pipe allowed to drip for about a minute after which they are run over dripping pans and allowed to remain until ready for baking. The excess enamel on the dripping pans flows back into the tank.

With the various grades of enamel this preliminary air exposure accomplishes different purposes. With a high grade, high temperature baking enamel this exposure to the air does not cause any hardening of the enamel but merely allows some of the excess enamel to drain. With a medium grade, benzine-thinned enamel the benzine evaporates, leaving a jelly-like coating that hardens in the furnace with medium temperatures. With a cheap enamel containing a larger percentage of benzine, the latter evaporates leaving an enamel that is but slightly tacky and which becomes hard with a slight baking.

After the preliminary air treatment the pipes are run into the baking oven. These vary in their construction and in capacity which is usually rated in terms of ½-in. pipe. An oven having a capacity of 25,000 feet of ½-in. pipe would hold about 4000 ft. of 4-in. pipe.

The design of the baking oven is dependent upon the enamel used. In general they are made of firebrick with ample ventilation for all fumes and gases evolved.

If a low temperature baking enamel is used steam coils may be placed in the bottom of the oven and adequate heat furnished by these to finish the drying of the enamel.

Where higher temperatures up to 700 deg. Fahr. are desired two general methods are in use, the direct and indirect.

The direct method is used where natural gas is available or other gas can be obtained at low cost. The gas is burned directly in the baking oven in a kind of hearth or brick that are heated to a white heat. The object is secure as complete combustion of the gas with as little excess of air as possible. The hot gases of combustion circulate among the pipe and bake the enamel. With small excess of air there is little danger of igniting the fumes evolved. With incomplete combustion soot would be deposited upon the tacky enamel and spoil it.

With the indirect method of heating the hot gases of combustion are led through radiators which heat the air to be used in baking the enamel.

The efficiency of the direct method is very high when compared to the indirect. With the latter there is no danger of spoiling the enamel with the products of combustion and there is no danger of an explosion should the oven door be accidentally opened during the "heat."

When a medium enamel which hardens slowly in the air is used the oven is run at a temperature of 300 deg. to 400 deg. Fahr. When the oven is first warmed a small amount of enamel may drip from the bottom of the pipe due to the thinning of the jelly-like film left after the evaporation of the solvents.

With one that must be baked at a temperature of 600 deg. Fahr. the operation is not as simple. When the oven warms the enamel thins and the excess will drip to the bottom of the furnace. This dripping will continue for some time, usually until the solvents have evaporated and the linseed oil has begun to harden. The excess is drained into a well from which it is periodically returned to the tanks, apparently having suffered no deterioration.

The securing of a uniform film of enamel over the surface of the pipe is a difficult problem. After baking a rack of ½-in. pipe, that have received one coat of enamel, the following imperfections will be noted:

1. The upper end of the pipe, both interior and exterior, has received a thinner and harder coating than the lower end.
2. The threads at the lower end are filled with enamel.
3. The surface of the exterior of the pipe that is very close to another pipe has a coating thin enough to be transparent, while the balance of the pipe has a heavier coating.
4. The interior surface of a piece of ½-in. pipe has received a thin coat while the same surface on a piece of 4-in. pipe is as heavily coated as the exterior.

These are the chief difficulties encountered in enameling conduit.

The coating at the upper end of the pipe is usually half as heavy as that at the lower end. This is caused by the upper part of the enameling oven becoming hotter first and the draining of the surplus enamel to the bottom of the pipe. The enamel flows slowly to the lower end, and, before it can all drip, it has begun to harden since the rate of heating is usually high. With slower heating this difficulty could be lessened. At the upper end of the pipe it is also harder than at the lower owing to the thinner film and higher temperature.

These imperfections may be remedied in the second application by upending the conduit on the racks. This is not generally done owing to the extra operation of changing couplings which would require that the racks be unloaded and reloaded. Some manufacturers depend upon the second coat being more uniform than the first and covering any pronounced difference in the upper and lower end.

The unevenness of coating due to the proximity of other pipe can obviously only be remedied by cutting down the capacity of the oven. Since the second coat of enamel covers this defect it is usually disregarded. If but one coat of enamel were used this defect would have to be remedied.

The difference of thickness between the interior and exterior coat is primarily caused by the lack of circulation in the interior of the pipe and consequent slow evaporation of the solvents and slow oxidation of the oils, allowing more enamel to drain. The enamel film is also very thin at the top when compared to the bottom. As the size of the pipe increases these difficulties decrease.

The two coats of enamel are necessary to give a flexible coat of suitable thickness as required by the specifications and to overcome some of the defects mentioned. A coat of the requisite thickness could not be applied in one baking for the same reason that a thick coat of paint is never used.

The second coat is applied in the same manner as the first and results in a bright smooth surface. This coat is usually baked at a slightly higher temperature than the first giving a harder surface, yet flexible owing to the softer foundation. A third coat is sometimes required but such an additional film is of doubtful value as an added protection.

The conduit is now ready for the market after an inspection of the bore to discover obstructions. This inspection is carried out by flashing a light through it.

The enamel interior provides a smooth raceway for wires. Its generally excellent appearance, its cleanliness, smooth interior and its cheapness makes the black pipe very popular among the installers.

The racks used for dipping the pipe soon become covered with enamel and unfit for use. This can be easily removed by burning in a scrap fire.

Elbows are enameled by running wires through the bores and dipping them as with pipe.

The enameling plant should be so planned that the process may be carried on without interruption during the different operations. The layout should allow enough space to provide for the hanging of an oven-full of green pipe and enough dripping space to take care of an oven-full of dipped pipe. The mechanism should be so arranged as to allow a batch of baked pipe to be removed from the oven while a second batch is run into it. During the baking of this, the first can be given its second dip and allowed to drain.

Since the quality of the enamel is dependent in a large measure upon the temperature control of the ovens, recording gauges should be used to keep an accurate record of the temperature at various parts.

Methods of Manufacture of Galvanized or "White Pipe"

While the general practice in the manufacture of "black pipe" is essentially the same at all plants, the practice in the "white" or galvanized pipe industry varies widely. This difference is due primarily to the three galvanizing methods used, these being hot galvanized, electro-galvanized and sherardized. Approved conduit of all these three types are on the market, the electro-galvanizing predominating since the one sherardized conduit is patented, and there has been but one **hot galvanized conduit** approved by the underwriters.

The specifications of the Board of Underwriters have been quoted and are easily complied with. In direct contrast are the rigid specifications of the Navy Department which exclude hot galvanizing.

"2, h. All steel conduits shall have the exterior surface galvanized and the interior surface either enameled or galvanized and enameled. All galvanizing shall be done either by electro-plating process or dry galvanizing process, and shall show no signs of rust when conduit is immersed in warm salt water (90 deg. C.) for 48 hours. The outer surface of conduit shall be free from paraffin or other material which would tend to prevent the adhesion of paint. Before any tests are made, conduit shall be washed thoroughly in carbon tetrachloride.

"3, d. 4. When conduit is both enameled and galvanized on inside tests under 3, (d) 1, 2, and 3 (acid tests) will not be applied."

The chief trouble that has been encountered in the manufacture of hot galvanized conduit has been the wiping of the interior of the conduit to secure a thin, flexible, and adherent coating. The present hot galvanized conduit on the market has a smooth wiped interior and exterior surface while the threads are clean, yet well coated and need no recutting. The coating is somewhat heavier than is found on electro-galvanized or sherardized pipe yet it is flexible and adheres well to the iron base.

This coating contains aluminium in varying amounts, often being as high as 10 per cent. The addition of this metal improves the hot galvanizing bath without materially increasing the cost owing to its low specific gravity. The aluminium gives the finished conduit a pleasing white appearance.

The presence of about 4 per cent of aluminium reduces the melting point of zinc from 788 deg. Fahr. to 716 deg. Fahr., and allows the bath to be run at lower temperature and decreasing the amount of zinc-iron alloy formed. Since 4 per cent is the eutectic percentage any other low percentage of aluminium will make the solidification occur over a shorter or longer range of temperature depending upon the composition and will, therefore, make it easier to wipe.

The interior of this hot galvanized conduit is not enameled but a peculiar blue black wash is used. It is a thin coating and is merely used as a distinctive finish and helps the fishing qualities slightly.

The one **sherardized conduit** is made by the sherardizing process and has a coating of zinc-iron alloy on the interior, exterior, and threads. While it is not as heavy as that obtained by the hot galvanizing process it is much heavier than that obtained with the electro-galvanizing. It adheres firmly to the iron base, does not flake and is hard, making it capable of withstanding rough usage.

Analyses of the zinc-iron alloy made at different times will show varying amounts of iron present. The iron varies with the metallic zinc in the zinc dust, thickness of coat, sherardizing temperature and length of time in the furnace. The amount of iron in the alloy has been subject to a great deal of discussion since the different investigators have found widely varying percentages. Patrick and Walker[2] found 11.70 per cent, Leighou and Calderwood[3] 18.15 per cent, while Cushman[4] found about 30 per cent. In none of these cases was it known under what conditions the alloy was formed. From a large number of analyses made by the author it was found that the above variables determined the iron content of the alloy formed. By controlling these factors any zinc-iron alloy containing from 8 to 30 per cent of iron may be obtained.

Sherardized conduit receives an exterior and interior coat of clear enamel. Previous to this practice a coat of clear enamel was put upon the interior only and the exterior was paraffined. The clear enamel was used to aid fishing while the paraffin was used to lay the objectionable loose zinc dust that remained on the pipe.

Electro-galvanized conduit is made by varying methods. Only the exterior is plated since the plating of the interior has not been put on a commercial basis. Usually the threads have little or no coating on them, the interior of the couplings are rusty and elbows are poorly coated. With one exception the zinc coating is thin.

One brand of conduit is made by flashing the cleaned iron pipe in a copper bath and plating over this copper with zinc.

Another manufacturer obtains a smooth velvety adherent coating by wire brushing the pipe before coating with zinc. A second brushes the conduit after plating and obtains a bright finish which is pleasing to the eye and does not discolor easily.

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[2] J. of I. & E. Ch., Vol. 8, No. 4, p. 239.

[3] Reports of Tests on Sherardized and Electro-galvanized Conduits, Carnegie Inst. of Tech.

[4] Efficiency of Zinc Coated Conduit Pipes, Inst. of Industrial Research. Washington.

All "white pipe" is enameled in the interior to help the fishing and with the cold galvanizing to provide against oxidation of the iron. In the Navy Specifications the acid tests do not apply to the enamel in the interior for that conduit which has a protective zinc coating beneath. This allows a very thin enamel to be used by those manufacturers who apply zinc to the interior wall while a good grade giving a heavy film must be used by others. This somewhat equalizes the costs.

The coatings used in the interior of conduit cover a wide range. The colored wash in the hot galvanized and clear enamel in the sherardized have been mentioned. Electro-galvanizers use a black enamel except one who uses a red iron oxide enamel paint which is of an excellent quality.

To enamel or paint the interior of conduit requires a special apparatus. A tank similar to the one used for black pipe is used. The pipes are let down into this on racks. The enamel is stored in a small tank about 10 to 15 ft. above. A circular spraying nozzle is let into the top of the pipe. A valve allows the enamel to flow and the head of enamel sprays it on the interior wall of the conduit. Enough is introduced to thoroughly cover the entire interior surface. The surplus drains to the bottom of the tank from where it is pumped back to the storage tank to be used again. This method of enameling is very effective and one man can work at the rate of 600 lengths of pipe per hour. The remaining procedure is similar to that of the black pipe.

Enameled or painted "white pipe" is now sold extensively. The enameling of this pipe does not present any difficulties beyond those found with the black pipe. The applying of a paint presents difficulties of a different nature. The pigments used settle quickly and some method must be devised to keep it evenly distributd throughout the oil. The stirring may be accomplished by means of a propeller. Even with stirring the conduit will not be evenly coated by the pigments. The more practical way of applying the paint would be by means of a spray. In this way the pigment would be more evenly distributed and not be washed away as it is when the conduit is withdrawn from the tank.

When sherardized pipe was paraffined the following method was used. A solution of paraffine of the requisite strength was made in warm benzine. This solution was contained in a horizontal tank capable of holding 5000 ft. of ½-in. conduit. Steam coils kept the solution hot to prevent the paraffine from freezing out. About 5000 ft. of ½-in. pipe, after enameling the interior, were dipped into this tank in one bundle. Any superfluous dust was washed off and settled to the bottom while a thin layer of paraffine remained on the pipe after the benzine had evaporated.

After the conduit has been galvanized and enameled it is inspected, labeled, bundled and is ready for shipment.

Black Pipe versus White Pipe

At present the relative merits of the various brands of "white pipe" are subject to a large amount of controversy. The "black pipe" has been almost entirely neglected, it being generally taken for granted that it is an inferior conduit. Large numbers of tests of galvanized pipe have been made both by partial and impartial investigators and the results made by the former are contradictory while those made by the latter agree fairly well.

If the "man on the job" were asked what pipe he would prefer there would be but one answer which would be "black pipe." He prefers it because of its clean, smooth surface, superior appearance, excellent fishing qualities and because it "takes" paint. He objects to the rough surface of the electro-galvanized because of the "acid" which he says eats into his skin. He objects to the hot galvanized pipe because of its rough surface and some even complain of the "acid." The sherardized paraffine finished pipe was objectionable because of the paraffine finish which became soft in warm weather. Without the paraffine the conduit was dusty.

The stiff competition in conduit manufacture has raised the standard to a high plane. Where, about six or seven years ago, most any kind of enameled pipe would have been acceptable, now this is no longer true and a good quality has to be made. By way of confirmation, one only needs to look at conduit installations of a few years ago and compare them with those of to-day.

As stated above the durability of the different kinds of "white pipe" has been the subject of much argument. The relative merits of black and galvanized pipe are not often mentioned and the writer wishes to emphasize the high merit of the former. Each class of pipe is best under certain conditions and before an installation is made these should be studied to obtain the greatest service per unit of cost.

Conduit is subject to a wide range of conditions. Outdoors it is subject to the action of the weather; it may be buried and here a variety of conditions may affect it, ranging from a dry to a wet, acid soil; it is subject to temperature extremes; it may be buried in cement, cinder, concrete or various plasters; it may be exposed to corrosive vapors, coal smoke, or gases; it may be attacked by oils, acids or alkalis, and it is always subject to mechanical injury in transportation during installation and sometimes in service.

Prof. C. F. Burgess[5] has shown that a high grade enameled conduit, the surface of which has not been injured, is superior to galvanized conduit under a variety of corrosive conditions. Those cases coming under the writer's observation have confirmed this, but only where a good grade of enamel was used.

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[5] Sherardizing Magazine.

Any enamel that conforms to the Navy Specifications as given above must be resistant to corrosive influences.

But under ordinary conditions of shipment and installation the exterior enamel is scratched and scraped, exposing the iron beneath and subjecting it to corrosion. This condition is necessarily important when comparing with galvanized conduit.

Under the following conditions enameled pipe is cheaper to install and will be fully as satisfactory as the galvanized. In room interiors where the conduit is afterward painted, under similar outdoor conditions, in walls of buildings including both plastered and concrete where moisture is not present; in short, any place where dry conditions prevail and any exposed iron is not subject to permanent corrosive conditions. This would cover a large percentage of installations.

By painting the enameled pipe after installation it could be made superior to non-enameled galvanized conduit under many conditions. Where the latter is installed and is exposed to acids and fumes the galvanizing soon is corroded. The resistance of unscarred enameled pipe to such conditions has been pointed out by Prof. C. F. Burgess[5]. By giving the scarred places a coat of slow air drying enamel after installation, the conduit could be made comparatively permanent.

Under exposure to alkalis there would be an advantage to the galvanized conduit but under such conditions even the latter shows a high rate of corrosion and brass, lead, or composition conduit are necessary. Under conditions where the application of this enamel after installation would be impractical or under peculiar conditions of exposure where the enamel would blister and peel the galvanized conduit would be better suited.

The importance of securing as permanent an installation as possible in modern buildings even at a much higher cost has been recognized by some engineers and architects. These men have specified conduit that is both galvanized and enameled, and, so insistent has been this demand, that manufacturers are turning out this class of conduit.

The importance of such a protecting coat over the galvanizing was first noticed in the testing of the paraffined sherardized pipe. The paraffine was primarily used for laying the dust but at the same time it increased the resistance to corrosion to a remarkable degree. It seems as though this increase in the life of the sherardizing would have been the important feature but was not recognized as such by the manufacturers. Tests[3],[5] on paraffined and non-paraffined conduit showed the marked superiority of the former, being fully as durable as the enameled conduit.

The writer believes that any enamel that is used over the galvanizing should be equal in quality to that used on "black pipe." A cheap enamel will soon disintegrate and leave the galvanizing exposed. And where such a conduit is installed the scarring of the enamel during installing will make it little better than the raw galvanized material. The painting of all scars is very important and should be rigidly enforced if the maximum of service is to be received.

The U. S. Government has recognized the value of such a double protection, especially on war vessels, and along the Panama canal, where galvanized conduit, usually sherardized, is painted after installing and is repainted regularly.

The value of the different galvanized coatings when used for conduit protection is a much discussed subject. With the constantly improving methods and with the new brands continually appearing, no data are ever complete.

Some of the earliest work was done by Prof. C. F. Burgess[3] at the Chemical Engineering Laboratories of the University of Wisconsin and showed the relative merits of hot, cold and dry galvanized and enameled conduit. Messrs. Leighou and Calderwood[4] of the Carnegie Technical Schools made some exhaustive tests in 1912 of the value of electro-galvanizing and sherardizing as a protection for conduit purposes.

The value of galvanizing is usually determined primarily by the amount of zinc per unit of area. The other important factors are homogeneity, purity, continuity and tenacity with which it clings to the iron.

The cold galvanized conduit is made by several manufacturers and the product varies. The first of such conduit showed up poorly under actual service conditions as well as in accelerated tests. This was the result of the light deposit of zinc and its uneven distribution. The threads and couplings were usually subject to immediate corrosion owing to the absence of zinc. The amount of zinc has been materially increased but even now the threads and couplings rust quickly. The writer has under his direct observation a large amount of cold galvanized conduit of recent installation and every length is badly rusted at the joints.

The copper flashed conduit employing a thin zinc deposit has shown no superiority over the ordinary electro-galvanizing under actual service conditions.

The sherardized conduit has been subject to many tests and has shown that when the alloy is formed *under proper conditions* it results in a coating that is superior to the electro-galvanized or hot galvanized material. The present practice of sherardizing shows a lack of uniformity of practice and results obtained. The theoretical alloy that should be obtained is one corresponding to $FeZn_{10}$, containing about 8 per cent of iron. Where this alloy has been obtained a coating highly resistant to corrosive action has resulted. The writer's experience has shown that a low temperature is necessary for the production of such an alloy, probably lower than any temperature used in commercial sherardizing plants of today with but one or two exceptions.

With the increase of iron content of the coating the more quickly will it corrode. With coatings containing from 25 to 30 per cent of iron the writer has found that the sherardizing affords little protection since it pits easily. Such a coating is obtained by using high temperatures and a lean zinc dust.

A peculiar property of this alloy is the formation of a blue black covering after being exposed to the weather for some time. Cushman[4] calls attention to the highly protective powers of sherardizing, through its ability to take on this highly resistant black coating, which he explains as being the formation of Fe_3O_4 from the oxidation of the iron in the alloy. He states that this oxide will greatly increase the life of the coating owing to its superior weathering qualities. This black appearance is especially found on exposed paraffined conduit.

The successful introduction of the hot galvanized conduit is of great importance since it is almost impossible to obtain a thin coating with this process. This conduit should, if the weight of coating and other factors are considered, have a long life. Hot galvanized pipe stands high in corrosion tests.[5] What effect the introduction of aluminium will have can only be conjectured.

The importance of the interior galvanizing is often over-estimated. In most cases few fumes and vapors come in contact with the interior and a coat of good enamel should be sufficient to protect against all corrosive influences.

The testing of galvanized conduit is usually done by the standard Preece copper sulphate method and the coats are usually spoken of as being so many "dips" in thickness.

The writer has tested the Preece method and has found that it is very reliable, cheap, and entirely satisfactory as a quick factory method for testing galvanized conduit. The heaviness of the coating is a straight line function of the number of dips and makes the factory control very simple.

But results obtained by this method on two different types of galvanizing are not comparable. It will be found that sherardizing of the same weight as electro-galvanizing will give twice the number of dips in copper sulphate.

The writer has often heard the statement that a coating standing one dip will be equal to three years of atmospheric corrosion. On the strength of the copper sulphate tests resulting from the above statement, a large amount of conduit has been sold. Some manufacturers, quickly realizing that the addition of certain materials to the coating would raise the Preece test without materially increasing the coat, began this practice. As a result of this the test when used by the salesman is practically worthless.

To arrive at a fair basis, depending upon the actual amount of zinc present, a new method has been proposed.[2] In this method the zinc or zinc iron alloy is removed by basic lead acetate. This method is very satisfactory where an accurate determination is desired and in the comparison of two unlike conduits. For routine factory testing it is not practicable since it involves several weighings with the balance. It may be used in occasionally checking up the copper sulphate tests. The actual amount of zinc present will not be indicative of the serviceability of the conduit for this will depend on the process.

From this description of the making of rigid conduit after leaving the tube mill the process is seen to be a product of the chemical engineer and electrochemist. Unfortunately they have not been instrumental in the early development of the processes that have only received their aid during the past decade.

How long the galvanized conduit will be supreme is a question of when some other cheap resistant coating may be applied to iron or some other resistant metal or alloy may be produced cheaply enough to compete with steel. The possibility of using a lead coating instead of zinc is an attractive proposition. Samples of such conduit have come to the notice of the writer from time to time and to all appearances should make an excellent conduit.

Chemical Engineering Laboratories, University of Wisconsin.

A paper presented in the Symposium on Electrodeposition of Metals, at the Twenty-Third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

THE ELECTRODEPOSITION OF COBALT AND NICKEL

By Oliver P. Watts.

In accordance with a request from the President of the Society, this paper was undertaken with the intention of including all solutions used for the deposition of cobalt and nickel. Lack of time, however, has prevented such a thorough search of the periodical literature as could insure this result. Because of the difficulty of making intelligible yet brief abstracts of lengthy metallurgical processes in which electrolysis is often but a single step, the various processes and patents which deal with the extraction of these metals from their ores have been omitted.

ELECTRODEPOSITION OF COBALT.

Cobalt and nickel present such striking similarities in both physical and chemical properties that it is not surprising to find similarities in their behavior under electrolysis. In this connection Langbein[1] says: "For plating with cobalt, the baths given under 'Nickeling' may be used by substituting for the nickel salt a corresponding quantity of cobalt salt."

Hollard et Bertiaux[2] says: "In our numerous analyses we have never found any difference in electrolytic properties between nickel and cobalt." Many other writers give similar testimony.

While there is a general agreement in regard to the similarity of conditions and solutions suitable for the electrodeposition of cobalt and nickel, there is the widest disagreement concerning the relative hardness, color, etc., of these metals, as shown by the quotations which follow:

Brochet[3] says: "Cobalting has been proposed in place of nickeling when a deposit of the greatest hardness is desired."

McMillan[4] says: "The deposit of cobalt is similar to that of nickel; it is equally brilliant, but is somewhat harder."

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[1] For references, see the end of the paper.

On the other hand, Langbein says: "Cobalt precipitated from its chloride solution does not yield a hard coating."

Watt[6] says: "When deposited by electrolysis under favorable conditions, cobalt is somewhat whiter than nickel, but acquires a warmer tone after being exposed to the air for some time." . . . "Gaiffe says that, when deposited from a solution of the double sulphate of cobalt and ammonium it is 'superior to nickel in hardness, tenacity and beauty of color.' Wahl remarks: 'The electro-deposits of this metal which we have seen equal, if they do not surpass, those of nickel in whiteness and brilliancy of lustre.' Electrolytic cobalt[7] is somewhat softer than nickel."

S. P. Thompson[8] finds that articles plated with cobalt tarnish much less quickly in the atmosphere of London than silver or nickel plate; while Watt[9] quotes Stolba to the effect that cobalt salts treated like nickel "yield metallic deposits of a steel gray color, less lustrous than nickel and more liable to tarnish." In the same article Watt says: "I have invariably found that, while cobalt admits of being burnished without difficulty with a steel burnisher, nickel yields but little to the tool."

In the account of the deposition of nickel many authorities will be quoted in regard to the extreme difficulty or impossibility of obtaining deposits of that metal more than a few hundredths of a millimeter in thickness. E. Bouant[10] says: "Electrolytic deposits of cobalt are easily obtained, even of very great thickness, so that the electrodeposition of cobalt is as easy as that of copper."

A partial explanation of the above contradictions is given by Watt:[9] "The whiteness of electro-deposited cobalt depends greatly upon the nature of the electrolyte employed. Again, the density of current influences the color of the deposit; the strength of the solution also greatly affects the color of the deposit." It is evident that not only is the color of the deposit influenced by these and other factors, such as temperature, acidity, alkalinity, etc., but also that the hardness, brittleness and other physical properties of both cobalt and nickel are dependent upon the conditions above mentioned.

ELECTROPLATING WITH COBALT.

Concerning cobalt plating solutions, Watt says:[9] "Nearly all those who have devised formulæ for cobalt baths for electrodeposition prefer to employ solutions which are either neutral or more or less alkaline, but, so far as I am aware, in no case acid. . . . I have found that certain solutions were greatly improved when put in a faintly acid condition. . . . In working solutions which are more or less acid some little care is necessary to prevent the film from stripping or peeling off the receiving surface."

For ease of comparison the original composition of the baths which follow has been re-calculated to the basis of grams of solid taken per liter of water, where they were not already expressed in this way. Current densities are given in amperes per square decimeter, and temperatures on the centigrade scale.

1. Becquerel's solution:[11] 37.5 grams of cobalt chloride, neutralized by ammonia or potassium hydroxide, gives a brilliant, white, hard and brittle deposit. A very weak current must be used.

2. G. W. Beardslee's solution[12] consists of 30 to 45 grams of cobalt chloride per liter of water, made very faintly alkaline with ammonia. He claims that this bath gives a thick deposit which is very white, exceedingly hard, tenaciously adherent and not liable to tarnish. "I do not, however, limit myself to the precise method or agents above described, but employ any others which will produce similar results in substantially the same manner. What I claim and desire to secure by letters patent is: Electroplating with the metal cobalt so as to form a useful coating of this metal that is tenacious, compact, adherent, and flexible, and of sufficient thickness to protect the surface upon which it is deposited." Although plating with cobalt had been known for thirty years, the United States Government at this late date seems to have turned the practice over exclusively to Mr. Beardslee.

3. Boettger's solution[11] consists of 400 g. cobalt chloride, 200 g. ammonium chloride, 200 g. ammonia. It is claimed to give a brilliant deposit.

4. Watt[11] (page 519) recommends 37.5 grams of cobalt chlo-

ride, without any additions, as giving good deposits at low current density, but states that heavy deposits become dull.

5. Another solution by Watt[11] (page 519) consists of 37.5 grams cobalt chloride and 22.5 grams of ammonium chloride per liter. This gives a very white and very bright deposit, but requires a smaller current than No. 4.

6. The substitution of an equal weight of sodium chloride for the ammonium chloride causes the deposit to continue bright longer than in bath No. 5.

7. E. D. Nagel[13] patents the following for plating with cobalt, nickel, or both metals in combination:

"Four hundred parts by weight of pure sulphate of the protoxide of nickel (or cobalt) is combined with 200 parts by weight of pure ammonia to form a double salt, which I dissolve in 6,000 parts of distilled water, and add 120 parts ammoniacal solution of specific gravity 0.909. A platinum anode is used, and the solution is heated to 38° C."

8. Watt[11] (page 354) gives 30 to 45 g. of the double sulphate of cobalt and ammonium, made alkaline by ammonia, and states that the solution gives a fine white deposit.

Isaac Adams[14] says: "I have found that a solution made and used in the manner described in the books will not produce such a continuous and uniform deposit of cobalt as is necessary for the successful and practical electroplating of metals with cobalt. . . . I have found, further, that the simple salts of cobalt, such as are recommended by Becquerel and others, are not such salts as can be used in practical electroplating with cobalt. I have found out, also, that the simple salts of cobalt, when associated with another electrolyte—such as the chloride of ammonium, or the sulphate of ammonia, or the chloride of magnesium, or the sulphate of magnesia—can be used so as to produce good results in practical cobalt-plating.

"I have found, further, that, in order to produce the best results, the cobalt solutions should, in use, be neutral, and (except in covering poorly conducting surfaces) in no case acid. I find, further, that when solutions of cobalt are used—such as are mentioned in Smee—and contain an excess of ammonia, they become changed, by contact with the air, into such salts of cobalt as are not suitable for practical electroplating with cobalt. I have found, further, that the electrodeposition of cobalt does not necessarily take place in solutions in which exist salts of alkalies—such as the nitrates of soda or potash, or free nitric acid."

Adams' solutions:[14]

9. 22.5 g cobalt chloride.
   15 g. ammonium chloride.

10. 22.5 g. cobalt chloride.
    15 g. magnesium chloride.

11. The sulphates of cobalt and ammonia.

12. The sulphates of cobalt and magnesia.

13. Watt[11] (page 354) gives 30 to 45 g. of cobalt ammonium sulphate, made alkaline by ammonia, and states that this gives a fine white deposit.

14. Watt[11] (page 518) also gives 37.5 cobalt sulphate per liter, and specifies a current density of 0.2 to 0.4 ampere per square decimeter.

15. Brochet[3] recommends 100 grams of the double sulphate of cobalt and ammonium, making 21 grams of cobalt per liter. Specific gravity 1.057. Specific resistance 22.1 ohms.

S. P. Thompson's[15] solutions:

16. 60 g. cobalt sulphate.
    30 g. magnesium sulphate.
    60 g. or less ammonium sulphate.

17. 100 g. double sulphate of cobalt and ammonium.
    50 g. magnesium sulphate.
    6.2 g. citric acid.
    12.5 g. ammonium carbonate.

These solutions are claimed to give "deposits of greater tenacity, density, and brilliance of tint, than have heretofore been obtainable with certainty." . . . "The solution for the deposition of cobalt may consist of the sulphate or chloride of cobalt, or of the double sulphate or chloride of cobalt and ammonium, to which has also been added the sulphate or chloride of magnesium, or other suitable soluble salt of magnesium, or a mixed soluble salt of magnesium and ammonium may be added to the solution of cobalt salts. Citrate of magnesium is a useful salt.

. . . Citrate of ammonium, or simply citric acid, may be added to the solution."

18. Maigne and Mathey[16] give:

28.6 g. cobalt chloride.
14.3 g. potassium cyanide.
143 g. sodium thiosulphate (hyposulphite).

The first two are dissolved separately, the solutions are mixed, the cobalt cyanide is washed, collected and dissolved in a solution of the thiosulphate in one liter of water.

19. The same authors (p. 334):

20 g. cobalt chloride.
10 g. potassium sulphocyanide.

20. Kayser's[17] solution:

67 grams cobalt sulphate.
67 grams ammonium sulphate.
33 grams boric acid per liter.

21. Langbein's[5] solutions consist of:

40 grams of the double sulphate of cobalt and ammonium.
20 grams boric acid.

At an E. M. F. of 2.5 to 2.75 volts, and a current density of 0.4 ampere per square decimeter, this bath is claimed to give a hard deposit suitable for electrotypes.

22. The solutions of Joseph Vandermersch[18] for the deposition of cobalt, nickel, copper, brass, manganese, cadmium, zinc and other metals are claimed to give deposits of any thickness and any weight. He says: "Heretofore in depositing nickel on iron and copper it has been possible to get only thin coatings (0.01 to 0.02 mm.). I obtain thick deposits by adding to a solution of nickel (or cobalt, etc.) sulphate as a base, one or several acids—benzoic, salicylic, boric, gallic, pyrogallic, and others of similar qualities—which gives a perfectly pure and white nickel deposit, but still in thin films only.

Therefore I add to the above bath 10 drops per liter, more or less, of sulphuric acid, and get deposits of any thickness and of any weight. I may also add sulphurous, perchloric, chloric, formic, lactic, acetic, or other acid instead of sulphuric and get a similar effect. But sulphuric acid is best.

The same results are obtained with cobalt.

The process applies not only to nickel sulphate, but also to nickel chloride, nickel nitrate and all other nickel salts.

Instead of benzoic acid, etc., any compounds of these acids may be used, *e. g.*, calcium benzoate, etc. The chlorides, bromides, iodides, or other compounds of these acids may be used instead.

In the second operation, the sulphuric, sulphurous, or other acid may be replaced by compounds of salts of these acids, *e. g.*, sulphates. The sulphuric, lactic and other acids may be replaced by any other acid, provided they contain oxygen, and not only acids may be used for this purpose, but also all bodies capable of being added to the bath, provided they contain oxygen, such as alcohols, ethers, aldehydes, gums, sugars, creosote, glycose, glycerine, etc.

The second operation may take place before the first, the same result being obtained.

Acids capable of furnishing in a single operation the deposit of required thickness may, if desired, be employed, *e. g.*, phosphoric, permanganic, manganic, or other acids which are highly oxygenated, and which, when added to the nickel salts of any kind, give an unlimited deposit; but this result is far from equaling that of benzoic, aromatic and oxygenated compounds, superoxygenated by another body as above described. . . . It is however in all cases required as a total result that the bath be so constituted that it forms an ether, an alcohol, or an oxygenated acid, or an oxygenated compound in such a manner that hydrogen produced in consequence of decomposition of water by the electric current, is absorbed by the composition of the bath."

23. M. Kugel[19] deposits "tough, rollable, cobalt or nickel of any desired thickness by adding to any desired nickel-salt (or cobalt) solution, a strong mineral acid which is not changed in its chemical composition by the current. The most suitable acids are perchloric, perbromic and sulphuric. The acid concentration ranges from 2 to 20 percent normal or 1 to 10 grams per liter. The temperature must be kept above 30° C., and

current densities of 10 to 20 amperes per square decimeter may be used without harm to the deposit,—"a correspondingly lively movement of the electrolyte, in order to mix well, being of course necessary."

24. Alexander Classen[20] deposits more rapidly and compactly than has heretofore been possible, the metals cobalt, nickel, copper, iron, zinc, cadmium, bismuth, lead, tin, and antimony, by converting solutions of the chlorides or sulphates, by means of a solution of neutral potassium oxalate, into soluble potassium double salts. A suitable bath for cobalt consists of:

50 grams cobalt sulphate.
80 grams ammonium oxalate.
20 grams potassium oxalate.
1 liter water.

The baths are used hot.

25. E. Placet and J. Bonnet[21] claim the employment of polyatomic acid salts, alone or mixed with neutral salts, to obtain deposits of cobalt, nickel, chromium, aluminum, copper, iron, tungsten, molybdenum, antimony, tin, silver, etc., and the alloys of these metals electrolytically. They specify particularly the use of the bisulphates, biphosphates and biacetates" (?), and give the following bath for the deposition of chromium:

100 to 150 g. chrome alum.
100 to 150 g. acid sulphate of potassium, sodium, or ammonium, per liter of water.

It is evident at a glance that several of the metals listed cannot be deposited from these baths, and there is, from the chemical standpoint, no reason why the use of an acid salt should prove any more beneficial than equivalent amounts of the free acid and normal salt. The substitution of acid salts for free acid is claimed as the particular merit of the invention.

Watt[22] experimented with many different solutions for the deposition of cobalt. Those which he considered best were published in his book, and have already been mentioned in this paper. The others follow:

26. Cobalt acetate faintly acid gives a deposit which, at the end of an hour, is very bright, and pure white.

27. Cobalt and ammonium acetates gives a dull, brownish deposit.

28. The same as No. 27, made slightly alkaline, gives the same result as No. 27.

29. The same as No. 27, strongly acidified by acetic acid, gives a brilliant white deposit for two hours.

30. Cobalt citrate, acidified, gives a bright, but slightly yellowish deposit, and good anode corrosion.

31. Cobalt and ammonium citrates, neutral, gives a dull and dark deposit.

32. The same as No. 31, but acidified, gives a bright deposit. After 12 hours deposition the deposit is dark gray and nodular. The single citrate is better.

33. Cobalt borate, neutral, gives a bright and very white deposit, which finally loses its lustre and becomes dull. Gas is evolved at the cathode.

34. Cobalt tartrate, neutral, gives a deposit which turns black at the end of 10 minutes.

35. Cobalt tartrate, acidified, gives a bright and white deposit, and good anode corrosion.

36. Cobalt and potassium tartrates made by dissolving cobalt carbonate in a hot solution of cream of tartar, gives a white deposit, streaky on the front, but good on the back of the cathode. The result was the same in three different trials.

37. Cobalt phosphate gives only hydrogen at low current density. At higher currents a good deposit is obtained and much hydrogen is evolved.

38. Cobalt carbonate dissolved in a solution of ammonium carbonate gives at first a brilliant white deposit, becoming dull in 10 minutes. There is a vigorous evolution of hydrogen.

39. Cobalt salicylate gives a dark, but polished deposit.

40. Cobalt nitrate, a weak solution, gives on brass a malachite-green deposit of great beauty, which falls from the plate in transparent flakes.

41. Cobalt and ammonium nitrates gave a thick green deposit on brass.

42. Cobalt carbonate and sodium pyrophosphate were heated together, producing a solution of faint pink color. This gives a very adherent, dark deposit along with much hydrogen.

43. 42 g. cobalt sulphate and 30 g. potassium sulphate per liter, heated, gives a bright deposit, which peels off in 20 minutes Gas is evolved at both electrodes.

44. 42 g. cobalt sulphate and 18 g. magnesium sulphate per liter gives a bright and remarkably white deposit which becomes dull after a long time. No gas is evolved.

45. Excess of oxalic acid, added to a solution of cobalt sulphate, gives no deposit at low currents, but a bright deposit with evolution of hydrogen at high current.

46. Cobalt oxalate digested with a warm solution of ammonium carbonate gives no deposit of metal with one or two Daniell cells, but with three cells gives a brilliant, silver white deposit, and much hydrogen. In 15 minutes the deposit is streaked and in 30 minutes it is covered with dark streaks except on the edges.

47. Cobalt carbonate and potassium carbonate evolves much gas and yields a dark, smooth deposit of cobalt.

48. Cobalt sulphate and excess of ammonia gives a dark deposit. No gas is evolved.

49. Cobalt hydrate is very sparingly soluble in a strong solution of potassium cyanide, and three Daniell cells give only a trifling film of cobalt, and much gas.

50. Cobalt sulphocyanide. Potassium sulphocyanide, dissolved in alcohol, was added to a solution of cobalt sulphate, the clear solution decanted from the potassium sulphate, evaporated to dryness, and the residue dissolved in water. Three cells gave a slight deposit of cobalt on brass.

Many "per-salts" were tried. Calcium hypochlorite solution was added to a solution of cobalt sulphate, and the precipitate was washed and dissolved in the desired acid.

51. Cobalt per-citrate, tartrate, oxalate, acetate, chloride, sulphate, phosphate and borate all give bright, adherent deposits with three cells. Gas is evolved.

Gaïffe[5] has proposed the use of cobalt instead of nickel for facing valuable electrotypes on account of the complete solubility of the former metal in dilute sulphuric acid, thus permitting the removal of the film of cobalt and its replacement by a fresh deposit without injury to the copper.

DEPOSITION OF AN ALLOY OF COBALT AND NICKEL.

Owing to the difficulty of separating cobalt and nickel electrolytically as well as chemically, it should be an easy matter to deposit an alloy of the two metals. Nagel[23] deposits an alloy of the metals from a mixed solution of their ammonium double sulphates, made alkaline by ammonia, and heated to 40° C. He uses a platinum anode.

A similar trial was made in the experimental laboratory of the Brass World[24] for the purpose of getting a deposit harder than nickel, "since alloys are always harder than pure metals." The electrolyte consisted of a solution of 70 parts nickel sulphate, 30 parts cobalt sulphate, with ammonium sulphate sufficient to form double salts, acidified by boric acid and made up to 6° Bé (sp. g. 1.0432). E. M. F., 2 volts. The deposit contained both nickel and cobalt, and was very hard. It was suggested for facing electrotypes, as the electrolytic iron commonly used, rusts.

The writer found in his filing cabinet another bath, from an unknown source, which is claimed to deposit the hardest alloy of the two metals, consisting of 75 percent nickel and 25 percent cobalt. The bath consists of:

Nickel ammonium sulphate	147	grams
Cobalt ammonium sulphate	40	"
Ammonium sulphate	56	"
Water	1,000	"

The following bath is given by Langbein[5] (p. 307):

Nickel ammonium sulphate	53	grams
Cobalt ammonium sulphate	13	"
Boric acid, cryst	22	"
Water	1,000	"

The only obstacle to the general use of cobalt in place of nickel for plating appears to be its high price. Rumors have frequently reached us that cobalt was about to be put on the market at the same price as nickel. Fink[25], in 1912, says that cobalt can be bought for less than one-third what it cost ten years ago, yet in that same year the metal purchased for use in the writer's laboratory cost $5 per pound, just a dollar higher than it cost two years before, while in 1889 Watt, in England, bought the metal in the form of anodes for only $3.90 per pound.

In an account of the Cobalt mining district Gibson[26] says: "The enforced production of cobalt from these mines has brought about a reduction in the price of cobalt oxide and is likely to lead to still further reductions."

ELECTROCHEMICAL ANALYSIS.

Solutions for Estimation of Cobalt:

52. The double oxalate of ammonium and cobalt according to Classen:[27]

0.3 g. cobalt, present as sulphate.
4 to 5 g. ammonium oxalate.
120 c.c. in volume.
1 ampere per square decimeter.
2½ to 3½ hours at 60 to 70° C.
3.1 to 3.8 volts.

Perkin[28] (page 98) states that the deposit contains carbon.

53. Solution of Fresenius and Bergmann. Classen[27] gives:

0.5 g. cobalt as sulphate.
5 to 6 g. ammonium sulphate.
40 c.c. ammonia (s. g. 0.96).
150 to 170 c.c. in volume.
0.7 ampere at 20° to 25° C.

The presence of chlorides, nitrates, fixed organic acids and magnesium compounds acts injuriously. Neumann[29] (page 113) states that this is the only solution employed in practical analysis.

54. Cobalt and ammonium chlorides have been proposed by Oettel. According to Neumann[29] (page 112) a suitable solution is:

1 g. cobalt chloride (0.248 g. cobalt).
5 g. ammonium chloride.
30 c.c. ammonia.
150 c.c. total volume.
1.5 amperes.
5 to 6 hours.

For the determination of cobalt a larger amount of ammonium chloride is required than in the case of nickel. The presence of nitrates is harmful.

55. Cobalt potassium cyanide is stated by Smith[30] (p. 129) to give complete precipitation. He adds 0.1 g. more of potassium cyanide than is necessary for precipitation and re-solution.

2 g. ammonium carbonate.
150 c.c. in volume.
1.5 amperes at 60° C.
6 to 6.5 volts.
3½ hours.

Neumann[29] (p. 113) states that it is impossible to secure a quantitative separation of cobalt from solutions containing an excess of potassium cyanide.

56. Neumann[29] (p. 112) states that exact results are given by:

1 g. cobalt sulphate (0.21 g. cobalt).
15 g. ammonium carbonate.
2 to 4 c.c. ammonia.
150 c.c. total volume.
1 ampere at 3.7 to 3.9 volts.
2½ to 3½ hours at 50° to 60° C.

57. Perkin[28] (p. 97) adds 3 g. ammonium tartrate to the solution of the cobalt salt, begins electrolysis at 0.2 ampere, and after an hour increases the current to 1 ampere per square decimeter. Time, 4 to 5 hours. The deposit often has a brilliant, burnished appearance. The results are slightly high, owing to a small amount of carbon being deposited with the cobalt.

58. Perkin[28] (p. 98) claims that the most accurate results are obtained by adding to the solution of the cobalt salt:

2 c.c. of a 5 percent solution of phosphoric acid,
20 to 25 c.c. of a 10 percent solution of di-hydrogen, sodium phosphate, stirring during the latter addition to prevent precipitation of a double phosphate. Hydrogen di-sodium phosphate cannot be used on account of the formation of an almost insoluble cobalt salt. Electrolysis should begin at 0.2 ampere in the cold solution. After an hour the current may be raised to 1 ampere and the solution warmed to 60° C. If a brown deposit forms on the anode it may be removed by adding 0.1 to

0.2 gram of hydroxylamine sulphate or chloride. Formaldehyde acts more slowly. Time, 4 to 6 hours. The deposit is usually brilliant.

59. Vortmann[30] adds tartaric or citric acid and an excess of sodium carbonate to the solution of the cobalt or nickel salt, then electrolyzes at 0.3 to 0.4 ampere. The deposit may contain traces of carbon.

60. Smith[30] (p. 129) obtains perfectly satisfactory results by adding an alkaline acetate to the cobalt solution. For rapid precipitation with a rotating anode he uses (p. 135):

Cobalt sulphate = 0.331 g. metal.
25 c.c. ammonia.
10 c.c. acetic acid, 20 percent.
5 amperes at 6 volts for 25 minutes.

The deposit is brilliant, and there is no precipitation on the anode.

61. Sodium formate is a very satisfactory electrolyte.[30]

Cobalt sulphate = 0.3535 g. metal.
2.5 g. sodium carbonate.
4 c.c. formic acid, 98 percent.

Heat to boiling, remove the flame and electrolyze with rotating anode at 5 amperes and 6 volts. Time, 30 minutes. The deposited cobalt is brilliant. A slight anode deposit may be removed by a few drops of a mixture of 5 c.c. glycerine, 45 c.c. alcohol, 50 c.c. water. A few drops of formic acid should be added from time to time to prevent the solution from becoming alkaline.

62. Lactic acid or a lactate makes an excellent electrolyte.[30] No precipitation occurs on the anode, and the cobalt deposit is exceedingly brilliant and adherent. A large excess of lactic acid retards precipitation.

2.2 g. sodium carbonate.
5 c.c. lactic acid, conc.
5 amperes at 8 volts precipitates 0.32 g. cobalt in 25 minutes.

63. Ammonium lactate is even superior to the preceding electrolyte.[80]

0.331 g. cobalt as sulphate.
30 c.c. ammonia.
7 c.c. lactic acid.
125 c.c. in volume.
6 amperes at 5 volts.
25 minutes is sufficient for complete precipitation.

64. Smith[80] uses a mercury cathode for the rapid determination of cobalt from its sulphate or chloride. At 4 amperes, 6 volts and 1,000 R. P. M. of anode, 0.35 g. of cobalt is precipitated in 15 minutes. It is necessary to add 10 c.c. of toluene or xylene to the chloride solution to prevent attack of the platinum anode.

65. Ammonium succinate can be employed, but some carbon is apt to be precipitated with the cobalt. Sodium succinate should not be used.

Separation of Cobalt and Nickel: Several solutions have been proposed for the difficult problem of separating cobalt and nickel by electrolysis.

66. Basse and Selva[31] add to the neutral or feebly acid solution of the metals an organic substance, such as tartaric or citric acid, glycerine, dextrose, etc., to prevent precipitation of the metals by excess of alkali; a large excess of caustic soda is added, and the solution is electrolyzed at a current of 0.3 to 1 ampere (per square decimeter?). Cobalt, iron and zinc are deposited, while nickel remains in solution. Ammonium carbonate is then added to the solution, and the nickel is deposited electrolytically.

67. G. Vortmann[32] adds to a neutral solution of the sulphates of the metals alkali or alkali-earth sulphates, and about 1 percent sodium chloride, and electrolyzes with frequent reversals of the current. Nickel remains in solution, and cobalt separates as hydroxide.

Neumann[29] (p. 215) says that this method is not suited to quantitative analysis.

68. Vortmann[29] also proposes to electrolyze solutions containing tartrates of the alkalies and a little potassium iodide. Neumann condemns this process also, and states that there is no reliable method for the electrolytic separation of cobalt and nickel.

Classen[27] (p. 241) ascribes to Vortmann the use of a solution containing sodium potassium tartrate, strongly alkaline by sodium hydroxide, but says that the essential data for repeating his experiments are lacking.

Bancroft[33] tested Vortmann's separation in an alkaline tartrate solution. He states that in this solution "the decomposition voltage of cobalt is about one volt lower than that of nickel." He finds that cobalt peroxide tends to precipitate at the anode, but this can be remedied by a high current density at the anode or by the addition of a few drops of concentrated nitric acid. In the latter case a little nickel peroxide may precipitate at the anode at low current densities. With a Classen dish as cathode and an E. M. F. of 1.9 to 2.0 volts between the electrodes, a good deposit of cobalt is obtained which gives no test for nickel, but some cobalt is always left in solution. If the voltage is raised to take out the last traces of cobalt, some nickel is also deposited. Heating the solution makes matters worse. The addition of potassium iodide, as recommended by Vortmann, is unsatisfactory. Addition of hydroxylamine sulphate, hydrogen peroxide, formaldehyde or sodium bisulphite helps a little, but does not remove the last traces of cobalt in a reasonable time. Nickel peroxide precipitates more readily the more carbonate and the less tartrate there is present, but, as cobalt peroxide tends to come down with the nickel peroxide, it is best to deposit nearly all the cobalt first, then to add sodium carbonate, and electrolyze with low current density at the anode. Proceeding in this way it was possible to separate one gram of cobalt from 0.1 g. nickel in eight days' electrolysis.

69. A. Coehn and E. Salomon[31] electrolyze neutral solutions of the sulphates or nitrates of cobalt and nickel, when the cobalt separates at the anode as peroxide.

70. A. Coehn, in a later patent,[35] by the addition of a persulphate to the former electrolyte, secures the precipitation of cobalt alone.

71. A. Coehn and E. Salomon,[36] to prevent cobalt and nickel from precipitating on the cathode when carrying out the above process, add to the solutions some metal more easily precipitated, *e. g.*, copper. In this case cobalt precipitates as peroxide on the anode, nickel remains in solution, and copper is deposited on the

cathode. Nitrate and sulphate solutions are well adapted to the process, which works better at elevated temperatures, e. g., 60° C. E. M. F. 1.5 to 2 volts. Current 0.1 ampere per square decimeter.

72. Perkin[28] (p. 170) says: "Many attempts have been made to separate cobalt and nickel electrolytically, but none of the methods so far published can be said to give very satisfactory results. The only method which can be at all recommended is that of A. Coehn and M. Glaser:[37] "The process depends upon the simultaneous deposition of the two metals—nickel at the cathode and cobalt at the anode. . . . The cobalt must be prevented from being precipitated on the cathode. Now, as hydrogen is only deposited 0.22 volt higher (lower?) than cobalt, too high an E. M. F. must not be employed, or else one must employ some method in which the deposition takes place at a lower potential than that at which the H ions are discharged, *e. g.*, the addition of a carbonate to the solution." To the neutral solution, containing not more than 0.1 g. cobalt, add 0.1 to 0.2 g. potassium dichromate and 3 to 4 g. potassium sulphate, make up to 500 c.c., and electrolyze at 0.10 to 0.15 ampere for 10 hours. E. M. F. 2.3 to 2.4 volts. All the nickel is deposited as metal at the cathode, and all the cobalt as peroxide at the anode. The peroxide is dissolved in acid, neutralized and precipitated as metal.

73. Balachowsky's method. Classen[27] gives:

0.3 g. of the metals in acetic acid solution.
3 g. ammonium sulphocyanide.
1 g. urea.

Ammonia to neutralize the free acid.

0.8 ampere per sq. decimeter, 1.0 volt, at 70 °to 80° C. Time, 1½ hours to precipitate the nickel. This contains sulphur, and should be dissolved in nitric acid, filtered and re-precipitated. The solution containing cobalt is boiled with nitric acid, filtered, and the cobalt deposited by any regular method.

Smith[30] (p. 266) uses:

10 g. ammonium sulphocyanide.
3 g. urea.
300 to 350 c.c. total volume.

After removal of the nickel the solution containing cobalt is evaporated to dryness several times with nitric acid, and the residue taken up with water, before depositing the metal.

74. Method of Alvarez.[38] The salts of cobalt and nickel are dissolved in cold water, recently boiled, and saturated at 0° C. with sulphur dioxide, forming a yellow cobalto-cyanide, $Ni_2CO(CN)_6$, which becomes green after washing and drying. Dissolve 0.5 g. of this salt in 100 c.c. of water, add 40 c.c. of ammonia of sp. g. 0.927 and 5 g. of ammonium sulphate. Electrolyze at 4 amperes per square decimeter and 3.4 to 4 volts for 2 hours. A brilliant deposit of nickel is obtained, free from cobalt, but containing carbon.

At 50 to 60° C., 1 ampere at 3.8 volts, in one hour precipitates both metals from a solution of:

1 gram of $Ni_2Co(CN)_6$ in 100 c.c. water.
50 c.c. ammonia.
10 g. ammonium sulphate.

P. Brulylants[39] criticises the method as not detailed enough for successful use. He obtains both metals in the deposit and also in the residual solution.

Smith[30] obtained unsatisfactory results with this process.

To sum up, it appears that all electrolytic methods so far devised for separating cobalt and nickel fail in the hands of all save their inventors.

ELECTRODEPOSITION OF NICKEL.

The quotations which follow give the opinions of different authorities upon the nature of electro-deposited nickel, and some of the difficulties encountered in plating with this metal.

Langbein[5] (page 246) says: "Hot fats strongly attack nickel, while vinegar, beer, mustard, tea, and other infusions produce stains; hence the nickeling of culinary utensils or the use of nickel-plated sheet iron for that purpose cannot be recommended." Bouant[10] (page 186): "After having considered nickel as dangerous in the preparation of food, it is now recognized, on the contrary, to be harmless. Nothing prevents the extension of nickeling to utensils of copper, an operation doubtless more expensive than tinning, but giving much more durable results."

"To decrease the resistance of the nickel solutions, conducting salts are added to them, which are also partly decomposed by the current. . . . The use of sodium acetate, barium oxalate, ammonium nitrate, ammonium-alum, etc., we consider unsuitable, and partly injurious, and are of the opinion that with few exceptions potassium, sodium, ammonia, or magnesia, are best for bases of the conducting salts. The presence of a small amount of free acid effects without doubt the reduction of a whiter nickel than is the case with a neutral or alkaline solution. Hence a slightly acid reaction, due to the presence of citric acid, etc., with the exclusion of the strong acids of the metalloids can be highly recommended. . . . An alkaline reaction of nickel baths is absolutely detrimental."—Langbein.[5]

"Lowering of the acidity, and elevation of the temperature, current density and nickel content of the bath tend to produce a fine-grained and matte deposit. Addition of alkalies and salts of magnesium have a beneficial effect. Addition of ammonium salts hinder the production of thick deposits. . . . Deposits from chloride solutions are always crystalline and coarser grained than those from sulphate solutions. Their hardness is about the same. The observation that the deposit from a chloride solution deteriorates more readily than one from a sulphate solution is explained by the difference in fineness of grain. In the presence of magnesium sulphate, the deposit contains 0.2 to 0.4 percent magnesium. This deposit is no harder than ordinary nickel plate, but is very flexible and well suited to the production of electrotypes. A bath containing magnesium salts ought to be more acid than other baths, to prevent the deposition of oxide. A higher acid content explains the fact that nickel deposited from solutions containing ethyl-sulphuric acid are very hard. Sulphate solutions give more flexible deposits than chloride baths. Deposits from solutions containing sodium salts are especially flexible, probably because of their finer grain. Iron renders the nickel deposit very brittle."—K. Engermann.[40]

"A solution of chloride of nickel is used as electrolyte. By this method it is possible to prevent the contamination of electrolytic nickel with sulphur, as would be the case were a sulphate solution used as the electrolyte."[41]

In spite of the recommendation by various experimenters of baths containing only nickel salts, there is a very general belief that for a successful nickel plating bath the salt of some other metal must be present, to form a double salt.

"Indeed it has been heretofore held as impracticable to nickel-plate with a single salt."—J. Yates.[37] "On the other hand, the simple acid salts of nickel have not hitherto been found to answer for the purpose of electrodeposition, from the fact that such solutions refuse to yield a reguline or cohesive deposit of metallic nickel."—J. Powell.[42]

Brass World[43] published a number of experiments with nickel sulphate solutions, made by an experienced practical plater to settle the question of whether or not single nickel salts can be used for plating. The conclusion is, "It is apparent, therefore, that single nickel salts cannot be used alone for plating."

The writer cannot subscribe to this result, for in 1904 he tried the deposition of nickel from a solution of 140 grams of commercial nickel sulphate per liter. Several trials gave black deposits, but finally a good deposit resulted. The solution was slightly diluted and 4 drops of sulphuric acid added. At the end of 38 hours electrolysis, with a current density of 5 amperes per square decimeter, falling to zero at the end, because of the complete solution of the anode, the deposit was excellent. Another trial of the same bath for 8 hours at 6 amperes per square decimeter gave a deposit of excellent appearance and firmly adherent. The current efficiency, however, was low.

Brochet[3] (page 229) says: "At the cathode the ion $Ni^{\cdot\cdot}$ ought to be discharged, and the metal pass into the molecular state and be deposited. In reality the reaction is much more complex, and the electrolysis of a pure salt of nickel generally gives poor results. With the sulphate there is the production of a slight black deposit, accompanied by an abundant evolution of hydrogen. With the chloride there is a deposit of nickel hydrate mixed with the oxychloride, and a similar evolution of hydrogen. A mixture of the sulphate and chloride of nickel gives much better results. The addition of an alkali-salt: potassium, sodium, ammonium, seems to be necessary to secure a good deposit; but then the series of reactions is entirely different. A complex salt is formed."

"It is a practice commonly adopted to momentarily use a high

E. M. F. until the work is just covered with nickel, and then to reduce the E. M. F.. This is called "striking," and 5 to 6 volts may for a few moments be used for this purpose. The E. M. F. is then quickly reduced to 2 or 3 volts."—Field.[44]

It is well known that there is greater difficulty in obtaining a satisfactory deposit of nickel on some metals than on others. Sackur[45] contends that: "A metal is more difficult to nickel, the farther its potential lies from that of nickel. Zinc, for example, possesses a higher electromotive force than brass, and this, in turn, more than iron. Potassium cyanide solution has a lower E. M. F. of decomposition than nickel chloride, and this again smaller than the sulphate. Good nickeling depends only on the choice of the right E. M. F., not upon the composition of the bath." This is an excellent illustration of the pitfalls of error which lurk within the covers of our electrochemical authorities—errors all the more insidious from the grain of truth in them.

One trouble, which was encountered in the earliest commercial nickel-plating, and it seems to have persisted to the present, in spite of the numerous remedies proposed, is the tendency of the deposit to peel off from the underlying metal.

In 1871 Keith[46] says: "The objection to nickel-plated goods thus far is that the deposit is so brittle that it cannot be bent, nor on many articles stand necessary wear even if not bent, and that it will also scale or peel off." In spite of the cure for this trouble announced by Keith, Peters[45] (page 153) writing in 1900, says: "When deposits of electrolytic nickel exceed a fraction of a millimeter in thickness they usually separate from the cathode in thin brittle leaves."

"The usual methods of electrolytically separating nickel from aqueous solutions of its salts do not permit of the production of deposits of more than one-hundredth of a millimeter in thickness, since with a longer continuance of nickeling the layer formed comes off in thin scales. This disadvantage can be avoided by using a heated electrolyte, as has been long known; but a thick nickel plate thus produced shows a crystalline structure as compared with the rolled nickel of commerce, is very brittle, and is therefore not suited for direct manufacture or technical utilization without being first melted over again."—M. Kugel.[20]

Turning from patentees, who may be regarded as prejudiced witnesses, we find D. H. Browne,[47] saying: "The bug-bear encountered by all who attempt to produce sheets of nickel thicker than that used by nickel platers has been the tendency of nickel to crack and curl off in rolls, like wood shavings."

"Two of the difficulties which are often encountered in electroplating (with nickel) are either the formation of gray pulverulent deposits, or else the deposit does not adhere, but cracks and curls from the cathode. . . . The former difficulty has been found to be due to employing too high current density and too high E. M. F., whereas the latter difficulty is due to the electrolytes being too acid and at too low a temperature, or else to a film of grease or dirt on the cathode."—E. F. Kern.[48]

"Nickel well deposited is extremely hard, so hard that it cannot be burnished, and is somewhat brittle. Thick coatings are especially liable to flake off in use, unless exceptionally well deposited, and even the thinnest films will part from surfaces which are not chemically clean."—McMillan[4] (p. 217).

The cause of this brittleness and peeling of nickel deposits is indicated in the following quotations: "Using a neutral or ammoniacal solution of pure sulphate of nickel there is an abundant disengagement of gas from the anode; soon followed by an increasing production of hydrogen at the cathode, and the deposited nickel becomes detached, curling up like wood shavings."—M. Gresy.[49]

"The deposition of nickel requires a neutral bath. The presence of much free acid causes deposition of hydrogen, and the deposit of nickel in scales. Peeling of the nickel deposit is due to occlusion of hydrogen, which always exists in deposits of nickel and cobalt."—A. Brochet.[50]

"It is commonly considered that the curling up of electrolytic nickel plate is due to the co-deposited hydrogen."—Schoch.[51]

"The difficulty of obtaining thick nickel deposits is due to hydrogen evolved along with the metal and absorbed by it, causing brittleness."—A. Hollard.[52]

Another trouble occasionally referred to is the formation of pits on the surface of the deposit.

"The trouble you experience from dark and pitted deposits is due to occluded hydrogen. This trouble develops when the solution is low in metal and hydrogen gas forms very rapidly upon the surface of the articles being plated. This gas theoretically burns holes in the deposit, causing the pitting noticed."[53]

"The occlusion of hydrogen tends to make the deposit somewhat brittle, and more or less porous, and hydrogen gas clings to the surface of the deposited metal in the form of very fine bubbles, thereby making the surface more or less warty and rough. . . . By maintaining in the bath a small amount of material which will combine with free hydrogen, *e. g.*, chlorine, the occlusion of hydrogen, etc., is prevented. . . . The chlorine may be introduced as a gas, by adding fresh bath saturated with chlorine, or in case of a chloride electrolyte by using a small insoluble anode to which a portion of the current is shunted. Free bromine may be used, but gives inferior results."—T. A. Edison.[54]

Photographs showing such pitting of iron[55] and nickel[56] deposits have been published.

The remedies most frequently proposed for the curling and brittleness of electrolytic deposits of nickel are strict neutrality of the bath, and electrolysis at high temperatures, varying between 30° and 100° C. H. J. Brownell[57] secures a deposit of nickel which will stand drawing, bending, spinning, etc., of the plated metal. "The article to be plated being heated by immersion in water or otherwise to a temperature of nearly 100° C. (212° F.), and then subjected to a hot nickel-plating bath." Foerster,[58] by heating from 50° to 90° C. an absolutely neutral bath containing 140 g. nickel sulphate per liter, obtained deposits 0.5 to 1.0 mm. in thickness. The current density was 2 to 2.5 amperes per $dm.^2$ Other methods of preventing the curling of nickel, depending on the addition of particular substances to the electrolyte, will be mentioned later.

Purity of Nickel Anodes.

Calhane and Gammage,[59] analyzed commercial anodes from two different establishments and found 7.57 and 7.52 percent iron in them, and 92 percent nickel. Using these anodes, the deposit always contained iron, varying in amount between 0.07 and 0.75 percent.

The following is a formula given for the making of nickel anodes:[60] 92 parts nickel, 4 parts tin, 4 parts old files.

O. W. Brown[61] finds copper present in a nickel anode: "The presence of the copper, rather than being a detriment, seems to be advantageous in allowing a high anode current density to be used.

"Commercial nickel anodes contain, in addition to nickel, iron, tin and carbon. These are introduced intentionally to render the anode 'soft,' *i. e.*, so that it will dissolve easily in the solution during plating."[62]

Since such anodes are largely used in this country it is evident that much of the nickel plate produced here contains a small amount of iron. It is to this iron that Bancroft[63] ascribes the ready rusting of nickel-plated objects when exposed to the weather: ". . . All our nickel plate contains iron. I am confirmed in that belief by the fact that the nickel-plating on the Weston instruments, which I assume to be as good as any that would be put on the market, rusts red in the laboratory. I take it that this is due to iron in the nickel plate. . . . If a bicycle is left out over night it will rust." The writer does not regard the above allegations as proved until rust has formed on such nickel plate deposited on copper or some other surface which is in itself entirely free from iron.

Passivity of Nickel Anodes.

It has long been known that rolled nickel anodes do not dissolve satisfactorily in the standard plating solution, nickel ammonium sulphate. This phenomenon was brought to the attention of this Society by O. W. Brown.[64] Brochet[3] (page 228) says: "Nickel is a passive metal, that is to say that to a certain degree and under certain conditions it dissolves incompletely and acts as a noble metal—as an insoluble anode. Sulphuric acid is then formed at the anode, and nickel dissolves in an amount less than that required by Faraday's law." Speaking of nickel anodes, McMillan[4] (page 222) says: "Nickel anodes must be as pure as it is possible to obtain them. They are to be had cast or rolled. Cast anodes being the more readily soluble are more likely to neutralize the acid set free by electrolysis at the anode, and hence the natural tendency of the (ammoniacal) nickel bath to become alkaline asserts itself. Rolled anodes are more likely, by insufficiently neutralizing the acid, to cause the bath to become acid." Bancroft[63] points out that a pure nickel anode may be made to corrode satisfactorily in nickel ammonium sulphate by adding to the solution a small percentage of nickel chloride or ammonium chloride. He recommends the use of anodes of pure nickel and the complete elimination of iron from the nickel bath. Brochet[65] says: "The greater or less passivity of the anode depends on the physical nature of the metal, *i. e.*, the hammering or rolling to which it has been subjected, not on its purity."

On the contrary, Kern[48] says: "Another cause of gassing is the use of pure metal anodes in nickel-ammonium sulphate electrolyte, as the pure metal does not readily dissolve. However, pure nickel anodes may be successfully used in this electrolyte if a small amount of chloride salt is added, the presence of which causes the anode current efficiency to approximate 100 percent." Langbein[5] (pages 247 and 254) objects to the addition of chlorides or nitrates to baths for nickeling iron: "Iron objects nickeled in such a bath come out faultless, but in a short time, even if stored in a dry place, portions of the nickel layer will be observed to peel off, and by closely examining them it will be seen that under the deposit a layer of rust has formed which actually tears the nickel off." E. Weston[66] says: "It has been found that the solution of the double chloride of nickel and ammonium is better adapted for coating iron with nickel than the double sulphate solution, the latter answering better for brass."

In the electrolytic refining of iron the writer found that deposits from a chloride electrolyte rusted very much worse than those obtained from a solution containing only sulphates.

NICKEL PLATING BATHS.

For convenience the baths will be classified as follows:

I. Baths containing single salts of nickel.
II. Baths containing double salts.
III. Miscellaneous baths.
IV. Baths for deposition of malleable nickel.
V. Baths producing thick deposits.
VI. Agents for the production of smooth deposits.
VII. Nickel electrotypes.
VIII. The nickeling of zinc.

I. Baths Containing Single Salts of Nickel.

a. Neutral Baths:

Under this title will be grouped the baths formed by simple solution of the nickel salt without rendering it distinctly acid or alkaline, as well as those baths whose neutrality is specifically stated.

75. Yates' acetate solution.[67] Nickel acetate is dissolved in water to a strength of 8° or 10° Bé. (1.058 to 1.074 sp. g.). It is claimed to have the advantage over other solutions of a larger proportion of metal of not being subject to the irregular decompositions which render the continued operation of other baths so difficult, and to permit of direct nickeling on metals which it has heretofore been impracticable to nickel without a previous coating of copper. Plate steel, cast and wrought iron are mentioned as examples of this. With care, zinc may also be nickeled directly in this bath.

In referring to the fifty different nickel baths tried by Alexander Watt,[68] a number placed in parenthesis after the title of the bath indicates the numbering in his paper.

76. Watt's acetate bath (1). This consisted of 120 grams of neutral nickel acetate per liter. At a current density of 2.4 amperes per square decimeter a uniform but somewhat dark deposit was obtained. At the end of an hour's deposition a steel burnisher was applied, which brightened the surface, showing that the metal was softer than that obtained from the ordinary double sulphate solution.

77. Watt's[68] nickel benzoate solution (46). This solution yields a bright deposit, soft enough to be burnished.

78. Watt's[68] nickel borate solution (48). This yields a white deposit.

79. Nickel chloride solution[68] (22). 15 grams of nickel chloride per liter gave a brisk evolution of hydrogen and a deposit of metal not quite so white nor so fully adherent as the deposit from the double sulphate.

80. Nickel citrate solution[68] (6). This was prepared like most of the other salts of this set of experiments, by digesting moist nickel carbonate with a hot solution of the acid. The first

deposit was not of satisfactory whiteness, but this was improved by increasing the current.

81. Nickel lactate[68] (12). This salt is readily soluble, and gives a deposit of fairly good color.

82. Nickel nitrate[68] (16). Nickel carbonate was dissolved in nitric acid diluted with two volumes of water until a neutral solution was obtained. Neither a deposit of metal nor of hydrogen was obtained with one, two or even three Daniell cells in series. There was a slight evolution of oxygen at the anode.

83. J. Mathieu's propionate solution.[69] He used a solution of nickel propionate of about 5° Bé. (sp. g. 1.0357). No results are stated, nor are any claims made in regard to the superlative excellence of the product.

84. Nickel salicylate[68] (47). This gives a white deposit.

85. Nickel sulphate[68] (18). A solution was made by dissolving 100 grams of the crystals per liter of water. The deposit was of good color, but was not so adherent as deposits from the double sulphate of nickel and ammonia.

86. Nickel sulphate, neutralized by lime or calcium carbonate.[70] To 100 parts of an acid aqueous solution of nickel sulphate he adds 3.75 to 7.5 parts of hydrate of lime to exactly neutralize the acidity of the sulphate. To avoid the danger of an excess of alkali he prefers, however, to neutralize by the carbonate of lime. "This solution produces a brighter metallic deposit than the solution in general use, and without the addition of ammonia in any form."

87. Nickel sulphocyanide[68] (20). Moist nickel carbonate was dissolved in a strong solution of potassium sulphocyanide, and this was electrolyzed with the current from three cells. A dark steel-gray deposit was immediately formed, which did not alter during a half hour's deposition. Gas was evolved at both electrodes.

88. Nickel tartrate[68] (11). The solution prepared by digesting moist nickel carbonate in a strong, hot solution of tartaric acid is a poor conductor, and three cells in series were required to produce a deposit of an indifferent color. It was noticed that the cathode became more fully coated with metal on the back than on the front.

b. Acid Baths:

89. Nickel acetate.[71] The solution contains about 60 grams of nickel acetate per liter, and is maintained strongly acid by acetic acid. "These solutions thus prepared and used do not become depleted in using, and require no addition of nickel to keep up their strength other than that derived from the nickel of the anode."

90. Nickel citrate[68] (26). The solution was prepared by electrolyzing a strong solution of citric acid with a nickel anode. The deposit was very bright, of a good white color, much softer than is usual with nickel, and received a high polish under the steel burnisher.

91. Nickel formate.[72] The solution contains nickel formate with excess of formic acid. Among its claims to merit are: "The solution needs no replenishing with salts of nickel, the nickel being supplied from the anode. No precautions need be taken to see that the solution is free from the presence of potash, soda, alumina, lime or nitric or other acid. The deposit may be of any thickness, and will always be firm, flexible and white."

c. Alkaline Baths:

92. Nickel ammonio-acetate[68] (32). Ammonia was added to a strong solution of nickel acetate until the liquid acquired a deep blue color. The deposit was bright, of a good color and very adherent.

93. Nickel ammonio-carbonate[68] (35). Nickel carbonate was dissolved in strong ammonia, diluted and electrolyzed. The deposit was white, and retained its original brightness after an hour's deposition.

94. Nickel carbonate[68] dissolved in a strong solution of ammonium carbonate gave a rather dark deposit.

95. Nickel ammonio-chloride[68] (30). Strong ammonia was added to a solution of nickel chloride until the solution acquired a deep blue color. The deposit was white and very bright. Very little hydrogen, but much oxygen was evolved.

96. Nickel ammonio-citrate[68] (33). Ammonia was added to a strong solution of nickel citrate. The deposit was white, bright

and very adherent. The anode kept perfectly clean during the electrolytic action.

97. Nickel ammonio-ferricyanide[68] (45). Nickel ferricyanide was dissolved in strong ammonia. The filtered and diluted solution gave a prompt and fairly white deposit on brass.

98. Nickel hydroxide in ammonia[68] (15). This solution gave a yellowish deposit of nickel, without hydrogen. Oxygen was abundantly evolved at the anode, which became coated with a brownish film.

99. Nickel ammonio-nitrate[68] (31). Excess of strong ammonia was added to a solution of nickel nitrate. The nickel deposit was rather dark in color, and after a half hour the anode had a deep brown color.

100. Nickel ammonio-sulphate[68] (19). An experiment was tried to ascertain the effect of small and increasing additions of ammonia to the sulphate solution. The current from three cells was used, and a fresh brass cathode was used after each addition of ammonia. After the first addition of ammonia the deposit appeared much brighter than that obtained from nickel sulphate alone, and this characteristic was maintained until the solution acquired a deep blue color. The anode was almost black, and a flocculent precipitate formed in the solution.

The evolution of oxygen or the formation of nickel oxide on the anode, mentioned in many cases, indicates that those particular baths are not suited to practical use because of poor corrosion of the anode. In only one case, No. 96, is there mention of good anode corrosion in these alkaline baths.

II. Baths Containing Double Salts.

In connection with these baths it will be of interest to review the patents of Adams under which for many years nickel plating was monopolized. His first U. S. Patent, 93,157, of Aug. 3, 1869, claims:

"1. The electrodeposition of nickel by means of a solution of the double sulphate of nickel and ammonia, or a solution of the double chloride of nickel and ammonium, prepared and used in such a manner as to be free from the presence of potash, soda, alumina, lime, or nitric acid, or from any acid or alkaline reaction."

"2. The use, for the anode of a depositing cell, of nickel combined with iron to prevent the copper and arsenic which may be present from being deposited with the nickel or from injuring the solution."

"3. The electroplating of metals with a coating of compact, coherent, tenacious, flexible nickel of sufficient thickness to protect the metal upon which the deposit is made from the corrosive agents with which the article may be brought in contact."

"4. The deposition of electrotype-plates of nickel to be removed from the surface on which the deposit is made and used separately therefrom."

It is easy to see how it was possible to monopolize nickel plating under this unjust patent. Even today manufacturers of anodes have not recovered from its baneful influence, but are still furnishing anodes in accordance with claim No. 2, to the great detriment of the nickel plating industry.

Adams' patent, 100,961, March 22, 1870, is remarkable for its contradictory claims. "This improvement consists in the use of three new solutions from which to deposit nickel by the electric current: First, a solution formed of the double sulphate of nickel and alumina, or the sulphate of nickel dissolved in a solution of soda, potash, or ammonia alum, the three different varieties of commercial alum; Second, a solution formed of the double sulphate of nickel and potash; Third, a solution formed of the double sulphate of nickel and magnesia, *with* or without *excess* of *ammonia*. . . . I prefer to use these solutions at a temperature above 100° F. (38° C.), but do not limit my invention to the use of these solutions at that temperature. I therefore claim:

"1. The electrodeposition of nickel by means of a solution of the double sulphate of nickel and alumina, prepared and used in such a manner as to be free from the presence of ammonia, potash, soda, lime or nitric acid, or from any acid or alkaline reaction."

"2, . . . A solution of the double sulphate of nickel and potash, prepared and used in such a manner as to be free from the presence of ammonia, soda, lime, or nitric acid, or from any acid or alkaline reaction."

"3. . . . A solution of the double sulphate of nickel and magnesia, prepared and used in such a manner as to be free from the presence of potash, soda, alumina, lime or nitric acid, or from any acid or alkaline reaction."

In U. S. Patent 136,634, March 11, 1873, Adams' claim was still further extended. "I now claim . . . The electrodeposition of nickel, or the electroplating with nickel, by means of a solution of either of the soluble salts of nickel, such solution being prepared and being used, substantially, free from the presence of potash, soda, lime, alumina, and nitric acid, or either of them, and free from acid and alkaline reaction, or from either."

a. Neutral Baths:

In this class will be included baths made by merely dissolving normal salts, as well as those solutions which have been carefully neutralized.

The bath most generally used is a solution of nickel ammonium sulphate.

101. Pfanhauser's solution[73] (page 361). 75 grams of nickel ammonium sulphate per liter. Current density, 0.3 ampere per dm.² Temperature 15 to 20° C. Resistivity 24.6 ohms. 3.5 volts for 15 cm. between electrodes. Temperature coefficient 0.0176 for 1° C. Specific gravity 1.047. Current yield 91.5 percent. Deposit per hour 0.0034 mm. Cast anodes of ½ to ¾ the area of cathode should be used. The deposit is hard, good for plating iron or steel. Langbein[5] says the cast anodes rapidly render the bath alkaline, necessitating a frequent correction of the reaction. Brochet[3] (page 237) says: "This bath is poor in metal, even in case of the saturated solutions (98 grams at 18° C.). It is better to replace a part of the double sulphate by the single sulphate." He recommends:

102. Solution of single and double sulphates:[3]

Nickel sulphate	166 grams.
Nickel ammonium sulphate	55 grams.

Specific gravity 1.101, resistivity 23.9, at 18° C., nickel per liter 39 grams. "Baths rich in metal possess the advantage of greater covering power and are less influenced by cold. The addition of ammonium sulphate is sometimes recommended to increase the conductivity of the bath; this should not be done, since it results in the impoverishment of the bath in metal." —Brochet.[3]

103. The double sulphate with ammonium sulphate:[5]

Nickel ammonium sulphate....	50 grams
Ammonium sulphate	50 grams

"E. M. F. at 10 cm. 1.8 to 2 volts. Current density 0.35 ampere. The bath deposits rapidly, and all metals (zinc, lead, tin, and Britannia, after previous coppering) can be nickeled in it. Upon rough castings and iron, a pure white deposit is difficult to obtain. On account of the great content of ammonium sulphate in the bath, the deposit piles up, especially on the lower portions of the objects, which readily become dull, while the upper portions are not sufficiently nickeled."—Langbein.[5]

104. Pfanhauser[73] gives:

Nickel sulphate	50 grams
Ammonium chloride	25 grams

Specific gravity 1.0357 (5° Bé.). Resistivity 17.6 ohms. Temperature coefficent 0.025. E. M. F. for 15 cm. 2.3 volts. Current density 0.5 ampere. Current yield 95.5 percent. Deposit per hour 0.0059 mm. Cast anodes half the area of cathode. Langbein[5] gives 57 grams and 29 grams, respectively, of the same salts, and states that the deposit is soft and white, that heavy deposits cannot be obtained because of the danger of peeling, and that the bath is not suited to the direct nickeling of iron.

105. Bath with magnesium sulphate:[5]

Nickel ammonium sulphate ..	56 grams.
Magnesium sulphate	26 grams.

"E. M. F. 4 volts at 10 cm. Current density 0.2 ampere. Good for plating on iron, and may be used for the direct nickeling of zinc. The deposit is soft, and of a yellowish tinge. The bath does not remain constant, but fails after working three or four months, even cast anodes being but little attacked."—Langbein.[5]

Watt experimented with a solution containing the sulphates of nickel and magnesium. At first the deposit was decidedly yellow in tone, but became whiter after a few hours' use of the solution.

Adams' patent of the double sulphate of magnesium and nickel has already been noticed.

106. To a solution of nickel ammonium sulphate Watt[68] gradually added a concentrated solution of ammonium citrate. A bright deposit of a slightly yellowish tone was obtained, which retained its brightness during deposition for a long time, but finally became dull. The deposit was soft enough to be burnished. There was a brisk evolution of gas at the anode, and a few bubbles of hydrogen clung to the cathode.

107. Langbein[5] gives a somewhat similar bath, as do C. H. Procter[74] and Pfanhauser:[73]

	Langbein	Procter	Pfanhauser
Nickel sulphate	26.0 grams	30 grams	40 grams
Ammonium chloride	17.5 "	30 "	0 "
Potassium citrate	17.5 "	18 "	35* "

* Sodium citrate.

Langbein specifies for copper and copper alloys: Current density 0.45 to 0.5 ampere, E. M. F. at 10 cm. 1.5 to 1.7 volts. For zinc, current density 0.8 to 1 ampere, E. M. F. 2 to 2.5 volts.

Pfanhauser gives a current density of 0.27 ampere, E. M. F. at 15 cm. 3.6 volts. Specific gravity 1.039 (5½° Bé.). Resistivity 51.7 ohms. Temperature coefficient 0.0348. Current yield 90 percent. Deposit per hour 0.00301 mm. Rolled anodes. The bath yields a soft white deposit, and is especially suited for plating pointed objects like knives.

108. An English solution:[16]

Nickel ammonium sulphate..	100 grams.
Ammonium acetate	50 grams.

109. Another English solution:[16]

Nickel ammonium acetate...	100 grams.
Ammonium chloride	20 grams.
Glycerine	5 grams.

110. Nickel and ammonium chlorides:[5]

Nickel chloride, cryst.	37.5 grams.
Ammonium chloride	37.5 grams.

The bath is neutralized by ammonia. E. M. F. at 10 cm. 1.75 to

2 volts; for zinc, 2.8 to 3 volts. Current density 0.5 ampere. "The bath deposits readily, and is especially liked for nickeling zinc castings."

111. H. P. Dechert's solution:[75]

Nickel chloride, cryst. at least	141 grams.
Calcium chloride solution of 30° Bé. (sp. g. 1.261).....	1 liter.

The advantages claimed for this solution are very low resistance, elimination of hydrogen bubbles from the surface to be plated, thus removing the danger of spotting, a permanent and enduring solution, and a smooth, close and tough deposit of nickel.

112. Watt[68] gradually added to a solution of nickel sulphate a solution of ammonium tartrate, and obtained a very bright and very white deposit of nickel.

b. Acid Baths:

E. Weston[66] in his patent claims: "1. The electrodeposition of nickel by means of solutions of the salts of nickel containing boric acid, either in its free or combined state."

"2. A solution of the single or double salts of nickel to which has been added boric acid, either in its free or combined state." The exact composition of the baths is not stated by Weston. He claims that the addition of boric acid or its compounds prevents the deposition of sub-salts upon the cathode, renders the solution more constant and stable in composition, diminishes the liability to the evolution of hydrogen, permits the use of a more intense current, and improves the character of the deposit by rendering it less brittle and by increasing the tenacity with which it will adhere to a metal surface.

Langbein[5] (page 249) says: "Boric acid, recommended by Weston as an addition to nickeling baths, has a favorable effect upon the pure white reduction of the nickel, especially in nickeling rough castings. . . . Numerous experiments have shown that the deposit of nickel from nickel solutions containing boric acid is neither more adherent nor softer and more flexible than that from a solution containing small quantities of a free organic acid. Just the reverse, the deposit is harder and more brittle in the presence of boric acid.

"Weston recommends the following composition for baths:[5]

"113.	Nickel chloride	26 grams.
	Boric acid	10.5 grams.
"114.	Nickel ammonium sulphate	38 grams.
	Boric acid	19 grams.

"Both solutions are said to be improved by adding caustic potash or caustic soda so long as the precipitate formed dissolved. These compositions, however, cannot be recommended, because the baths work faultlessly for a comparatively short time only."

115. Pfanhauser[73] gives:

Nickel ammonium sulphate	40 grams.
Ammonium chloride	15 grams.
Boric acid	20 grams.

Current density 0.5 ampere. E. M. F. for 15 cm. 2.8 volts. Resistivity 20.85 ohms at 15° to 20° C. Temperature coefficient 0.0156. Current yield 89.5 percent. Deposit per hour 0.00556 mm. Specific gravity 1.0357 (5° Bé.). He, too, speaks of the difficulty of regulating the bath, and recommends cast anodes of half the surface of the cathode.

Maigne and Mathey[16] ascribe to Weston the two baths which follow:

116.	Nickel chloride	50 grams.
	Boric acid	20 grams.
117.	Nickel sulphate	50 grams.
	Boric acid	17 grams.

118. Bath of Julius Weiss:[16]

Nickel sulphate	40 grams.
Ammonium chloride	20 grams.
Citric acid	2 grams.

119. Langbein[5] (p. 253) gives:

Nickel ammonium sulphate	64 grams.
Ammonium sulphate	20 grams.
Citric acid	4.4 grams.

E. M. F. 2 to 2.2 volts at 10 cm. Current density 0.34 ampere. The materials are dissolved in boiling water, and ammonia is added until blue litmus paper is only slightly reddened. Very careful regulation of the current is required to avoid peeling off. The anodes should be cast and rolled in equal numbers. According to experiments by Dr. Langbein it is better to decrease the amount of ammonium sulphate to 2 grams.

This bath is operated so nearly neutral that it closely resembles bath No. 107.

120. J. H. Potts[76] uses:

Nickel acetate	28 grams.
Calcium acetate	16 grams.
Acetic acid, sp. g. 1.047 (35 percent)	8 grams.

Potts claims: "I have succeeded in producing a nickel-plating solution having the advantages of the presence of free acid and of great density, and yet free from the objections which have been heretofore made to acid solutions. . . . To the presence of the acetate of lime I also attribute the fact, which I have discovered in practice, that in the use of my solution no such care and nicety in the regulation of the electric current are necessary as in the use of the ordinary solutions. . . . Another advantage of my solution is the entire freedom of iron work plated in it from liability to corrosion after removal from the the cleansing bath of warm water in which it is necessary to place it after leaving the plating solution, thus obviating a very serious objection heretofore made to the presence of free acid in a nickel-plating solution—an objection which has been found to exist in the use of ordinary solutions." Watt[11] (p. 297) quotes Wahl as follows: "It gives satisfactory results without that care and nicety in respect to the condition of the solution and the regulation of the current which are necessary with the double sulphate solution. The metallic strength of the solution is fully maintained without requiring the addition of fresh salt, the only point to be observed being the necessity of adding from time to time (say once a week) a sufficient quantity of acetic acid to maintain a distinctly acid reaction. It is rather more sensitive to the presence of a large quantity of free acid than to the opposite condition, as in the former condition it is apt to produce a black deposit, while it may run down nearly to neutrality without notably affecting the character of the work. The deposited metal is characteristically bright on bright surfaces, requiring but little buffing to finish. It does not appear, however, to be so well adapted for obtaining deposits of extra thickness as the commonly used double sulphate of nickel and ammonium. On the other hand, its stability in use, the variety of conditions under which it will work satisfactorily and the trifling care and attention it calls for make it a useful solution for nickeling."

121. "W. Baker and J. Unwin[77] dissolve nickel hydrate in tartaric acid and add potassium hydrate or ammonia nearly to neutralization, so that a double salt is formed."[17]

122. Placet and Bonnet's nickel solution, see bath No. 25, this paper.

123. For Nagel's nickel solution see bath No. 7.

124. For Kugel's nickel solution see No. 23.

c. Alkaline Baths:

125. Roseleur's solution:[16]

Nickel ammonium sulphate ..	40 grams.
Ammonium carbonate	30 grams.

126. Desmur's solution:[11]

Nickel ammonium sulphate ..	70 grams.
Sodium bicarbonate	8 grams.

The bath is worked nearly at the boiling point. If, after working for some time, the deposit becomes dark, a small lump of sodium sulphide will remedy it. "Of all the solutions of nickel which I have tried," says M. Desmur, "this has, without doubt, given me the best results both as to quickness of working and whiteness of deposit, which is equal to that of silver. Nickel deposited from this solution can be burnished."

121. Bischof and Thiermann's[78] solution:

Nickel sulphate	86 grams.
Ammonium sulphate	67 grams.
Ammonia, sp. g. 0.905......	110 grams.
Volume	1 liter.

Platinum anode. E. M. F. 2.8 volts. Current density 0.5 ampere.

128. Prior's solution.[79] He adds to nickel chloride solution ammonium chloride, sodium chloride and potassium hydrate until the solution is strongly alkaline.

129. Gutensohn's solution.[80] He claims to deposit nickel, aluminum, copper, lead and zinc from a solution of the phosphate of the desired metal dissolved in a solution of sodium hydrate to which ammonia is added.

130. F. Weil[81] dissolves nickel hydroxide in Seignette's salt and sodium hydrate.

III. Miscellaneous Baths.

Although even traces of nitrates are declared by Adams to be harmful in the nickel bath, several solutions have been used or patented in which a nitrate is the principal or an important ingredient.

131. Boden's solution:[16]

Nickel nitrate	27 grams.
Sodium sulphite	333 grams.
Ammonia	27 grams.

132. George Brucker[82] patents a solution composed of:

100 parts saturated solution of nickel in nitric acid.
3 parts cream of tartar.

133. Watt[68] (17) added ammonium nitrate to a neutral solution of nickel nitrate but obtained only a slight discoloration of the cathode. No hydrogen was liberated, but small bubbles of gas appeared at the anode.

134. Watt[68] (43) also tried the addition of ammonium citrate to the solution of nickel nitrate, but without any favorable action.

The double cyanide solution, used for the deposition of so many of the metals, in the case of nickel is conspicuous by its absence from all save two of the books on electroplating so far referred to in this paper. Watt[11] says, page 298: "This was one of the earliest solutions used for depositing nickel, and is capable of yielding an exceedingly white deposit. Though neither so economical nor so susceptible of yielding stout deposits of nickel as the ordinary double sulphate or double chloride, it may be advantageously employed when only a thin coating of a fine white color is desired. It is stated to be somewhat extensively used in some large nickel-plating works in the United States." Nickel cyanide is dissolved in a strong solution of potassium cyanide and a small excess of the latter is added. "The solution should be as concentrated as possible, almost to the point of saturation."

135. Thomas and Tilley[83] in 1854 patented a nickel bath consisting of a solution in potassium cyanide of the washed precipitate from a solution of nickel in nitric acid.

Watt[68] failed to get a deposit of nickel in the three experiments which follow:

"A solution was prepared by digesting recently precipitated phosphate of nickel in a moderately strong solution of cyanide of potassium. With the current from three cells, no metallic deposit was obtained, but a red salt formed at the cathode. A deposit of a black color appeared on the anode. There was a copious evolution of gas at both electrodes."

"A solution was prepared by adding recently precipitated and moist carbonate of nickel to a strong solution of cyanide of potassium. . . . There was much hydrogen given off, and the solution failing to yield a good film was abandoned."

"To a strong solution of cyanide of potassium moist ferricyanide of nickel was added. . . . No deposit of nickel could be obtained even when the cathode was briskly agitated in the bath. There was a brisk evolution of gas at both electrodes."

It looks like a case of too much free cyanide in the above solutions.

136. Bates[84] black nickel solution:

"Nickel salts"	120 grams
Cyanide of potassium	75 grams
Ammonia	108 grams
Water	1,000 grams

The nickel salts are dissolved in water, the cyanide added with stirring until the precipitate formed is dissolved, then the ammonia added—which should turn the solution to a light blue color. Nickel anodes are used. "The object of my invention is the electrodeposition of a black nickel which shall be as compact, coherent, tenacious, and flexible as the best deposit of white nickel."

Many "black nickel" solutions contain sulpho-cyanides, compounds of arsenic, antimony, or other substances whose presence in other baths, containing no nickel, causes a deposit similar to "black nickel." Until proved by analysis, the writer doubts that "black nickel" is either nickel or one of its compounds. Hence modern "black nickel" solutions are not included in this paper.

137. Adams' sulphite solution:[85]

Nickel sulphate	37.5 grams.
Ammonium sulphite or bisulphite	22.5 grams.

"The resulting products are sulphite of nickel and sulphite of ammonia, and a residuary product of sulphate of ammonia. This solution may also be made from the nitrate, chloride, or acetate of nickel by adding the proper quantity of sulphite or bisulphite of ammonia. It may be used with special advantage where the nickel plate forming the anode in the solution contains zinc. Nearly all commercial nickel contains more or less zinc, the presence of which tends to increase the evolution of hydrogen on the deposited plate. There is less tendency to this evolution of hydrogen with this solution than with those heretofore described in books."

138. Langbein[5] gives a phosphate solution:

Nickel phosphate	19 grams.
Sodium pyrophosphate	80 grams.

E. M. F. at 10 cm. for copper 3.5, for zinc 3.8 volts. Current density for copper 0.5, for zinc 0.55 ampere. "The bath yields a very fine dark nickeling upon iron, brass, and copper, as well as directly, without previous coppering, upon sheet zinc and zinc castings. For the same purpose a nickel solution compounded with a large quantity of ammonia has been recommended. However, experiments with this solution always yielded lighter tones than the above bath."

139. Powell's pyrophosphate solution:[86]

Nickel phosphate	22.5 grams.
Sodium pyrophosphate	26.2 grams.
Nickel citrate	15. grams.
Sodium bisulphite	7.5 grams.
Ammonia, 16 percent	37.5 grams.

"One great advantage arising from the use of my solutions is that the various metals and their alloys are electronegative to a solution containing pyrophosphates or phosphoric acid; hence, no decomposition or local action occurs when they are immersed in the bath. Thus zinc articles, which cannot be plated in a solution of double sulphate or chloride of nickel and ammonia, are beautifully plated with a firm adhesive layer of metal by using my solutions, and the deposit is white in color and very ductile."

140. Nickel fluosilicate:[87]

Nickel fluosilicate	100 grams.
Aluminum fluosilicate	50 grams.
Ammonium fluoride	50 grams.

The deposit is claimed to be smooth, dense, coherent, and adherent. It is advisable to add ammonium fluoride from time to time during use to prevent the separation of silica.

141. A bath with sodium chloride:[3]

Nickel sulphate	50 grams.
Nickel ammonium sulphate	50 grams.
Sodium chloride	10 grams.

Sp. gravity 1.064 (8½ Bé.). Resistivity 23.4 ohms. Nickel per liter 18 grams. "The addition of 10 to 15 grams of boric acid per liter preserves the whiteness of the nickel deposit, which the presence of the chloride tends to make it lose."

Organic salts and compounds have been largely used, either as the basis of the bath, or as an addition for the purpose of improving the permanency of the bath or the nature of the deposit.

142. Watt[68] added sodium chloride to a strong solution of

nickel acetate, and with two cells obtained a good white deposit of nickel on brass.

143. To a strong neutral solution of nickel acetate Watt[68] added potassium acetate. The deposit of nickel was very uniform and white. There was only a moderate evolution of gas at the anode, and none at all on the cathode.

144. To a solution of nickel sulphate Watt[68] added a solution of nickel acetate. The deposit was bright, very white, and brightened under the burnisher without excessive pressure.

For other acetate baths see solutions 75, 76, 89, 92, 108 and 109.

Citric acid and citrates are frequently used in the nickel bath.

145. Pfanhauser[73] gives:

Nickel sulphate	40 grams.
Sodium citrate	35 grams.

E. M. F. at 15 cm. 3.6 volts. Current density 0.27 ampere. Specific gravity 1.0394 or 5½° Bé. Resistivity 51.7. Temperature coefficient 0.0348. Current yield ·90 percent. Deposit in one hour 0.00301 mm. Rolled anodes should be used of twice the cathode surface. This bath is equally good for nickeling iron, steel and brass, and is especially good for nickeling pointed objects. The deposit is white and ductile.

146. Langbein[5] gives a similar bath:

Nickel sulphate	48 grams.
Sodium citrate	30 grams.

"E. M. F. at 10 cm. 3.0 volts. Current density 0.33 ampere. This bath is claimed to be especially useful in preparing nickel electrotypes, but Langbein's experiments proved it to possess the disadvantages of all nickel baths prepared with large quantities of organic salts. For the special purpose for which it is recommended no better results were obtained than with any other nickel bath rationally composed for heavy deposits. It is very suitable for nickeling objects with sharp edges and points. The deposit is quite soft, and in grinding such nickeled instruments, peeling off of the nickel happens less frequently than with instruments nickeled in other baths."

147. Watt[68] added citrate of ammonia to a solution of citrate of nickel. Three cells caused a somewhat dull deposit, but on diluting the solution the color and brightness of the deposit were much improved. The deposit was readily brightened by the burnisher. The anode was covered with a greenish coating, which dissolved on standing at rest in the solution. Addition of a slight excess of citric acid kept the anode clean.

148. J. E. Chaster[88] patents a bath consisting of a solution of nickel ammonium citrate. It is to be used about three-fourths saturated. Its particular advantage over the double sulphate is claimed to be its lower E. M. F. of decomposition.

149. Watt[68] also tried the effect on the deposit of continued additions of nickel citrate to a solution of nickel sulphate. Even a small addition of the citrate caused a whiter deposit than that from the sulphate and a larger amount caused the deposit to continue bright, instead of becoming dull after a short deposition as it usually does in a solution of nickel sulphate. The metal felt soft under the burnisher, and a brilliant polish was obtained.

For other citrate baths see solutions 80, 90, 96 and 107.

Jas. Powell[89] patents the addition of benzoic acid or benzoates to any of the salts of nickel, claiming that it renders the solution more stable, causes proper corrosion of the anodes and yields a tough, cohesive and reguline deposit of beautiful silvery-white nickel. As an example of his solution he cites:

150.	Nickel sulphate	34 grams.
	Nickel citrate	15 grams.
	Nickel phosphate	15 grams.
	Benzoic acid	7.5 grams.

The four solutions which follow are also ascribed to Powell:[16]

151.	Nickel sulphate	27 grams.
	Nickel citrate	20 grams.
	Benzoic acid	6.5 grams.
152.	Nickel chloride	14 grams.
	Nickel citrate	14 grams.
	Nickel acetate	14 grams.
	Nickel phosphate	14 grams.
	Benzoic acid	7 grams.

153.	Nickel sulphate	20 grams.
	Nickel citrate	20 grams.
	Nickel benzoate	7 grams.
	Benzoic acid	1.8 grams.
154.	Nickel acetate	20 grams.
	Nickel phosphate	7 grams.
	Nickel citrate	20 grams.
	Sodium phosphate	14 grams.
	Sodium bisulphite	7 grams.
	Ammonia	32.5 grams.

For Watt's benzoate bath see solution No. 77.

155. Placet's bisulphate, biphosphate and biacetate solutions have been given under bath No. 25.

156. Villon's solution:[16]

Nickel ammonium sulphate	50 grams.
Nickel ammonium oxalate	20 grams.
Ammonium phosphate	10 grams.

157. Keith's solution.[90] "For preventing and overcoming this brittleness . . . I add to a solution of nickel . . . one or more of the salts, either single or double, . . . which are formed by the union of the various organic acids, acetic, citric and tartaric, with the alkalies and alkaline earths, ammonia, soda, potassa, magnesia or alumina. . . . The result is a deposit possessing elasticity, toughness and all the hardness, brilliancy and other qualities of pure nickel. . . . These various organic acid salts may be added interchangeably and collectively, though I prefer to use, in case of the double salts of nickel, the organic acid salts which have for their bases the alkali or alkaline earth which is associated with the nickel in its double salt. . . . Of the salts which can be used to accomplish the desired effect I prefer the tartrates. . . . To twenty volumes of a solution of the double sulphate of nickel and ammonia of a gravity of 7° Bé. (sp. g. 1.0507) I add one volume of a solution of an equal gravity of neutral tartrate of ammonia in water. These solutions may for some purposes be made alkaline—for instance, in the electroplating of brass and iron, wherein local action would interpose provided the solutions were left in an acid condition."

158. An English formula:[5]

Nickel sulphate	52.5 grams.
Tartaric acid	28 grams.
Caustic potash	7 grams.

For other tartrate baths see solutions Nos. 80 and 112.

159. Classen's oxalate bath may be found under solution No. 24.

Jules Meurent[91] secures highly adherent deposits of metals or their alloys by adding to an aqueous solution of the chloride of the metal to be deposited "a compound of a metal of the alkalies containing oxygen, and adding thereto a solution of chloride of ammonia and a carbohydrate," and electrolyzing. He specifies the addition of the following: Arabit, arabinose, xylose, rharmose, or isodulcite, saccharin, isosaccharin, metasaccharin, mannite, dulcite, sorbite, triose or glycerose, tetrose or erythrose, pentose, mannose, glucose, galactose, fructose, sorbinose, formose, acrose, methylenetan, glucoazone, isoglucosamine, osone, glucosone, glucosamine, the mannoses, methylerose, mannoheptose, glucoheptose, methylheptose, manoctose, nonose, mennononose, saccharose, lactose, maltose, mycose or trehalose, melibiose, raffinose or melitose, melitriose, melectose, also the following mono-acids, the biacids and the tribasic acids: The acids arabonic, aposorbinique, trioxyglutaric, saccharonic, trioxyadipinic, desoxalic, oxycitronic, dioxypropantricarbonic, as also the aldehydes and the ketones, hexavalents—that is to say, the acids mannitic, gluconic, dextrinic, mannonic, galactonic, etc., the saccharic, mucic, isosaccharic acids, etc. "I add also all the class of gums comprising especially arabine, gum arabic, the gums of the country obtained from plum trees, cherry trees, apricot trees, etc., wood-gum, vegetable mucilage, anisie bassorin, pectic mathers. I add also the classes of collagenous and chandrogenous matters containing ossein, glutine or gelatine, and all kinds of glues, as also chondrin and chitine.".

160. Meurent's nickel solution:

Nickel sulphate	50 grams.
Ammonium chloride	25 grams.
Citric acid	5 grams.
Gum arabic	50 grams.

"If the bath is too acid, it is necessary to neutralize it. Seventy-five grams of sugar or 100 grams of glucose may replace the gum arabic."

IV. Malleable Nickel.

E. Weston,[66] in his patent mentioned on page 132, claims to obtain from the solution below "A new article of manufacture—a deposit of nickel which is so tough, malleable and ductile that it can be worked in much the same way as brass or copper are worked by the operations of rolling, punching, drilling, spinning, drawing," etc.

161. Weston's solution consists of five parts of chloride of nickel and two parts of borate of nickel. The amount of water is not stated in the portion of the patent available.

162. Villon's solution of malleable nickel:[16]

Nickel ammonium sulphate .	60	grams.
Nickel ammonium oxalate..	20	grams.
Ammonium phosphate	10	grams.
Palladium oxalate	0.1	gram.

163. Kern's[92] fluoborate solution contained 8 percent metallic nickel as nickel fluoborate. In 300 hours at 1.2 amperes per square decimeter the deposit weighed 290 grams and was 5/16 inch thick. "It was bright, smooth, malleable, solid and adherent."

Two solutions previously given are claimed to yield malleable deposits: No. 23, Kugel's, and No. 139, Powell's. Deposits from the following solutions are said to be soft enough to burnish: Nos. 76, 77, 90, 106, 122, 126, 144, 147, and 149.

V. Baths Producing Thick Deposits.

Brochet,[3] Langbein,[5] Maigne and Mathey,[16] and Peters[17] all give the following:

163. Formula used in Belgium:

Nickel sulphate	50	grams.
Ammonium tartrate, neutral	36	grams.
Tannin	0.25	gram.

E. M. F. 3.5 volts; current density 0.3 ampere.

"The bath is said to yield a very white, soft and homogeneous deposit of any desired thickness, without roughness or danger of peeling off."

164. Nickel ethyl sulphate.[93] "By the use of an electrolyte which contains nickel ethyl sulphate, or the ethyl sulphates of the alkalies or alkaline earths, deposits of any desired thickness can be produced if the bath be constantly agitated by mechanical means or by the introduction of hydrogen. Agitation by blowing in air is not permissible on account of oxidation of the ethyl sulphates. Experiments with such ethyl sulphate combinations by Dr. G. Langbein & Co. resulted in formulas for prepared nickel salts, from which thick deposits of nickel capable of being polished can in a few minutes be obtained in the cold way. The salts are known in commerce as Mars, Lipsia, Germania and Neptune. In an electrolyte of given composition, which has to be kept slightly acid with acetic acid, nickeling may for weeks be carried on at the ordinary temperature without any peeling off of the deposit, and in this respect this bath surpasses all other known baths. In the course of six weeks Dr. Langbein has produced upon guttapercha matrices galvanoplastic nickel deposits 6 millimeters in thickness."—Langbein.[5]

165. A. Hollard's solution.[94]

Boric acid	65 grams.
Hydrofluoric acid (43 to 46 percent)	142 grams.
Nickel carbonate	excess.
Water	1,000 grams.

The boric acid is dissolved in 125 c.c. of boiling water, cooled, put in a rubber jar and the hydrofluoric acid added. The nickel carbonate is slowly stirred in until it remains undissolved, and then stirred for 24 hours by a motor to completely neutralize the acid. It is then filtered. At first the deposit is curly, but after three or four days of continuous operation it works satisfactorily. One may deposit nickel as thick as desired, and the deposit may be used for electrotypes on wax, guttapercha, etc. Nickel can be deposited directly on cast iron and on aluminum.

The writer can confirm Hollard's statement of the suitability of the nickel fluoborate electrolyte for thick deposits. About two years ago the writer began experiments with fluoborate solutions of several metals, obtaining deposits of considerable thickness. Last fall, as the laboratory nickel solution was not working satisfactorily, about three gallons of the fluoborate solution were added to the 30-gallon nickel tank as a corrective. The solution then gave light deposits of excellent quality, but heavy deposits, run for a week or more, were badly pitted by gas bubbles which clung to the cathode. Although he has never collected and analyzed the gas, the writer is inclined to consider the trouble due to air absorbed while the solution stood idle in

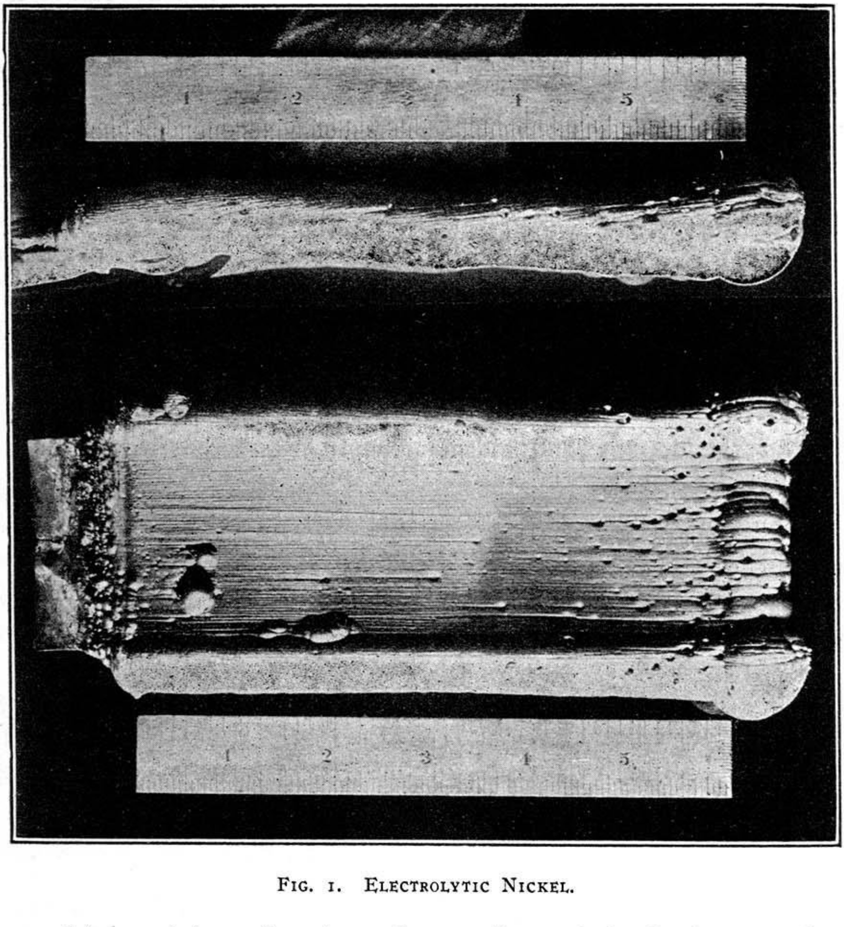

FIG. 1. ELECTROLYTIC NICKEL.

the summer. After several weeks of occasional use the pitting had diminished considerably, and an attempt was made to secure a really thick deposit of nickel.

Since the regular anodes, over a foot long, were left in the tank, there was naturally an excessive deposit on the bottom of the cathode. The deposit weighs 1,500 grams, and the cathode has a maximum thickness of 30 mm. The edge is 17 to 22 mm. in thickness. The bath operated at room temperature without stirring, and no additions were made to the solution during the 85 days of deposition. The current density averaged about 0.8 ampere per square decimeter. The deposit was brilliant and very satisfactory except for the pits caused by the gas bubbles. Although the cathode was lifted from the solution every few days for examination, there was no trouble from peeling. The deposit is very hard and somewhat brittle. In comparison with those deposits of copper, iron and lead of equal thickness which have come under the observation of the writer, the smoothness and freedom from protuberances of this deposit is remarkable. It is evidently not necessary that the entire bath consist of nickel fluoborate in order to obtain thick deposits.

Of the baths previously described, No. 22, No. 91 and No. 146 are claimed to give thick deposits at ordinary temperatures.

The heating of the electrolyte to prevent curling and peeling of the deposit has already been mentioned, and doubtless the thick deposits claimed for bath No. 22 are due to the elevated temperature specified.

VI. Agents for the Production of Smooth Deposits.

"A small addition of gelatine or transparent white glue will give an exceedingly bright lustre to the nickel deposit, providing the deposit is not too heavy."—C. H. Procter.[95]

Bruce adds carbon disulphide to the nickel bath to prevent the deposit from becoming dull when it reaches a certain thickness. "This is not advisable."—Langbein[5] (p. 261).

Classen[96] obtains brilliant mirror-like electrolytic deposits of the metals by adding to the plating baths glucosides, phlorglucosides, or extract of althæa, or Panama licorice extract.

J. A. Nussbaum[97] obtains smooth, dense deposits of metals by adding to aqueous solutions of their ordinary salts small quantities of colloids, which wander toward the cathode, *e. g.*, seed mucilages (linseed), mucilage from roots or bulbs (salep), vegetable gums, albumin, glutin, chondrin, mucin, etc.

"I found that by the addition of potassium cyanide to an alkaline electrolyte of nickel the deposit of nickel formed was smoother than that obtained by using other solutions. The addition of ammonium carbonate in place of ammonia produced smoother deposits when from 1 to 2 percent of cyanide was present."—E. F. Kern.[98]

"Other conditions being the same, we shall get the smallest crystals the greater the potential difference between the metal and the solution. This is the recognized explanation for the excellent character of deposits from cyanide solution."—Bancroft.[99]

Q. Marino dissolves nickel ammonium sulphate in glycerine at 60° to 80° C. instead of in water. Foerster and Langbein[5] (p. 250) find that the deposits do not possess the good qualities claimed by the patent. "The owners of the Marino patents have apparently themselves recognized the disadvantages of the glycerine electrolyte, and have applied for a patent, according to which 15 to 20 percent of glycerine is to be added to solutions of metallic salts in water. The glycerine is claimed to act as a depolarizer, and allow of the production of lustrous nickel deposits of great homogeneity. By experiments made in this direction it was found impossible to produce a better technical effect with such an addition of glycerine than without it, in properly prepared baths."—Langbein[5] (p. 250).

VII. Nickel Electrotypes.

Of the baths mentioned, Nos. 23, 91, 146, 164 and 165 are claimed to be suitable for the production of electrotypes, etc., in nickel.

VIII. The Nickeling of Zinc.

Owing to the corrosion of zinc by many of the common nickel baths much difficulty has been experienced in plating nickel directly upon zinc. Recourse has frequently been had to a preliminary coating of copper or brass from a cyanide solution.

"Some manufacturers nickel the cleansed sheet wthout previous coppering or brassing, and claim special advantages for such direct nickeling. Sheet-zinc directly nickeled does not show the warm, full tone of sheets previously coppered or brassed. The nickel deposit upon brassed sheets shows a decidedly whiter tone than on copper sheets, and brassing would deserve the preference if this process did not require extraordinarily great care in the proper treatment of the bath, the nickel deposit readily peeling off. This peeling-off of the deposit may be prevented by avoiding too large an excess of cyanide, and by regulating the current so that no pale yellow or greenish brass is deposited." —Langbein[5] (p. 298).

The following baths are said to be suitable for the direct nickeling of zinc:

Nos. 107, 109, 138 and 139.

Electrolytic Determination of Nickel.

The methods and conditions described under Nos. 52, 53, 54, 55, 56, 57, 59, 60 and 61 for cobalt, may also be used for nickel.

No. 58, given by Classen[27] (p. 162) is stated by Perkin[28] to be less satisfactory for nickel than for cobalt, and to give rather low results.

166. Ammonium hydrate and ammonium borate.[28] Dissolve the nickel salt in 30 c.c. of water and add 70 c.c. of a solution containing 50 grams of ammonium borate dissolved in 700 c.c. of water and 300 c.c. of ammonia (sp. g. 0.88). Current 0.5 to 1 ampere at 30° C. If a slight anode deposit forms, a few cubic centimeters of strong ammonia will remove it. Time 3 to 4 hours. The method is very accurate, but the deposit is not so fine in appearance as in other methods.

There remains for consideration a few alloys of nickel with iron, zinc and other metals, but these have been purposely omitted. Although these alloys have been deposited from their various baths, they have not as yet reached any commercial importance, and it was not deemed advisable to incorporate them in this article, already bulky beyond expectation.

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SOME SOURCES OF ERROR IN GAS CALORIMETRY.

By O. L. KOWALKE.

Previous to five years ago the quality of municipal gas was judged according to two standards,—the candle power and the calorific. In the spring of 1908 the Railroad Commission of Wisconsin called into conference the representatives of gas companies to determine the proper standard for quality of gas. It was shown at the conference that practically all gas sold was used for producing heat, and that the calorific standard was the most logical one. The question now arose as to how the calorific value should be determined, what calorimeters were best suited, and what the proper conditions for testing were. As a result of this conference, the staff of the Chemical Engineering Department in co-operation with the Committee on Calorimetry of the American Gas Institute made an extended series of tests of the efficiency of various calorimeters on the market, and the factors affecting their accuracy.

The American Gas Institute adopted the following definition of heating value:—(See Proc. Am. Gas Inst., Vol. III, 1908, p. 383).

"The heating value of a gas is the total heating effect produced by the complete combustion of a unit volume of the gas, measured at a temperature of 60 degrees Fahrenheit, and a pressure of 30 inches of mercury, with air of the same temperature and pressure, the products of combustion also being brought to this temperature."

"In America the unit of volume is the cubic foot and we recommend that the heating value be stated in terms of British thermal units per cubic foot of gas."

The present discussion deals particularly with continuous flow calorimeters,—namely, calorimeters through which the cooling water, gas and air flow continuously. There are several other efficient types of calorimeters whose operation is radically different from the continuous flow type, but since the latter has the widest use the discussion will be confined to it.

It is apparent that there are several sources of error in a heating value determination, namely;—measurement of gas, correction to standard volume, temperature measurement, radiation losses, incomplete combustion, air humidity, and excess of air.

The gas supplied to the calorimeter is measured in a wet test meter. Aside from leaks in the case of the meter and incorrect water level, there are other sources of error. The temperature of the gas passing the meter must be accurately measured; hence the thermometer should read to single degrees, be quick to respond to changes in temperature, and be installed at the point where the gas leaves the measuring drum. An error of one degree in the measurement of the temperature of the gas means an error of about 1.8 B.t.u's. per cubic foot of gas.

Should the gas entering the meter be not saturated, there would be considerable evaporation during an extended series of tests, and the meter should be "slow" in its registration. The following data will illustrate this point. A meter was passing gas at the rate of 7 cu. ft. per hour, for six hours, with the gas and the meter at 80 degrees Fahrenheit. At the beginning the meter was 2.5 per cent fast and at the end was only 1.7 per cent fast. Had the meter not been checked, the results at the end would have been 0.8 per cent larger than at the beginning, a matter of about 5 B.t.u.

The standard unit volume of gas is one cubic foot of saturated gas at a temperature of 60°F. and 30 inches of mercury. It is seldom possible to meter gas under these conditions, but by proper corrections of temperature, barometer, and vapor pressure, the gas can be brought to this standard. The formula for making the correction is given as $\frac{17.64\,(h-a)}{460+t}$, where

h=barometer in inches of mercury

a=vapor tension at observed temperature, (t)

t=gas temperature observed, in degrees Fahrenheit.

Suppose that in the winter the temperature of the gas in the mains is 45°F. and that the gas is saturated. The gas is brought into the testing room where the temperature is 70°F., where it would now be only 41 per cent saturated. Were the gas saturated at 70°F., and the barometer at 29.5 inches of mercury, the correction factor according to the above formula would be 0.955.

Since the gas would be only 41 per cent saturated the correction factor, according to the formula above, would be 0.971 and would involve an error of about 10 B.t.u. During the winter it is necessary to pass the gas through a saturating bottle before passing the meter.

It can also be shown that an error of one-tenth of an inch in reading the barometer will mean an error of about 2 B.t.u. The gas coming from the main to the meter is usually under a pressure of from 2 to 6 inches of water. Each inch of water pressure corresponds to 0.073 inches of mercury which, for accurate work, should be added to the barometer reading. Failure to do so will mean a loss of about 1.5 B.t.u. for each inch of water pressure to which the gas is subjected.

The temperature of the water at the inlet and outlet must be accurately known; and the thermometers should show accurately the temperature difference. This will mean that a given interval on the scale of one thermometer should correspond exactly to the same interval on the scale of the other. It is practically impossible to build thermometers so that the bore is perfectly uniform, and the scale etched on the thermometer may not always accurately indicate the correct temperature.

Suppose that in a test the following data were obtained:—
Gas consumed (corrected)=0.1883 cu. ft.
Weight of water heated=7.39 lbs.
Observed average temp. of inlet water=65.38°F.
  Correction for bore=.33
Corrected temperature at inlet=65.05°F.
Observed ave. temp. at outlet of water=80.86°F.
  Correction for bore=.17
Corrected temperature at outlet=80.69°F.
Corrected rise in temp.=15.64°F.

Hence $\frac{15.69 \times 7.39}{0.1883}$=613.8 B.t.u. Had the correction for bore in the thermometer not been made the apparent rise would have been 15.48°F. and the heating value 607.5 B.t.u.

For work of great precision a further correction for the emergent stem of the thermometer is necessary. If the stem of the thermometer extends out of the bath in which the bulb is immersed, and if the surroundings of the stem are cooler than the bath, the reading will be low. The correction formula given in "Circular of the Bureau of Standards No. 8—1911", p. 15, is:

Stem correction=0.000088 N(T°—t°)
N=number of degrees emergent from bath
T=observed temperature of bath
t=mean temperature of emergent stem (taken as room temperature)

For a bath temperature of 85°F, room temperature of 70°F, and the stem submerged to the 32° mark, a correction of 0.06 degree must be added, which is equivalent to about 2 B.t.u.

Loss or gain of heat by radiation may be of considerable magnitude. In the following table is given the gain or loss in B.t.u. absorbed from or given to the room during the time required to burn one cubic foot of gas. To obtain these data no gas was burned in the calorimeter, the room temperature was kept at 70°F., but the temperature of the water flowing through the calorimeter was varied.

Temp. Water Flowing	B. t. u. Gain	B. t. u. Loss
40° F	8.0	
50° F	5.0	
60° F	3.5	
70° F	0.0	
80° F		2.0
90° F		2.0

When gas is being burned in the calorimeter, there is some heat loss by conduction down the stem of the burner. This loss is small as compared to the heat radiated down the combustion chamber from the flame. The Bureau of Standards has suggested the use of shields on the burner stem, so arranged as to admit air for combustion, but to prevent heat radiation downward. Numerous tests in the Chemical Engineering Laboratories have shown that the loss in B.t.u. due to the absence of radiation shields is about 3 B.t.u. per cubic foot of gas. The burner should be well up in the combustion chamber and the flame should be above the point where the water enters the calorimeter.

Incomplete combustion also produces an error. The flame in the combustion chamber should never touch the walls of the chamber. Such a condition will keep the gas below the ignition temperature.

The magnitude of the error due to humidity and excess of air supply is not generally appreciated. Gas at room temperature and saturated with vapor enters the combustion chamber, together with an air supply at room temperature and room humidity. The gas is burned, forming carbon dioxide and water vapor, with the liberation of heat; and the products of combustion are cooled by the calorimeter water to a temperature about equal to that of the water at the inlet. During the cooling the water vapor is condensed to a liquid; and the products of combustion pass out of the calorimeter saturated with water vapor at the exhaust temperature. The amount of water condensed is equal to the amount formed during combustion only when the water entering with the gas and air is equal to the amount carried out by the products of combustion. Should the air and gas entering contain less water than the products leaving, then some of the heat of condensation of the water formed during combustion is lost. It is usually the case that the air and gas entering carry less water than the products leaving. In extreme cases, the water required to saturate the products may be more than the sum of that brought in by the air and gas, and that formed during combustion. In this case no water is condensed.

During the summer months the air is at an average of about 75°F. and perhaps 60 per cent saturated. In the winter air from out-of-doors, perhaps at 20°F. and 50 per cent saturated, is brought into the room and heated to 75°F, but no moisture is added. This air is now only about 12 per cent saturated. Hence in the winter this error due to humidity is apt to be much greater than in the summer.

It can be shown that during the combustion of a carburetted water gas, coal gas, or mixed gas, there is a contraction in volume. In a certain carburetted water gas (which may be taken as typical), the dry air needed for combustion of one cubic foot of dry gas is 5.286 cu. ft. The volume of the products of combustion, dry, is 5.037 cu. ft.

Total volume before combustion is 1.00 + 5.286 = 6.286 cu. ft.
" " after " " = 5.037 " "

Contraction = 1.249 cu. ft.
= 19.8 per cent.

Should the excess of air amount to 40 per cent, the contraction would be 15.3 per cent. The contraction in volume due to combustion makes it possible to operate a calorimeter with an exceedingly small error when the humidity is about 80 per cent, for room temperatures from 60° to 80°F. and for air excesses from 20 per cent to 60 per cent.

The following tables show the loss or gain in B.t.u. per cubic foot for a carburetted meter gas when burned with air of various degrees of humidity, temperature, and percentages of excess. The amounts of heat lost are indicated with a minus sign and the amounts of heat gained with a plus sign.

TABLES SHOWING LOSS AND GAIN OF B. T. U.

Table 1. Air 20 Per Cent Excess

Room Temp. F°	100%	80%	Humidity 60%	40%	20%
60	+1.1	+0.01	—1.0	—2.3	—3.5
70	+1.6	—0.01	—1.6	—3.2	—4.8
80	+2.2	—0.03	—2.2	—4.4	—6.6
90	+2.9	—0.03	—3.0	—6.0	—9.0

Table 2. Air 40 Per Cent Excess

Room Temp. F°	100%	80%	Humidity 60%	40%	20%
60	+1.1	—0.2	—1.6	—2.9	—4.2
70	+1.5	—0.3	—2.2	—4.0	—5.9
80	+2.1	—0.4	—3.0	—5.5	—8.0
90	+2.9	—0.6	—4.0	—7.5	—11.0

Table 3. Air 60 Per Cent Excess

Room Temp. F°	100%	80%	Humidity 60%	40%	20%
60	+1.1	—0.4	—1.9	—3.4	—5.0
70	+1.5	—0.6	—2.7	—4.8	—7.0
80	+2.2	—0.8	—3.7	- 6.6	—9.5
90	+2.9	—1.0	—5.0	- 9.0	—12.9

The amount of excess of air will vary with different calorimeters and also with the method of operation. The following percentages of excess of air have been obtained from the old style Junkers calorimeter:—53%, 57%, 46%, 11%, and 200%. In one test the improved Junkers Calorimeter showed 41% excess of air, while in another the Doherty Calorimeter showed an excess of 70%. The amount of excess air can be controlled by the damper on the exhaust flue. One way of doing this is to watch the indications of the outlet water thermometer while the damper is being manipulated, leaving the damper in that position which corresponds to the highest reading on the thermometer.

In conclusion it will be noted that some of the errors in gas calorimetry are of considerable magnitude. Most of the errors are in the same direction, and the cumulative effect is an error of several per cent. By careful attention to the details of operation, the result obtained with a continuous flow calorimeter can be made equal to the total heating value of the gas.

A paper presented at the Twenty-fourth General Meeting of the American Electrochemical Society, at Golden, Col., September 11, 1913, President E. F. Roeber in the Chair.

SOME OBSERVATIONS ON BASE METAL THERMOCOUPLES

By O. L. Kowalke.

The thermocouple as a means of measuring temperatures seems to be used by a large variety of industries, if one may judge from the records of sales. It is peculiarly adapted for this purpose because of (1) the small volume the junction occupies, (2) the robust nature of the couple itself as compared to a thermometer, (3) the simplicity of the measuring or indicating instruments, (4) the rapidity with which the measurement can be made. Up to about seven years ago the platinum couple, which had been thoroughly investigated and tried out, was almost alone in the field. Since then there have appeared on the market couples made of the baser metals, such as iron, nickel-chromium, nickel, cobalt and other alloys. These couples came into favor because of their cheapness as compared to the platinum couple both as to first cost of the outfit and the cost of renewals of the couple itself, the high electromotive force generated and the use of a robust double-pivoted millivoltmeter. Among the causes for the inaccuracy of the platinum couple were heterogeneity of the wires in the couple and their contamination by metals or gases from the place where the temperatures were to be measured. All but the first of the causes named can be avoided after the couple is made, but the wire must be made homogeneous before the couple is completed.

Since the voltage generated by the couple for a given temperature is the summation of all the electromotive forces due to the contact of two dissimilar metal portions, it can readily be seen that it is imperative that the metal be as homogeneous as possible if the electromotive force indicated be that resulting from the two metals at the hot junction. If, then, the couple is composed of metal which is not homogeneous, then at each junction of two dissimilar metals there will be set up a voltage which is a function of the temperature existing at that point. Should the position of the couple be changed with respect to its depth of immersion, then the resulting voltage will be changed even though the temperature had not changed at all. A couple made of wires which are perfectly homogeneous is apt to be rather expensive, and the only combination which seems to fulfill this condition is the platinum and platinum-rhodium couple.

It is possible to get a couple which is sufficiently homogeneous so that the indications are satisfactory for many commercial purposes where an accuracy of about 25 to 50 degrees is wanted. This condition is realized in the combinations of which base metal couples are made. Not all of the couples meet this condition with the same accuracy, and not all of the couples retain their original accuracy. Some couples appear to change or deteriorate with use more than others, due to oxidation, crystallization, segregation of the metal and other undetermined causes.

It was the purpose of this investigation to determine how electromotive forces of couples varied with the temperature, and how constant this force remained with successive heatings and coolings, and also when exposed to various temperatures for extended periods of time.

PROCEDURE.

Couples were purchased from five of the prominent makers, and were cut to lengths of about 18 inches. To each couple about three feet of flexible lamp cord was soldered, and the wires at the point of soldering and all other required points were carefully insulated from each other.

The couples under test were all compared with a platinum and platinum-rhodium couple No. 3P, which had been standardized against a similar couple, "B. S. No. 120," certified to by the Bureau of Standards. The latter couple had not been used since it came from the Bureau of Standards, and was used only to standardize couple No. 3P at the beginning and at the end of the series of tests.

Couple No. 3P changed slightly during the investigation, and a correction was made for the indications of each series of tests. It was assumed that the change was a progressive one, and the total error divided into equal parts and the proper correction made in the corresponding chronological series.

All couples were calibrated over the range given by the manufacturers in their catalogues, and only one base metal couple at a time was compared with the platinum couple No. 3P.

Series 1. All couples were first calibrated against No. 3P with a length of about four inches heated.

Series 2. All couples were again calibrated, but with a length of about 15 inches heated to determine the effect and presence of heterogeneity in the wires.

Series 3. All the couples were now subjected at one time to a constant temperature of 400° C. for a period of about twenty hours. After this treatment each couple was again separately calibrated with a length of 15 inches heated.

Series 4. A second treatment consisted in heating all of the couples together at a constant temperature of about 600° C. for a period of twenty-four hours. After this treatment each couple was calibrated separately, the idea being to determine the effect of heat treatment at 600° C. over that at 400° C.

Series 5. All the couples were now heated together for a period of twenty-four hours at a temperature of 800° C., and afterwards separately calibrated as before.

The calibrations and heat treatments as indicated in Series 3, 4 and 5 were made with each of the base metal couples heated for 15 inches of its length.

FURNACES.

Electrically heated tube furnaces were used in all of the tests. One furnace was 10 inches long, and the other was 20 inches long, each having a tube about one inch internal diameter, and were used for the calibration at 4 inches and 15 inches depth of immersion, respectively. A tube furnace about 2½ inches in diameter and 24 inches long, so that all should be treated together, was used for the heat treatments at the temperatures of 400°, 600° and 800° C. The current on the furnace was controlled by means of a bank of incandescent lamps, and could be adjusted so that the temperature remained stationary for an indefinite period.

METHODS OF MEASUREMENT.

All measurements were made on Leeds & Northrup Type K potentiometers, and only one base metal couple at a time was compared with the standard platinum couple, and the voltage of each couple was determined by a separate potentiometer, the standard cells for each potentiometer being checked for accuracy.

Asbestos discs slightly less than the diameter of the tube, perforated in the center, were slipped on each couple and served to keep the couples centered in the furnace. The two couples were then introduced into the furnace so that the junctions of the couples met. The temperature of the furnace was then raised to about 300° C. for the first point so that a good reading on the platinum couple could be obtained. From this point up the temperature was increased by intervals of about 100° C. At each point the temperature was maintained stationary so that constant readings on both couples were obtained for a period of about two minutes. Thus all lag in the indications of the couples was avoided. During the entire procedure the cold junctions of both couples were kept at zero degrees Centigrade by surrounding them with a bath of melting ice, care being taken to avoid a circulation of air about the cold junction.

COUPLES USED.

The base metal couples used in this investigation are designated as follows:

Couple No. 6A, composed of wires ⅛ inch square and covered throughout the length, excepting about 2 inches, with a winding of asbestos cord, over which there was applied a solution, presumably sodium silicate. This couple had for its negative element an alloy of nickel and chromium, and the positive element one of nickel and iron.

Couple No. 7A was made of No. 8 B. & S. gauge wires, the negative element being composed of nickel with a small amount of aluminum, and the other element a nickel-iron alloy. This couple was purchased with both wires bare, and for the purpose of test an asbestos sleeve was drawn over one of the wires.

Couple No. 18 was composed of two No. 10 B. & S. gauge wires, each of which was wrapped with asbestos thread and painted over with carborundum paint. The negative element was made of nickel with a small amount of aluminum, and the positive element of iron with a small amount of nickel.

Couple No. 19, composed of two No. 10 B. & S. gauge wires, one of which was covered with an asbestos sleeve over which there was a coating of carborundum paint. The negative element consisted of nickel containing a small amount of iron, and the positive element contained iron with a small amount of nickel.

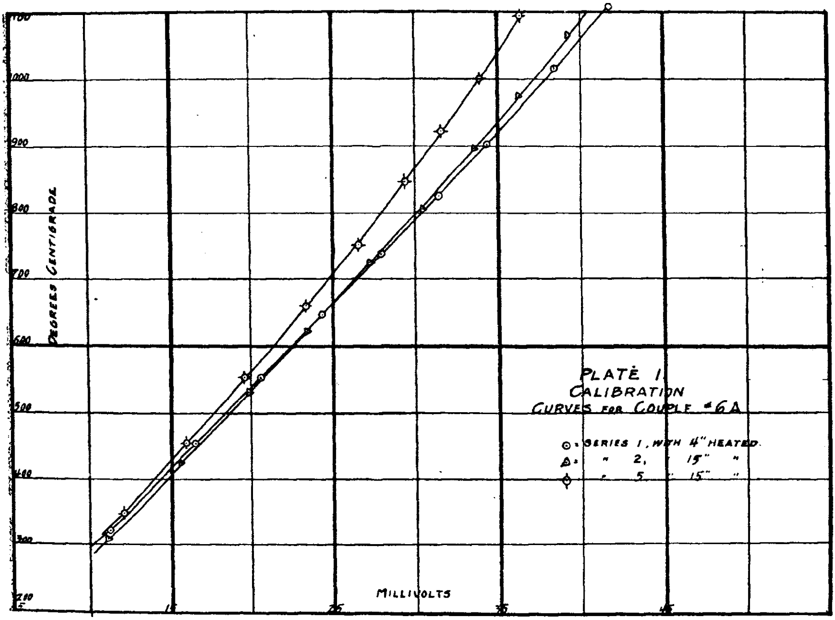

FIG. 1.

Couple No. 20 was made of two No. 16 B. & S. gauge wires, one of which was covered with an asbestos sleeve, and then a coarse asbestos cord was wrapped around both of the wires. No paint covering of any sort was used apparently on this couple. The negative element was a nickel-copper alloy, and the positive element an iron-manganese alloy.

OBSERVATIONS.

The results of the tests on couple No. 6A appear to show that this couple is resistant to oxidation, and was in about as good condition at the end as in the beginning of the series of tests. The asbestos covering appeared to be the most robust and satisfactory of the entire lot. The data of Tables I to V and the curve in Plate 1 show that there is a slight lack of homogeneity in the couple as evidenced by the variation in calibration with 4 inches and 15 inches, respectively, of the couple heated, the difference being about 25° at 40 millivolts. The treatments at 400° and 600° C. had little effect upon the calibration of the couple. The treatment at 800° C. had, however, a marked effect upon the calibration, throwing the curve up so that at 35 millivolts the difference between the indications of the initial and final calibrations was nearly 125° C. This large difference is due apparently to some marked change in the structure of one of the wires composing the couple.

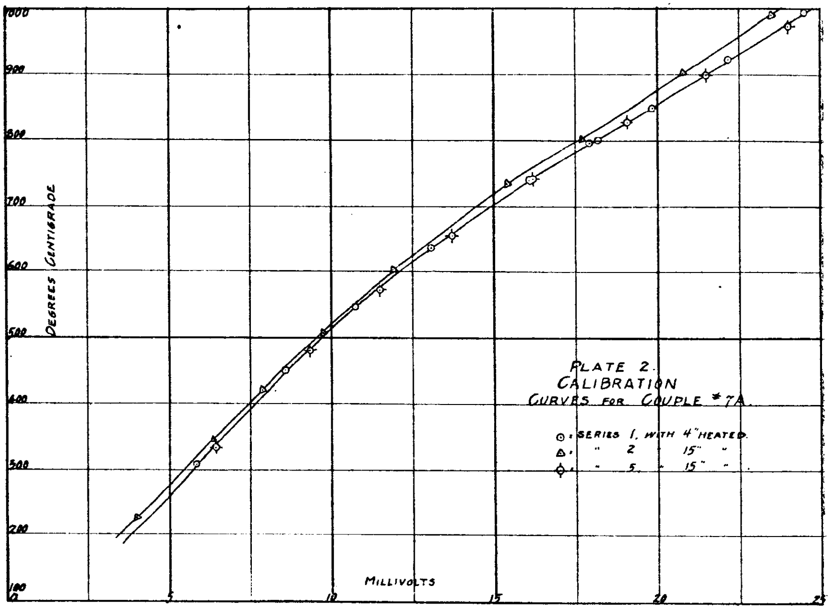

FIG. 2.

The data and curves for couple No. 7A are shown in Tables

I to V and Plate 2. From Plate 2 it is apparent that the calibration curves of this couple are far from being a straight line. The calibrations with 4 inches and 15 inches, respectively, of the couple immersed in the furnace coincide very closely up to 600° C. Above this point the curves separate so that at about 24 millivolts there is a difference of 25 degrees in the indications of the temperature, thus showing the effect of heterogeneity of the wires upon the indication of the couple. It is interesting, however, to note that the heat treatments at 400°, 600° and 800° C., respectively had very little effect upon the constancy with which this couple would indicate the temperature. This couple is robust, and stood the prolonged heat treatments and calibrations without any signs of damage; even the asbestos covering appeared to be in good condition.

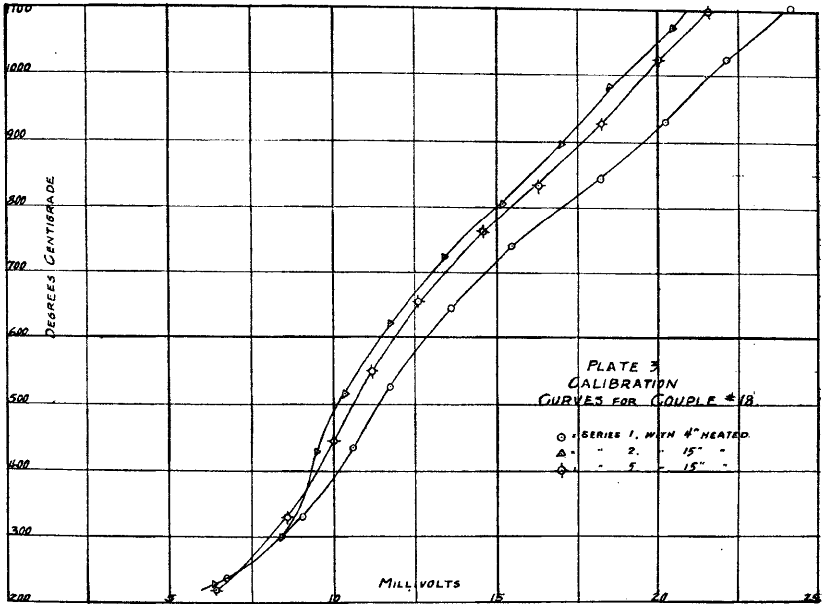

FIG. 3.

Couple No. 18 had a lower electromotive force than either of the two preceding ones. It was found that the iron wire in the couple started to oxidize during the second calibration. As a result of the heat treatment at 400° C. and the third calibration, one of the wires was badly swollen, and after the treatment at

800° it was oxidized so completely that it broke during the subsequent calibration. An examination of the wire revealed the fact that it was oxidized for a distance of about 6 inches beyond the hot junction. It seems likely that the metal of this wire had combined with the silicon of the carborundum paint and formed ferrosilicon. The other wire and its covering were in very good condition with the exception of the carborundum paint, which peeled badly during the first calibration. The data and curves for this couple are shown in Tables I to V and Plate 3.

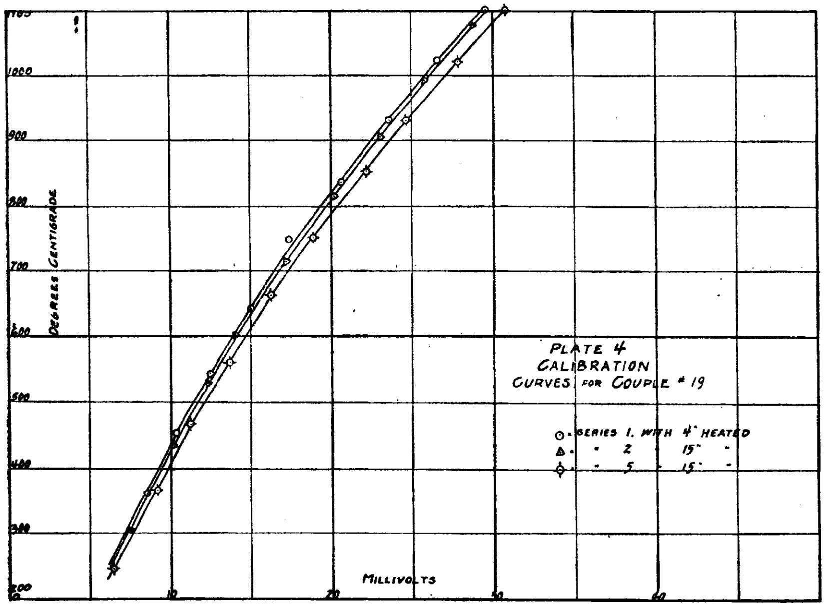

Fig. 4.

Inspection of Plate 3 will show that for an electromotive force of 20 millivolts there is an apparent difference in indication of the temperature by about 130° for a depth of immersion of 4 inches and 15 inches, respectively. This difference is due, no doubt, to a lack of homogeneity of the wires and certain recalescent effects. The calibration curve after the treatment at 400° C. falls between the first and the second calibration curves, showing that some of the heterogeneity has been partially removed. The calibration curves resulting from the treatments at 600° and 800° C. are thrown between the curve after the treatment at 400° and the first calibration with 15 inches of the couple immersed. It is also apparent that at 9 millivolts there is a point of a marked inflection and that the slope of the curve at this voltage is different for all the curves. Thus it would seem that there would be considerable difficulty in arranging a proper scale for the indicating instrument supplied with this couple.

Couple No. 19 showed very robust qualities, the metal being in fine shape at the end of the series of tests. The asbestos sleeve with which one wire was covered had been completely destroyed.

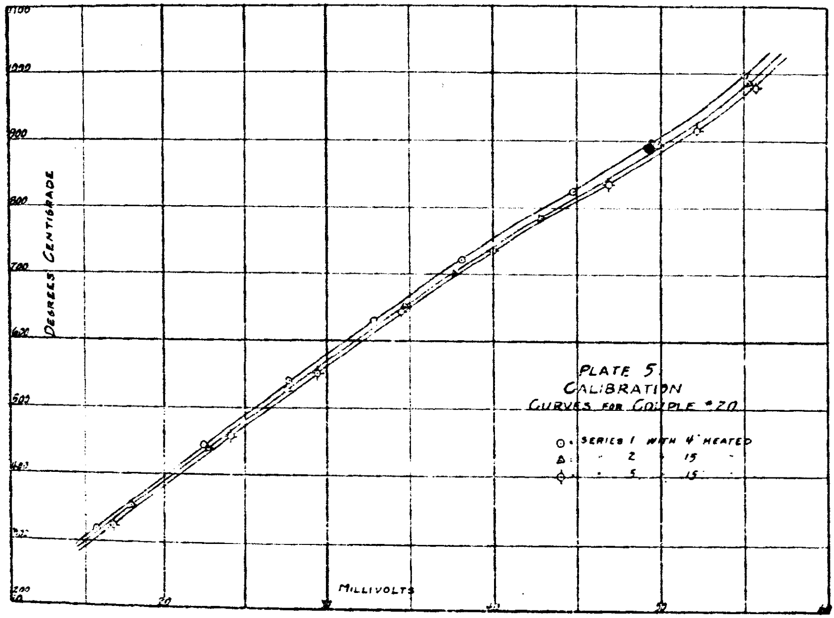

Fig. 5.

The data and curves in Tables I to V and Plate 4, respectively, show a gradual change in the calibration after each treatment, amounting to about 10 degrees at the higher temperature. The couple appears to be homogeneous, as there is only a slight difference in the calibration curves for a depth of immersion of 4 inches and 15 inches. The curve is very nearly a straight line. The discrepancy between the first and last calibrations is about 40° at 30 millivolts.

The data and curves of couple No. 20 in Tables I to V and Plate 5 show that the variation of millivolts with temperature is almost linear. This couple gives a higher electromotive force for a given temperature than any of the other couples. It is, however, less resistant to oxidation. This may be due to the fact that the wires composing the couple are only about one-half the diameter of the other couples. After the treatment at 800° C. one of the wires had been oxidized so that it was only about one-half its original size, while the other wire had swollen to about twice its normal size. Both wires had become very brittle and crystalline to within 6 inches of the cold junction. At the end of the last calibration one of the wires broke in two and spoiled the couple. The asbestos covering on this couple remained in fair shape during the entire series of tests. The calibration curves for 4 inches and 15 inches immersion show a slight variation in voltage for a given temperature, indicating that the couple is somewhat heterogeneous. This difference in temperature for a given voltage is less than 20°, which is doing very well for a couple made of this sort of material. The heat treatments at 400°, 600° and 800° C. did not seem to have very much effect upon the change in calibration. This difference is so small that it compares favorably with the changes which frequently take place in high-grade platinum couples.

TABLE I.

Data of Series 1. First Calibration. Couple 4 Inches in Furnace.

Couple No. 6A		Couple No. 7A		Couple No. 18		Couple No. 19		Couple No. 20	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
324	11.39	316	5.86	240	6.75	360	8.41	318	15.70
454	16.64	450	8.59	330	9.09	452	10.40	445	22.51
554	20.73	545	10.76	435	10.66	542	12.45	540	27.66
646	24.41	636	13.10	525	11.75	643	14.98	634	32.99
737	28.03	738	16.12	645	13.64	749	17.34	721	38.11
825	31.51	800	18.27	738	15.49	836	20.65	825	44.85
906	34.36	924	22.21	843	18.20	931	23.60	896	49.41
1018	38.45	993	24.52	933	20.28	1022	26.57	997	55.02
1115	41.43			1026	22.19	1107	29.58		
				1109	24.16				

TABLE II.

Data of Series 2. Calibration with 15 Inches of Couples Heated.

Couple No. 6A		Couple No. 7A		Couple No. 18		Couple No. 19		Couple No. 20	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
310	11.20	226	3.99	230	6.32	304	7.39	245	11.99
425	15.72	337	6.40	325	8.34	436	10.12	352	17.97
532	19.91	421	7.88	428	9.49	531	12.29	441	22.75
621	23.43	518	9.75	516	10.38	600	14.04	530	27.62
725	27.30	628	12.42	621	11.76	715	17.21	653	34.67
808	30.55	733	15.40	723	13.43	815	20.17	700	37.66
897	33.67	806	17.72	805	15.23	906	23.13	783	42.85
975	36.30	906	20.81	895	17.05	994	25.84	893	49.84
1067	39.19	987	23.47	981	18.51	1078	28.81	984	55.17
				1072	20.46				
				1174	22.77				

TABLE III.

Data of Series 3. Calibrations After Treatment at 400° C., with 15 Inches Heated.

324	11.81	315	6.02	218	6.33	321	7.88	323	16.55
429	16.05	440	8.28	346	8.79	441	10.36	445	23.10
534	20.42	540	10.49	436	9.81	528	12.36	543	28.52
618	23.56	621	12.47	520	10.87	639	15.25	634	33.87
723	27.26	709	15.22	628	12.27	719	17.56	724	39.11
808	30.45	808	18.47	713	13.86	825	20.59	815	45.19
912	33.97	895	21.34	825	16.43	900	23.10	900	50.66
991	36.63	993	24.81	900	18.20	998	26.37	997	56.54
1090	39.53			990	19.82	1085	29.37		
				1080	21.48				

TABLE IV.

Data of Series 4. Calibrations After Treatment at 600° C., with 15 Inches Heated.

343	12.71	355	7.08	213	6.04	355	8.94	316	16.38
454	17.09	436	8.68	358	9.32	450	10.83	429	22.30
546	20.76	545	11.04	471	10.32	555	13.33	546	28.83
657	24.80	642	13.41	540	11.05	650	15.80	637	33.83
758	28.66	739	16.17	635	12.21	746	18.31	736	39.77
834	31.36	819	18.64	729	13.82	843	21.64	810	44.75
921	34.33	917	21.69	834	16.14	911	23.85	894	50.16
1006	37.09	995	24.37	912	17.71	1013	27.32	985	55.25
1110	40.29			993	19.12	1096	30.19		
				1102	21.13				

TABLE V.

Data of Series 5. Calibrations After Treatment at 800° C., with 15 Inches Heated.

Couple No. 6A		Couple No. 7A		Couple No. 18		Couple No. 19		Couple No. 20	
C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.	C°	M. V.
350	12.20	332	6.47	222	6.42	246	6.35	324	16.88
455	16.12	476	9.31	330	8.61	365	9.02	459	24.12
553	19.78	571	11.51	446	9.96	465	11.18	553	29.40
658	23.40	654	13.73	554	11.18	562	13.61	645	34.59
752	26.61	740	16.19	655	12.61	662	16.30	735	40.09
845	29.49	827	19.12	763	14.65	750	18.88	835	46.93
922	31.72	900	21.53	838	16.34	854	22.22	928	52.70
1004	34.03	974	24.07	927	18.25	930	24.71	980	54.77
1095	36.40			1025	20.08	1020	27.95		
				1099	21.58	1102	30.83		

CONCLUSIONS.

This series of investigations seem to point to the fact that it is possible to obtain a base metal couple which is reasonably homogeneous and will give indications of temperature which are sufficiently constant to meet the needs of perhaps the greatest number of requirements for high temperature measurements in the industries.

There are some instances where the temperature is to be known to an accuracy better than 25°, and for such requirements it would be necessary to use a higher grade of equipment, and, furthermore, for such requirements it will be necessary to make frequent calibrations.

It would seem reasonable that the makers of thermocouples determine from the purchaser the particular conditions under which the couple is to be used and that the calibration of this couple be made for the same length of immersion at which the purchaser is going to use it.

A couple which will indicate an apparent difference of temperature amounting to about 130 degrees C. when immersed at different lengths in the bath or furnace is not giving the service that ought to be rendered.

From these tests it appears that not all manufacturers are careful in sending out couples which have been thoroughly annealed to remove all strains resulting from mechanical treatment. Once the couple has attained its permanent structure, there does not seem to be much change in the electromotive force.

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A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

THE EFFECT OF ADDITION AGENTS IN THE ELECTRODEPOSITION OF IRON.

By O. P. WATTS and M. H. LI.

The results set forth in this paper formed part of a thesis written by the junior author for the degree of Chemical Engineer at the University of Wisconsin, and are here presented as an addition to the rapidly growing literature dealing with the effects of small additions of foreign substances to solutions for the electrodeposition of metals.

Previous experience in refining iron had shown the senior author that, while an electrolyte containing only chlorides gave a much smoother deposit than one consisting of the sulphates of iron and ammonia, the iron produced rusted so badly after removal from the electrolyte that a pure chloride electrolyte was not considered practical.

It was found, however, that the admixture of some chloride with the sulphate electrolyte improved the smoothness of the deposit without causing excessive rusting of the iron produced.

When a solution of ferrous sulphate alone was used as an electrolyte its rapid oxidation caused the formation of excessive and harmful amounts of precipitate. The addition of 60 grams of ammonium sulphate per liter of solution considerably diminished this precipitate and resulted in the production of better cathodes than in its absence.

The electrolyte chosen as a basis for the addition of various substances consisted of 150 grams crystallized ferrous sulphate ($FeSO_4.7H_2O$) and 75 grams ferrous chloride ($FeCl_2.4H_2O$) per liter, and had a specific gravity of 1.125 at 20° C.

Fluosilicates and fluoborates have proved very successful for the deposition of lead and nickel, and a test of these electrolytes was therefore made for the deposition of iron. The solutions were prepared by dissolving iron in the respective acids and then neutralizing by ammonia.

A. Ferrous ammonium fluosilicate was electrolyzed with an anode of mild steel for 170 hours at 10 amperes per square foot (1.1 per sq. dm.) at room temperature (26° C.). The deposit was dark gray, streaky and very nodular. The electrolytic cell was half full of a white precipitate.

B. Ferrous ammonium fluoborate was electrolyzed similarly for 150 hours, with similar results as to deposit and electrolyte.

These electrolytes were very inferior to ferrous ammonium sulphate.

The next set of experiments consisted in a comparison of the effect of additions of the sulphates of ammonium, aluminum, magnesium and sodium to the above mentioned basic electrolyte (ferrous sulphate and chloride). The results are indicated in Table I.

TABLE I.

Time of electrolysis 90 hours, current density 1 ampere per sq. dm.

	Addition Agent	Result
C.	50 g. $(NH_4)_2SO_4$ per liter.	Deposit white, but pitted. Little precipitate in electrolyte.
D.	50 g. Na_2SO_4	Poor, gray and pitted deposit. Much precipitate.
E.	50 g. $MgSO_4$	Deposit gray, nodular and rusts badly. Much precipitate.
F.	50 g. $Al_2(SO_4)_3$	Deposit gray, streaked, and peeling off at top. Solution half filled with flucculent precipitate.

To prevent the formation of precipitates, 30 cc. of dilute sulphuric acid (1 volume of acid to 4 volumes of water) was added to each liter of electrolyte and the amounts of the sulphates increased to 120 grams. The results appear in Table II.

TABLE II.

Time, 140 hours, at 1 ampere per sq. dm.

	Addition Agent	Result
G.	120 g. $(NH_4)_2SO_4$ 30 cc. dil. H_2SO_4	Deposit bright, but nodular. Solution clear and yellowish.
H.	120 g. Na_2SO_4 30 cc. dil H_2SO_4	Deposit gray and very nodular. Gas evolved at cathode. Solution clear.
I.	120 g. $MgSO_4$ 30 cc. dil. H_2SO_4	Deposit dark gray with large nodules. Gas at cathode. Little precipitate.
J.	120 g. $Al_2(SO_4)_3$ 30 cc. dil. H_2SO_4	Deposit smooth and white at first, but finally gray and nodular. It rusted badly. Solution half filled with precipitate.

Since none of the other sulphates compared favorably with ammonium sulphate as an addition agent, the last named was used in all electrolytes for testing what further improvement could be made by organic substances.

TABLE III.

$$\text{Electrolyte:}\quad \left.\begin{array}{r} 150\text{ g. } FeSO_4.7H_2O \\ 75\text{ g. } FeCl_2.4H_2O \\ 120\text{ g. } (NH_4)_2SO_4 \end{array}\right\}\text{ per liter.}$$

Current density 1 ampere per sq. dm. Amount of addition agent is in grams per liter, and if not soluble in water was added as an alcoholic solution.

No.	Addition Agent	Time in Hours	Deposit
1.	0.5 g. acetanilide	170	Good, bright, but slightly pitted.
2.	0.5 g. acetphenetedin	170	Fair, good color, but much pitted.
3.	0.5 g. amidol	240	Fair, good color, but pitted.
4.	10 g. ammonium acetate 20 cc. dil sulphuric acid	120	Bad, black and worthless.
5.	23.4 g. ammonium citrate	120	Bad, dark and streaked.
6.	10 g. ammonium oxalate 20 cc. dil. sulphuric acid	120	Excellent, bright and smooth.
7.	20 g. ammonium oxalate	170	Very good, but inferior to No. 6.
8.	40 g. ammonium oxalate	40	Poor, brittle and peeling, contaminated by yellow precipitate.
9.	10 g. ammonium oxalate	290	Excellent.
10.	12.3 g. ammonium tartrate	50	Poor, slightly nodular and peeling off.
11.	0.5 g. benzoic acid	100	Bad, nodular and greenish. Gas at cathode.
12.	1 g. *beta*-naphthol	170	Poor; deposit of good color, but badly pitted.
13.	0.5 g. boric acid	200	Poor; deposit of good color, but badly pitted.
14.	2 drops bromoform	170	Poor, deposit white but badly pitted.
15.	2 drops creosote, white	170	Poor, of good color, but pitted.
16.	1 g. dextrine	170	Very good, white and smooth.
17.	0.5 g. eikonogen	220	Poor, of good color, but badly pitted.
18.	3 drops eucalyptol	170	Fair, brilliant, but nodular.
19.	4 drops formaldehyde (40 percent)	240	Excellent, bright and smooth.
20.	4 drops formin	250	Excellent, bright, smooth and compact.
21.	0.5 g. gallic acid	170	Fair, streaky.
22.	0.5 g. gelatine	100	Bad, corrugated, pitted and nodular.
23.	1 g. glucose	170	Good, slightly nodular.
24.	0.5 g. gum arabic	240	Poor, vertical streaks and grooves.
25.	0.5 g. gum copal	120	Poor, good color, but badly pitted.
26.	0.5 g. gum dammar	170	Poor, good color, but pitted.
27.	0.5 g. gum sandarac	170	Fair, brilliant, but pitted.
28.	1 g. gum tragacanth	100	Fair, brilliant, peels off.
29.	0.5 g. licorice	200	Poor, much pitted.

No.	Addition Agent	Time in Hours	Deposit
30.	...extract logwood	200	Poor, good color, but pitted.
31.	2 drops lysol	200	Bad, gray with very large pits.
32.	3 drops oil of cedar.	140	Poor, of good color, but pitted.
33.	8 cc. oil of cloves	150	Fair, of excellent color, but pitted.
34.	0.5 g. peptone	170	Bad, mossy.
35.	4 drops phenol	190	Excellent.
36.	2 drops pyridine	120	Poor, of fair color, but pitted.
37.	1 g. pyrocatechin	170	Excellent.
38.	1 g. pyrogallol	120	Bad, dark colored, rusts badly.
39.	0.6 g. pyrogallol	100	Poor, brilliant, but nodular.
40.	1 g. resorcine	170	Very good, white and smooth.
41.	0.5 g. resorcine	240	Very good, white, but slightly nodular.
42.	0.5 g. salicin	170	Poor, gray and pitted.
43.	1 g. salicylic acid	120	Bad, gray and rough, rusts badly.
44.	0.5 g. saponin	100	Bad, spongy and badly rusted.
45.	0.5 g. tannic acid	100	Poor, badly pitted.
46.	0.5 g. terpin hydrate	170	Fair, of good color, but many small pits.
47.	3 drops turkey red oil	170	Bad, dark and badly pitted.
48.	2 drops turpentine	170	Poor, light gray and badly pitted.

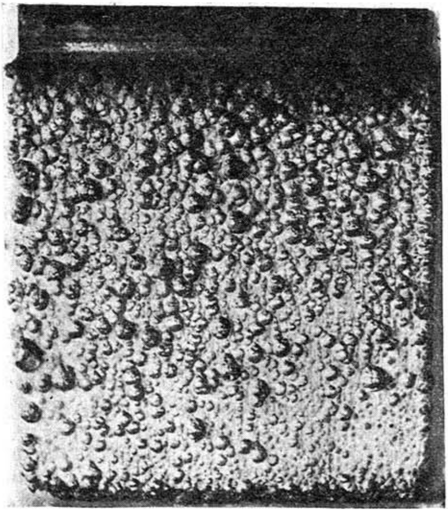

FIG. 1.

An objectionable tendency of electrolytic deposits is that they grow rough with increasing thickness, so that there is a limit, depending on the purpose for which the deposit is to be used, beyond which deposition cannot profitably be continued. Figure 1 shows a cathode of electrolytic iron a foot square and an inch or more thick, a very good deposit. Cathodes of copper or lead of equal thickness are fully as rough and nodular. This might be called the natural state of electro-deposited metal. It is the function of the successful addition agent to remedy this roughness. A, 10 and I in Fig. 2 show the nodular structure produced by several addition agents, the original electrolyte giving deposits free from nodules until the cathode attains at least three times the thickness of those shown.

For convenience the addition agents used have been classified according to certain well-marked physical characteristics of the cathodes. In each class the order indicates the relative quality of the cathodes in respect to that characteristic, *e. g.*, under pitted deposits each is more pitted than the one following, while those italicised show this action to an exceptional degree.

Nodular Deposits: *11*, *1*, 18, 41. Pitting caused by the clinging of bubbles of gas to the cathodes is a trouble to which thick cathodes of iron, nickel and zinc are subject. Copper and silver, whose discharge potentials in acid solutions are below that of hydrogen, are not subject to this trouble, so far as the writers have observed. 33, 47 and 31 in Fig. 2 show different degrees of pitting by gas bubbles. Although many of the addition agents are reported to cause pitting, there is a probability that experiments covering a longer period would have eliminated the pitting in several cases, for this has been found to grow less the longer electrolysis is continued, and seemingly it does not always keep step with exhaustion of the addition agent.

Pitted deposits: *31*, *C*, *25*, *47*, *48*, 17, 13, 42, 34, 46, 12, 21, 33, 27, 36, 3, 1, 29, 26, 30, 32, 15, 22.

Vertical grooves or striations is another trouble occasionally met with. Cathodes *24* and 5 were so afflicted.

"Brighteners" for silver and brass solutions have long been known among platers. Several addition agents produced bright deposits of iron, but these were extremely hard and brittle, and usually cracked and curled off from the starting sheet.

Bright deposits: *28*, *18*, *27*, 40, 8.

Several addition agents caused a badly rusted deposit, in the worst cases consisting entirely of iron rust.

Rusted deposits: *44*, *11*, 1, E, H, 43, 38, F, D, 5, J.

The color of the electrolyte at the end of the test was closely

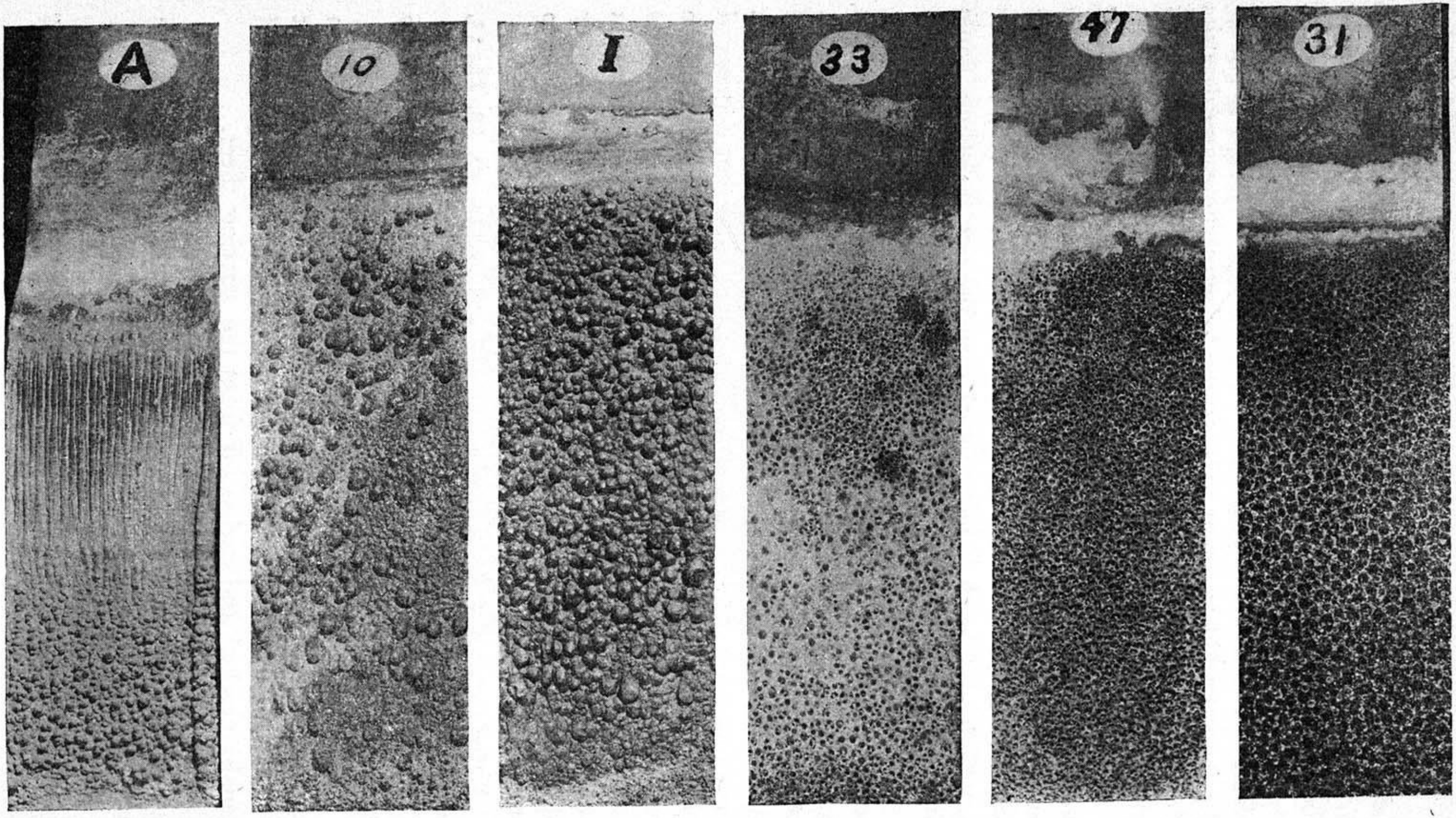

FIG. 2.

related to the quality of metal produced. A yellowish-green electrolyte almost invariably gave clean metal of a fine color, even though it might be too badly pitted to allow of the practical use of that particular electrolyte. A dark electrolyte fouled by much green precipitate usually yielded very bad looking mteal.

Yellowish-green electrolyte with little precipitate: 6, 7, 13, 15, 18, 19, 23, 25, 26, 27, 29, 30, 32, 33, 35, 36, 40, 45, 47, 48.

Ditto, with much precipitate: 2, 17.

Greenish electrolyte with little precipitate: 1, 3, 10, 12, 22, 31, 34, 40, 43, 46.

Ditto, with much precipitate: 20.

Bluish or dark green: 4, 5, 11, 14, 16, 21, 24, 28.

In order to test the best addition agents more thoroughly they were run continuously at 10 amperes per square foot for 21 to 30 days in series with a cell containing the electrolyte without any organic addition agent. The results are given in Table IV.

TABLE IV.

No.	Addition Agent	Days	Deposit
49.	None	30	Excellent, silvery, $\frac{7}{16}$-inch thick, slightly nodular.
50.	6 g. ammonium oxalate	30	Excellent, silvery and smooth. The best cathode of all.
51.	0.6 g. formin or hexamethylenetetramine	30	Excellent, bright and compact Slightly inferior to No. 50.
52.	0.5 g. resorcine	30	Very good, bright and solid, but slightly nodular near bottom.
53.	0.5 g. dextrine	30	Fair, excellent for first three weeks, then vertical grooves developed.
54.	4 drops formalin	21	Excellent, slightly nodular on the lower part.
55.	0.5 g. glucose	21	Fair, nodular near bottom.
56.	2 drops phenol	21	Excellent, white and solid, but with a few nodules near the bottom.
57.	0.2 g. tragacanth	21	Very good, slightly grooved, and thick on the edges.

The quality of metal in all of these deposits was excellent, and the only choice lay in smoothness and freedom from nodular structure.

Arranged in order of excellence, they are: *50, 51,* 56, 54, 49. The first two were distinctly superior to No. 49, which contained no addition agent. The others so closely resembled No. 49 that it is doubtful if these addition agents caused any improvement.

These experiments show that two organic addition agents, ammonium oxalate and formin, are capable of improving upon the remarkably smooth and satisfactory deposit given by the original electrolyte.

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A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

ADDITION AGENTS IN THE DEPOSITION OF ZINC FROM ZINC SULPHATE SOLUTION.

By O. P. WATTS and A. C. SHAPE.

This paper presents the effect of the separate addition of over two score different organic substances to a zinc plating solution.

The electrolyte was made by adding an excess of zinc to dilute sulphuric acid. The solution had an acid reaction and contained 25 percent of $ZnSO_4.7H_2O$. The amount of organic substance added was one gram per liter. Except when otherwise stated, the solutions were electrolyzed for two hours at about 22° C., with a zinc anode and an iron cathode, at a current density of about 10 amperes per square foot (1.1 amperes per sq. dm.). For comparison, the well-known Meaker galvanizing solution was electrolyzed under similar conditions.

The majority of the substances added had an injurious rather than a beneficial effect upon the deposit. The most common defect was the production of vertical grooves or striations, shown in various degrees by cathodes 25, 13 and 32 of the photograph. Cathode 1, from the Meaker solution, is typical of the best deposits. Cathode 47, a 16-hour deposit with eikonogen as addition agent, shows the mossy tufts which frequently appear on zinc deposits. Cathode 48 shows the effect of amidol in the same time, and resembles a thickly-planted apple orchard.

The results, arranged in tabular form, follow:

No.	Addition Agent	Current Density Amperes		Deposit
		Per Sq.Dm.	Per Sq. Ft.	
1	Meaker solution.	1.23	11.2	Excellent, non-crystalline, adherent.
2	$ZnSO_4$—no add'n	1.20	10.9	Poor, striated.
3	Acetanilide	1.17	10.6	Verv poor, badly striated.
4	Acetphenetidin .	1.26	11.5	Very poor, striated, dark.
5	Amidol	1.20	10.9	Poor, pitted.
6	Benzoic acid....	1.27	11.5	Good, non-crystalline, adherent.
7	Betanaphthol ...	1.27	11.5	Excellent.
8	Caffeine	1.20	10.9	Fair, crystalline.
9	Creosote	1.38	12.5	Fair, crystalline, slightly striated.
10	Dextrine	1.20	10.9	Poor, striated, granular.
11	Eikonogen	1.23	11.2	Very good, smooth, but dark.
12	Eucalyptol	1.20	10.9	Bad, striated, very dark.
13	Formin	1.20	10.9	Poor, striated.
14	Gallic acid	1.17	10.6	Very poor, striated.
15	Gelatine	1.32	12.0	Poor. crystalline, dark.
16	Glucose	1.17	10.6	Poor, striated.
17	Gum arabic	1.20	10.9	Fair, slightly striated.
18	Gum copal	1.27	11.5	Very poor, badly pitted.
19	Gum dammar ..	1,20	10.9	Very poor, striated, pitted, non-adh'nt.
20	Gum guaiac	1.14	10.4	Bad, striated, non-adherent.
21	Gum sandarac ..	1,20	10.9	Very poor, striated, pitted.
22	Gum tragacanth.	1.17	10.6	Very poor, striated, pitted, non-adh'nt.
23	Hydroquinone ..	1.23	11.2	Poor, striated, pitted.
24	Isinglass, Brazil.	1.27	11.5	Bad, striated, crystalline, dark.
25	Licorice	1.27	11.5	Very bad, striated, very dark.
26	Oil of cedar.....	1.23	11.2	Bad, striated, dark, non-adherent.
27	Oil of cloves....	1.27	11.5	Bad, striated, dark.
28	Oxalic acid	1.17	10.6	Poor, striated.
29	Peptone	1.23	11.2	Bad, dark, non-adherent.
30	Phenol	1.29	11.8	Fair, slightly striated and pitted.
31	Pyrocatechin ...	1.23	11.2	Very poor, striated.
32	Pyrogallol	1.23	11.2	Fair, slightly striated.
33	Salicin	1.20	10.9	Very poor, striated, pitted.
34	Salicylic acid....	1.27	11.5	Very poor, striated.
35	Salol	1.20	10.9	Very poor, badly striated.
36	Saponin	1.20	10.9	Very poor, striated.
37	Resorcine	1.13	10.3	Poor, striated, pitted.
38	Tannic acid	1.27	11.5	Very poor, gray, striated, granular, [pitted.
39	Tartaric acid ...	1.20	10.9	Poor, striated.
40	Terpin hydrate..	1.30	11.8	Fair, crystalline.
41	Turkey-red oil..	1.20	10.9	Poor, crystalline.
42	Turpentine	1.20	10.9	Bad, striated, non-adherent.

Addition agents which are insoluble in water were dissolved in alcohol before adding them to the electrolyte.

Those addition agents which gave the best results, *viz.*, gum arabic, benzoic acid, betanaphthol, caffeine, eikonogen, formin, pyrogallol and terpin hydrate, were tested repeatedly for different

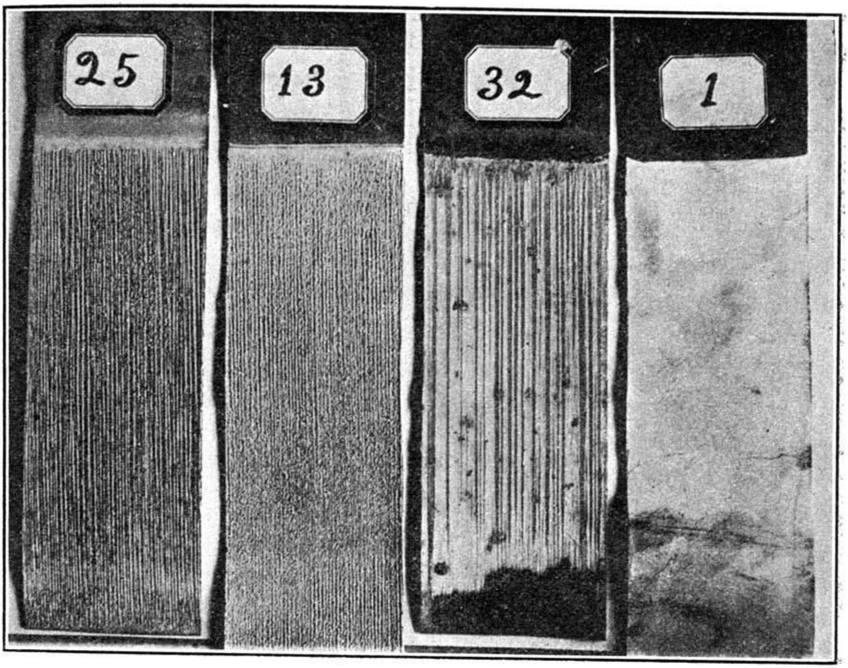

FIG. 1.

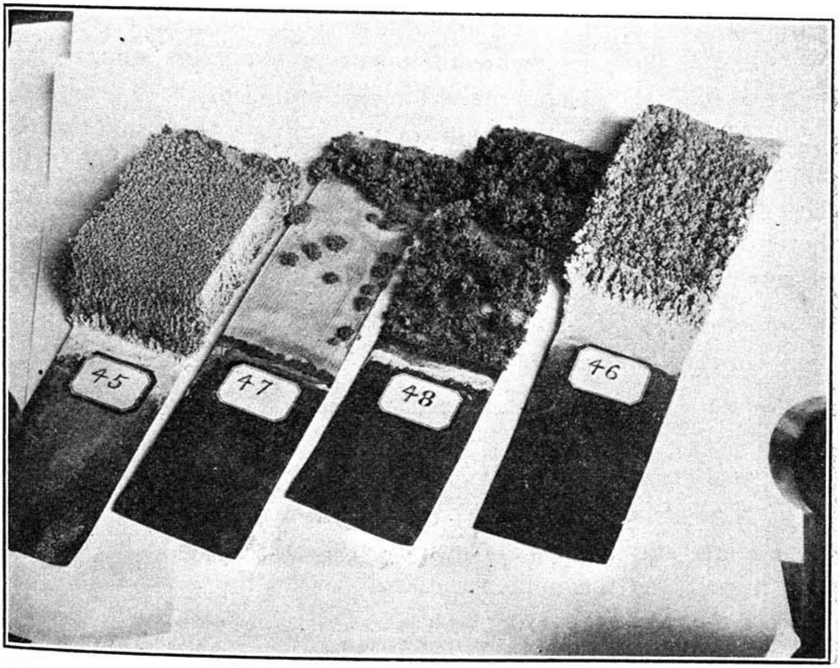

FIG. 2.

lengths of time. These tests resulted in the selection of betanaphthol, eikonogen and pyrogallol as the best addition agents.

Solutions containing these three reagents were electrolyzed for seven days at 0.5 ampere (10.5 amperes per square foot (1.16 amperes per sq. dm.)) in series with the Meaker solution. Although most experimenters have reported that addition agents are used up during electrolysis, and so require replenishing from time to time, it is claimed that the Meaker solution is self-sustaining and requires no additions to it during use.

After a number of hours' electrolysis of the above solutions, all except the betanaphthol became rough and unsatisfactory. It was only after several days that this deposit also became rough and spongy. Cathode 45 is the 7-day deposit from the Meaker solution, and cathode 46 that from the betanaphthol solution.

Whether or not failure of the electrolytes was due to exhaustion of the addition agents, and can be prevented by adding a fresh supply of these from time to time, was not determined in these experiments. There is, of course, also the possibility that some of the addition agents which failed under the conditions described may prove effective at a higher temperature or with some other zinc salt than the sulphate as electrolyte.

Although these experiments constitute but a preliminary and hasty survey, they have resulted in the finding of three promising addition agents for the deposition of zinc from a solution of zinc sulphate, *viz.*, eikonogen, pyrogallol and betanaphthol. The latter is best, and, so far as the writers have observed, has not heretofore been suggested as an addition agent for the deposition of any metal.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

J. N. PRING (*Communicated*): An investigation extending over some years, which has been carried out by Mr. U. C. Tainton and myself,[1] on the influence of colloids on the electrodeposition

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[1] C. f. Brit. Pat. 7235 of 1911. U. S. Pat. 1,059,233. Trans. Chem. Soc. London, **105**, 710 (1914).

of zinc, has shown that deposits similar to those reproduced in the paper of Messrs. Watts and Shape can be obtained under the following conditions: An electrolyte is taken of zinc sulphate together with from 10 to 20 grams of free sulphuric acid per 100 cc., and a small quantity of a colloid such as gum arabic. A current density at the cathode of between 20 and 50 amp. per square dcm. is employed. When using lead anodes, this current can be obtained with 4.5 to 5.0 volts in the above electrolyte. The current efficiency varies from 90 to 96 percent. With these conditions, considerable quantities of most impurities have no great deleterious effect on the deposition of the zinc. Moreover, iron, which is the most troublesome impurity in ordinary practice, remains for the most part in the electrolyte during electrolysis, on account of passivity or retardation phenomena. These conditions have been found to be the most favorable for conducting the extraction of zinc from solutions made from ores and for the purpose of electro-galvanizing, as deposits of very high luster are obtained with suitable colloids.

It would be of great interest if Messrs. Watts and Shape mentioned the current efficiency obtained in their electrolyses and also if measurements have been made with commercial solutions.

O. P. WATTS: Unfortunately, no determinations of current efficiency were made in our experiments, but the absence of noticeable evolution of gas at the cathode would indicate an efficiency of 95 percent or above.

I wish to congratulate Dr. Pring on two notable achievements: The deposition of zinc on stationary cathodes at 465 amperes per square foot, smooth and solid enough for galvanizing, and the attainment of current efficiencies of 90 to 95 percent from solutions containing 20 percent of free sulphuric acid, a degree of acidity which even copper refiners do not venture to use. Dr. Pring's experiments disclose new and undreamed-of possibilities in the electrometallurgy of zinc, and emphasize the importance of trying experiments which, in the light of our present imperfect knowledge of the laws of nature and the properties of matter, would seem sure to fail.

H. E. Holbrook,[2] using faintly acid zinc solutions, probably

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[2] B. S. Thesis, University of Wisconsin, 1912.

richer in iron than Dr. Pring's, found the same tendency for the iron to stay in solution. At 13 amperes per square foot, with stationary cathodes and soluble anodes, he electrolyzed for 30 minutes a solution containing 20 grams of zinc sulphate and 50 grams of ferrous sulphate per liter, and obtained a deposit containing 6.21 percent of iron. In a similar experiment the electrolyte contained 30 grams of each sulphate per liter, and the deposit was only 1.25 percent iron. Whatever may be the cause of this unexpected phenomenon, I do not see how passivity can explain the failure of the iron to plate out, once it has dissolved in the electrolyte.

A paper presented at the Twenty-fifth General Meeting of the American Electrochemical Society, in New York City, April 18, 1914.

POLARIZATION SINGLE POTENTIALS.

By Claude N. Hitchcock.

In a very interesting paper upon the decomposition of water, which appeared in a previous volume of the Transactions of this Society, J. W. Richards[1] obtained decomposition at an impressed electromotive force of only 1.15 volts instead of 1.67 volts, the value generally accepted for the decomposition point of water. This abnormal result was attained by the use of platinum electrodes differing greatly in size.

The experiments which follow were undertaken for the purpose of determining the potential at each electrode in such cases of decomposition of electrolytes below the normal decomposition point.

A description of the apparatus used and a word as to the mode of procedure will be considered before going into a detailed account of the experimental work.

Fig. 1 shows a diagram of the apparatus. A constant potential of ten volts was applied to a nichrome wire resistance coil *R*, from which any desired potential up to ten volts could be picked off by means of sliding contacts. By following out the connections in the above diagram the system will be easily understood. Key *K* requires a little explanation. This is a combination of a double-pole line switch and a short-circuit galvanometer key. With the lever in normal position, *m* and *m'* are connected to *n* and *n'* respectively by means of two side levers not shown, and *d* is connected by a top contact to *c*. When the lever is pressed down the electrolyzing circuit is broken and *c* is connected by a bottom contact to *b*.

The voltmeter used was an accurately calibrated instrument, from which readings could be obtained in millivolts. A milli-

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[1] Vol. 4, p. 120 (1903).

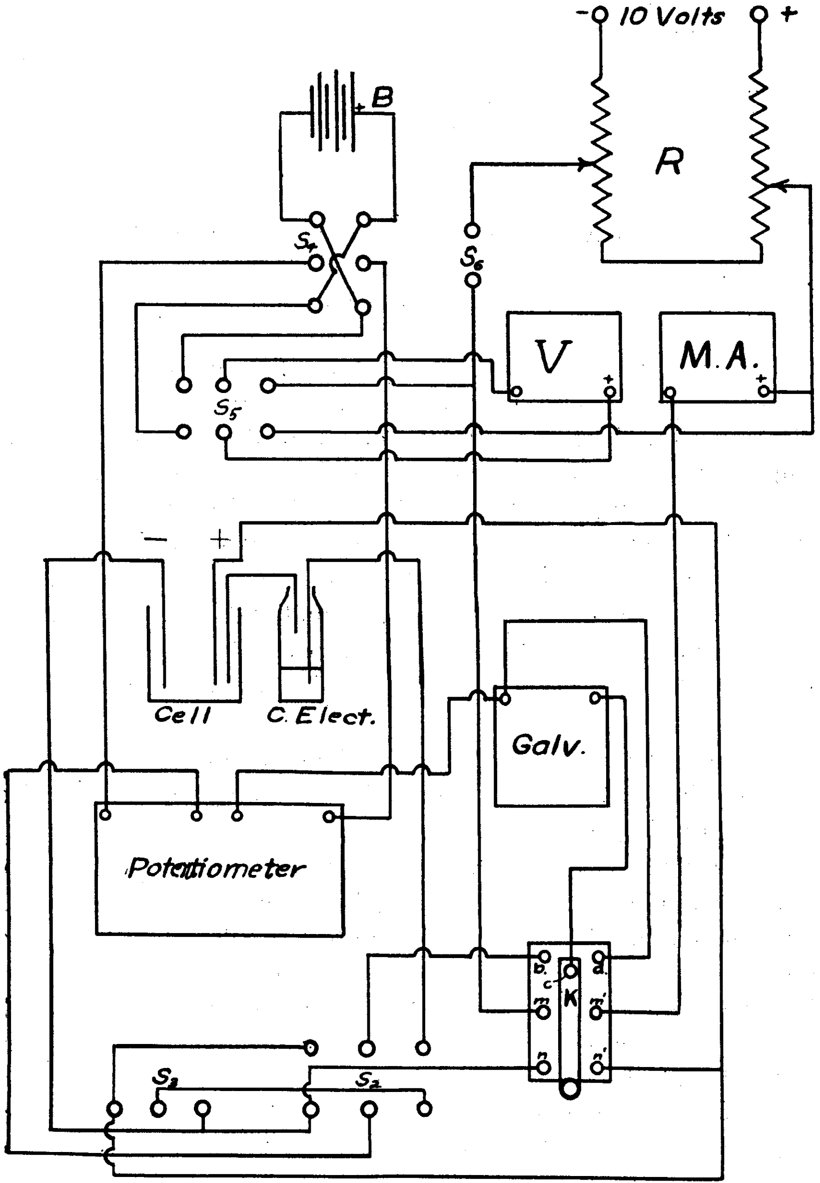

FIG. 1.

ammeter reading to hundredths of a milliampere was used, not so much to read exact values of current (for these experiments were not intended to deal with residual currents) as to indicate when that point in the experiment had been reached at which an appreciable current flowed through the cell.

Measurement of instantaneous values of polarization was accomplished with a potentiometer, this being a more accurate device than a millivoltmeter, as it drew from the system no current that would tend to destroy the maximum values of the counter electromotive forces. The calomel electrode had a potential of —0.56 volt, and it was frequently compared, during the series of experiments in which it was used, with another reserved for the purpose.

To manipulate the foregoing apparatus the cell and normal electrode were connected to the system as shown. To read total potential the switch S_3 was left open and switch S_2 was thrown to the left. By tapping the key K and adjusting the potentiometer, the galvanometer, an instrument sensitive to one micro-ampere, showed when the total potential was equal to that recorded by the potentiometer. In like manner the single potential of the cathode was found with switches S_2 and S_3 thrown to the right; and of the anode with S_2 thrown to the right and S_3 to the left. After obtaining initial values of total, cathode and anode potential, switch S_6 was closed and the sliding contacts arranged on R to pick off the voltage desired. The minimum voltage impressed on the cell was 0.2 volt, and from this starting point the electromotive force was increased at the rate of 0.1 volt per minute in increments of 0.2 volt, except around the decomposition point, where 0.1 volt increments were used.

The electrolyte used in most of the experiments was a normal sulphuric acid solution, made up from c. p. acid and distilled water. The solution was boiled to remove dissolved gases, cooled in a closed flask, and re-standardized with air-free water. Solutions used, differing from the above, will be noted.

Platinum electrodes were employed in all experiments. The regular procedure was to heat the electrodes to a red heat and plunge them into the electrolyte just before the experiment began.

Before attempting a study of electrolysis with electrodes of unequal size, it was deemed best to secure data under the standard conditions of equal electrodes.

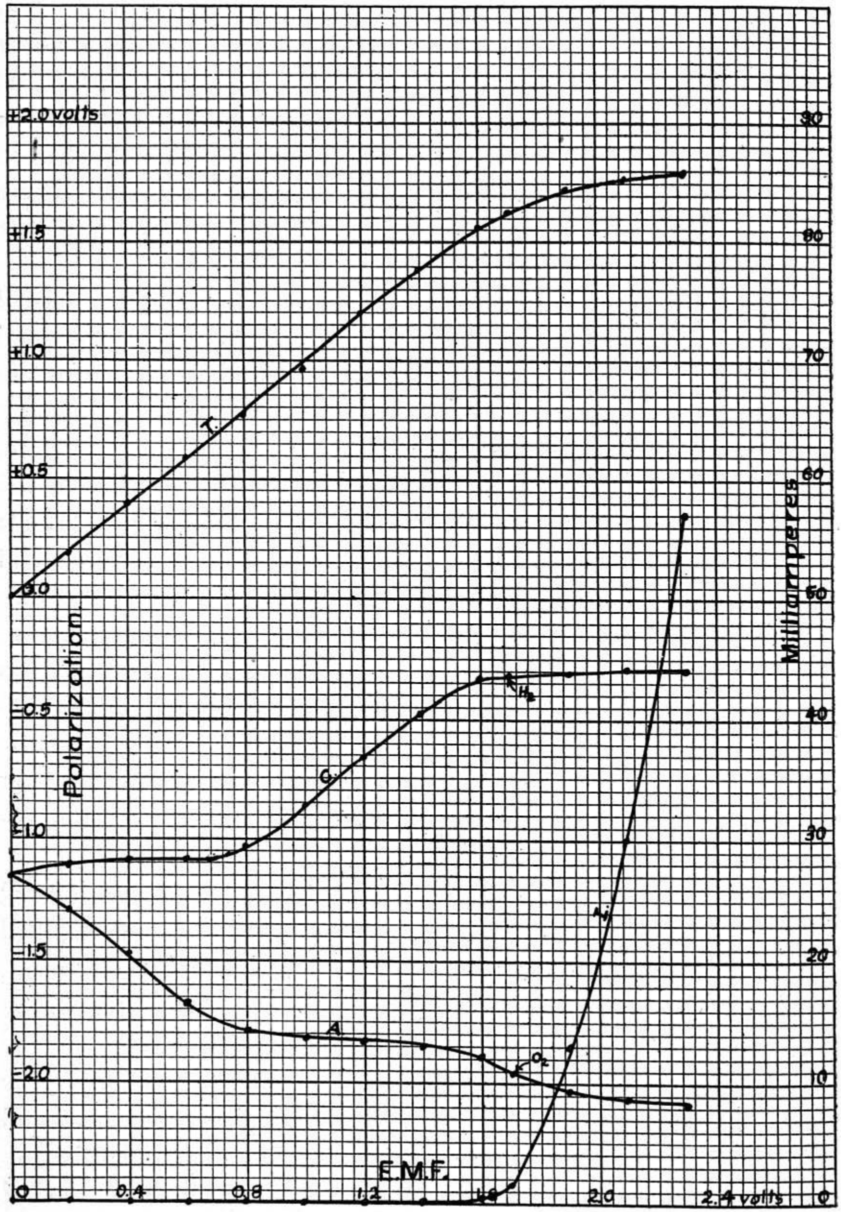
+2.0 volts
+1.5
+1.0
+0.5
0.0
-0.5
-1.0
-1.5
-2.0
Polarization
90
80
70
60
50
40
30
20
10
0
Milliamperes
T
C
A
H_2
O_2
M
E.M.F.
0
0.4
0.8
1.2
1.6
2.0
2.4 volts

Plate I.

EXPERIMENTS WITH ELECTRODES OF EQUAL SIZE.

No. 1.

Two platinum electrodes, each one centimeter square, were placed one centimeter apart in a cell holding 60 c.c. of electrolyte. The latter had stood exposed to the air for a short time before the experiment began, no precautions being taken to prevent absorption of air by the solution. Table I at the end of this paper gives the data secured, from which the curves of Plate I have been plotted. The curves plotted with total polarization as ordinates and impressed electromotive force as abscissae are denoted by *T* with a subscript corresponding to the number of the curve. The curves drawn with impressed voltage as abscissae and electrode potentials for ordinates are marked *C* for the cathode and *A* for the anode. Current Curves I are plotted with the same abscissae, and current values for ordinates. Current values plotted are the average that flowed during the two minute intervals between increments of electromotive force.

An inspection of this plate at once shows that the cathode curve is peculiar. Although the maximum change in potential of each electrode is about the same, up to an impressed electromotive force of 0.6 volt, the cathode still has almost its initial potential, while the potential of the anode has changed over 0.5 volt. If it be assumed (and there seems to be no escape from the assumption) that the successive changes in the potential of the anode are caused by the deposition of oxygen by that momentary current which is observed to flow every time the voltage is increased, it follows that twice as much hydrogen by volume must have been deposited on the cathode. Since little change in potential resulted, this hydrogen must have been removed as fast as deposited, and suspicion falls upon the air contained in the solution as being the depolarizing agent.

No. 2.

Another sample of the same electrolyte was, therefore, boiled to remove the dissolved gases and kept covered with a layer of kerosene during cooling and subsequent use. The results are shown in Table II and Curve I, Plate II.

Comparing the curves for this test with those for Experiment I,

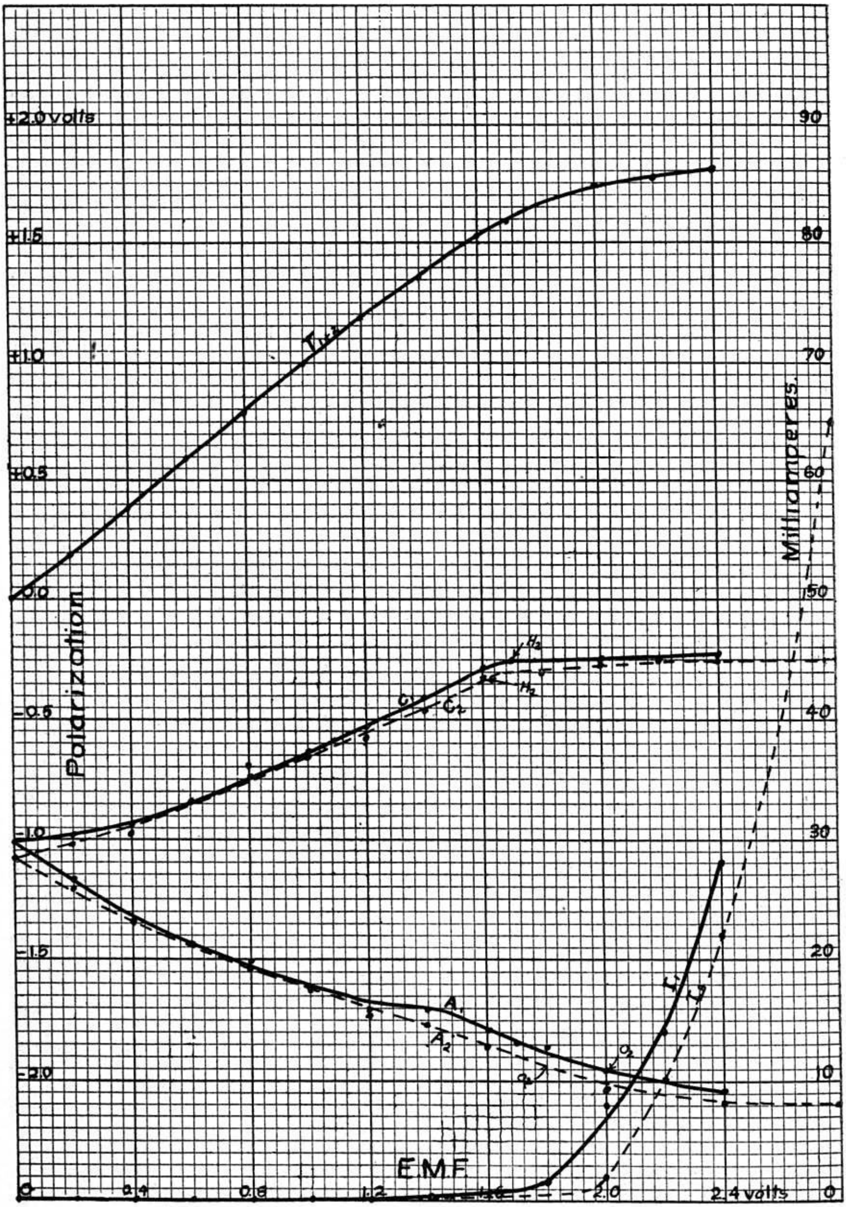

PLATE II.

it is at once evident that different conditions existed. Instead of remaining constant for the first few increments of voltage as before, the cathode potential here begins to rise as soon as electromotive force is applied to the cell. Taking into account the precautions used for exclusion of air, it is reasonable to conclude from the smaller degree of cathode depolarization observed in this experiment that where oxygen is dissolved in the electrolyte, owing to contact of the electrolyte with the air, depolarization results. That all oxygen had not been expelled from the electrolyte in the present case, however, seems probable, for the slight downward curvature of the cathode potential line suggests that some small depolarizing factor was still present. Before going to the next experiment, in which further elimination of dissolved oxygen was tried, it might be noted that the evolution of oxygen in this experiment occurred after hydrogen had begun to come off, due, no doubt, to the greater solubility of oxygen in water.

No. 3.

In this experiment the solution was made up as in the one before, but, instead of covering the electrolyte with kerosene, the cell and calomel electrode were placed under a bell jar and the experiment carried out under a reduced pressure of one-third of an atmosphere. This helped materially in removing the air dissolved in the electrolyte (see Table III and Curve II, Plate II). Not only was dissolved oxygen drawn out of the solution, but the appearance of gas at both electrodes at lower applied voltages than in experiment *No. 2* indicates that reduction of pressure removed some of the oxygen deposited at the anode which otherwise might have diffused over to the cathode, causing depolarization there. At any rate, depolarization is observed to occur at a constant rate at both electrodes. Both electrode potential curves approximate straight lines, a result not obtained by either of the foregoing experiments.

It is to be noted from the results of experiments *Nos. 2* and *3* that, altho the potential curves of cathode and anode vary considerably from each other in the two cases, still the total polarization curves for both coincide.

No. 4.

Finally, in order to add one more proof to the above conclusion on the depolarizing effect of dissolved oxygen, an experiment similar to *No. 1* was run, using a solution through which pure oxygen had been bubbled for five hours. Table IV gives the data taken, which, when plotted, gave total and single potential curves coinciding exactly with those of Plate I. We can therefore conclude that on standing exposed to the air for a short time the electrolyte used in these experiments became practically saturated with oxygen.

EXPERIMENTS WITH UNEQUAL ELECTRODES.

Having become familiar with the relations that exist between anode and cathode polarization when the electrodes are of equal size, and having established the effect of dissolved oxygen on such polarization, experiments were next undertaken with electrodes of unequal size.

No. 5.

A cell was arranged with a cathode one centimeter square and an anode one hundred times as large. The electrodes were placed one centimeter apart in a normal sulphuric acid solution (see Table V and Curve I, Plate III). In agreement with Richards' results,[2] gas was observed to come off from the cathode at 1.1 volts. From the presence of oxygen in the solution, however, depolarization of the cathode should occur as in experiment *No. 1*, yet the curves here appear more like those of experiment *No. 2*. The reason for this must be sought in the use of the large anode. Now, the current density at the cathode is one hundred times as great as at the anode. Two hundred volumes of hydrogen are discharged at the cathode per square centimeter for every volume of oxygen discharged per square centimeter at the anode, so that, even though the normal amount of oxygen in the solution did tend to depolarize the cathode as in experiment *No. 1*, still, with such large quantities of hydrogen a similar effect could not be produced. This large quantity of hydrogen distributed over a small area also accounts for the early saturation of the electrolyte around the electrode to such an extent that hydrogen appears as bubbles of gas. The opposite conditions at the anode are indicated by the slower rate of polarizing and the tardy evolution of oxygen.

At low values of applied voltage, larger current now flows

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[2] Trans. Am. Electrochemical Society, 4, 120 (1903).

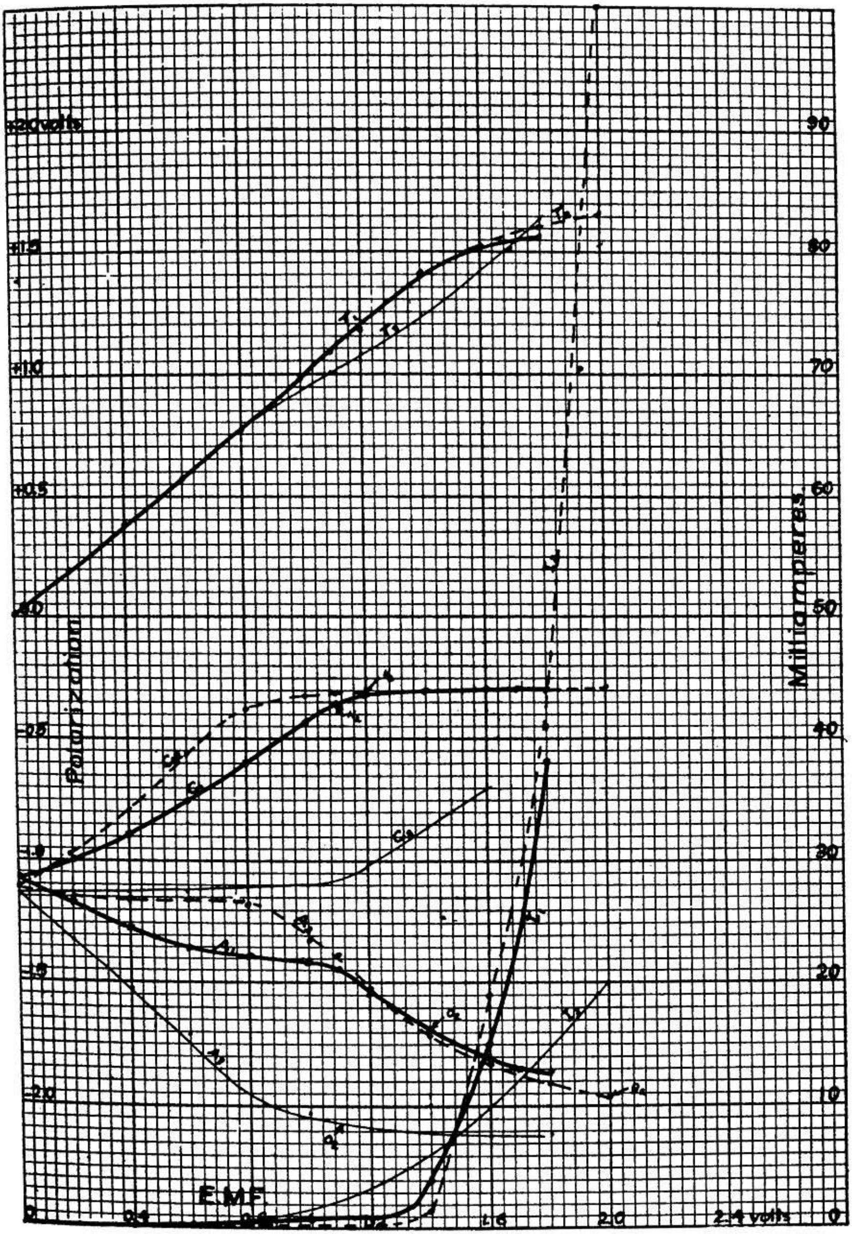

PLATE III.

than in the experiments with electrodes of equal size. The large amount of electrolyte in contact with the oxygen film at the anode dissolves the gas there with such facility that an appreciable current must flow through the cell to maintain even the lower degree of anode polarization observed.

No. 6.

This was a repetition of experiment *No. 5*, with the same solution. The electrodes were, however, removed, heated and replaced in the cell before use. Table VI and Curve II, Plate III, show the results.

A comparison with Curve I on the same plate shows that, whereas in the previous case there were evidences of depolarization occurring at the cathode, in this case there is practically none, for the anode potential remains constant up to an impressed E. M. F. of 0.8 volt, and only changes then because the potential of the cathode has approached close to its limit. It seems likely that this condition is due to complete removal of the oxygen in the solution by the hydrogen evolved during experiment *No. 5.* With the cathode thus free to be polarized without hindrance, it follows that, up to saturation of the electrolyte around the cathode with hydrogen, almost the entire polarization of the cell will occur at this terminal.

No. 7.

In this experiment the relative sizes of anode and cathode were reversed, causing a reversal of the characteristics of the anode and cathode curves from those of experiment *No. 6* (see Table VII and Curve III, Plate III). This experiment was performed with a fresh solution, so that the depolarizing effects of dissolved oxygen may again be expected; and, indeed, inspection of the curves plotted shows that this oxygen, together with the dissolving of hydrogen from the cathode by the electrolyte, served to eliminate entirely even that small polarization which might be expected to occur with so large a cathode. The cathode potential remains constant up to an impressed E. M. F. of 0.9 volt. This forces the polarization of the cell wholly on the small anode, with the result that the latter very soon reaches the discharge potential of oxygen, about —2.0 volts, and oxygen appears at an impressed electromotive force of 1.1 volts.

These latter experiments show very plainly that if for any reason the potential of one electrode lags behind its normal course, the potential of the other must change by a corresponding

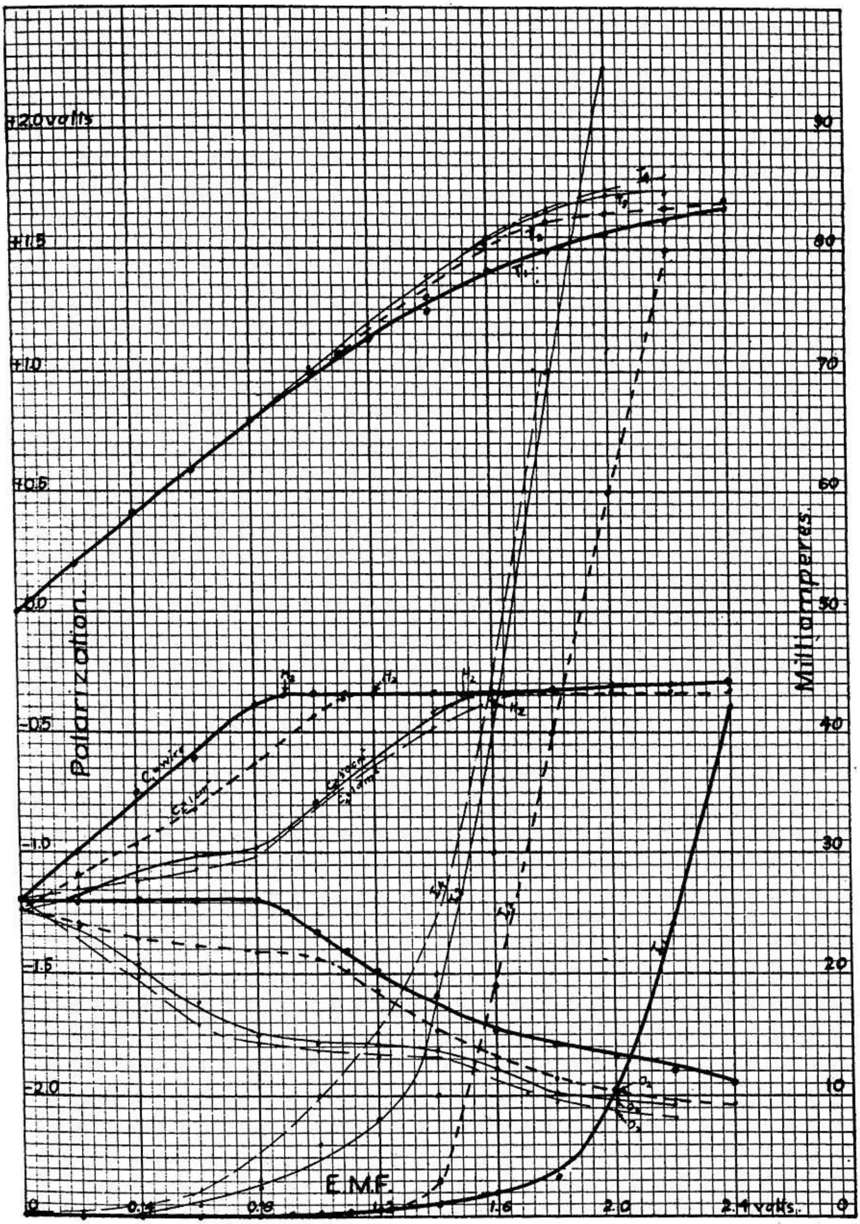

PLATE IV.

amount to make up for it. In all cases the total polarization must equal the sum of the separate electrode potentials.

EXPERIMENTS WITH CATHODES OF INCREASING SIZE.

It was found in the earlier experiments that hydrogen appeared at the cathode, as Richards stated, at values of impressed electromotive force far below the generally accepted decomposition point, 1.67 volts. To prove that the degree of lowering of decomposition point varies as the difference in electrode areas, the following experiments were performed. A platinum anode of constant size, one decimeter square, and a platinum cathode that varied from a wire 6.0 millimeters long by 0.75 millimeter in diameter to a sheet of platinum equal in area to the anode were employed. A fresh acid solution was used for each of the four experiments made, and the electrodes were heated and quenched each time, as usual. The data in Tables VIII–XI have all been plotted on Plate IV, to better disclose the results of the experiments.

It is apparent that in each case the potential of the cathode is —0.35 volt at the points where hydrogen is given off. This occurs regularly, and seems to be independent of the value of the impressed electromotive force. Current densities in milliamperes per square centimeter, at which hydrogen was first evolved at the cathodes from sulphuric acid, are found to be 1.5, 0.7, 0.3 and 0.25. Richards says:[3] "From a great number of experiments the conclusion is evident that current density at the electrodes is the prime factor in determining visible evolution of gas. * * * Measurements of current and area show that approximately 5 micro-amperes per square millimeter are necessary for the visible evolution of gas."

While the above statement is doubtless true for the conditions of Professor Richards' experiments, where the electrodes were a considerable distance apart and connection between them was made by a capillary tube, it requires modification when the electrodes are near together and in a relatively large volume of electrolyte which is exposed to the air, as is usually the case in practical electrolysis. Since a goodly share of the current flowing is used up in counterbalancing the effect of dissolved oxygen, it would perhaps be better to say that the gas evolution point is reached when the current density, minus the current per unit area used in off-setting depolarizing forces, has reached

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[3] *Loc. cit.*

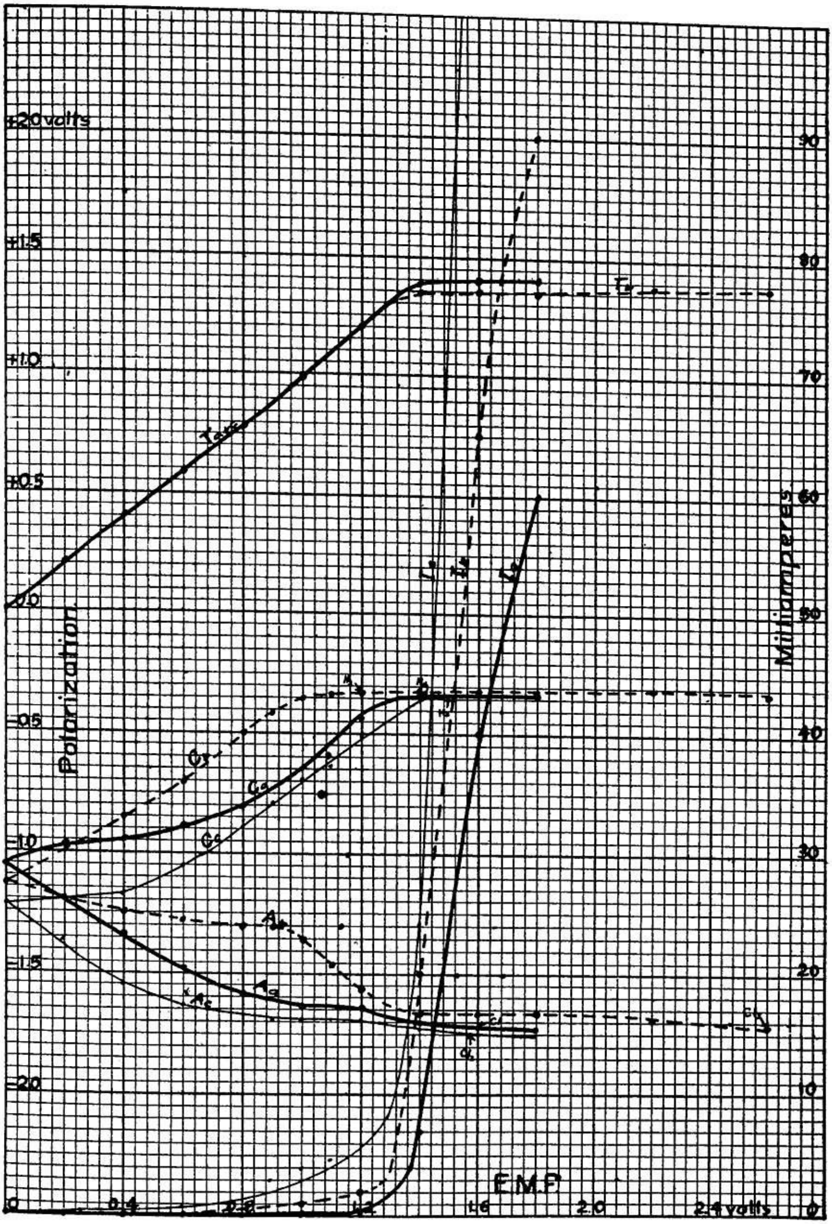

PLATE V.

some definite value. The evolution of hydrogen from normal hydrochloric acid required much higher densities, 7.0 and 2.0 milliamperes per square centimeter, than in sulphuric acid. This is explained by the greater solubility of chlorine, and consequently a more rapid removal of hydrogen from the cathode than was possible by the less soluble oxygen.

It is evident that the point at which a particular gas will be evolved at an electrode cannot in general be exactly defined either in terms of the impressed electromotive force or of the current density, but it can be expressed in terms of electrode potential. Whenever the cathode potential has risen to a particular value (in these experiments —0.35 volt) which may be called the discharge potential of hydrogen, evolution of that gas will occur, irrespective of the value of the electromotive force or the current density at that time. Similarly when the anode potential has fallen to the definite value of the discharge potential of oxygen, that gas will appear.

Variation of impressed electromotive force for gas evolution points was secured between 0.9 volt and 1.67 volts, using the electrodes described. Had there been greater differences in electrode size, it no doubt would have been shown that decomposition may take place at practically any voltage, provided the proper electrodes are employed.

It is of further interest to note the increase in current for a given voltage, below the decomposition point, as the cathode area is increased. With very large electrodes in an acid solution it would be possible to pass large currents through a cell and still obtain no visible decomposition of the electrolyte.

EXPERIMENTS USING HYDROCHLORIC ACID FOR THE ELECTROLYTE.

After the above work with sulphuric acid solution, three sets of data were obtained on cells filled with normal hydrochloric acid (not air free). The platinum electrodes were of the following dimensions:

Experiment	Cathode	Anode
a	1 square centimeter.	1 square centimeter.
b	1 square centimeter.	1 square decimeter.
c	1 square decimeter.	1 square centimeter.

From Tables XII to XIV and Plate V, it is seen that the results were very similar to those obtained with sulphuric acid. Again, hydrogen appears when the cathode reaches a potential of —0.33 volt, no matter what the size of the electrode or what the impressed voltage. The same occurrence is noted at the anode, where chlorine appears at —1.7 volts.

That chlorine is a very active depolarizer is shown by the results of experiment *c*. A large quantity of chlorine is deposited over a small anode area in this case, and is readily dissolved by the electrolyte and distributed throughout the cell. Coming in contact with the cathode, where the hydrogen concentration is small, it removes this so rapidly that the very large current shown is necessary to polarize the cathode at all. The same result is not obtainable with the other arrangements of electrodes, since with them there is not such free access of the chlorine to the cathode as in experiment *c*.

It will be noted that the initial potentials of the platinum electrodes in the three experiments were not the same. This was due to absorption of air by the electrolyte, the solution longest exposed giving the lowest initial potential.

ON THE USE OF PLATINUM ELECTRODES.

There has been much question as to advisability of using platinum for electrodes in a decomposition cell where gas is evolved. It has been claimed that, owing to the remarkable occluding powers of platinum for hydrogen and other gases, the potential of such an electrode must vary and, in varying, subject experimental work in which they are employed to a considerable degree of inaccuracy.

Several experiments were tried in order to determine if the potential of such electrodes changed as much as has been claimed.

No. 8.

A cell with platinum electrodes one centimeter square was set up and 0.2 volt impressed over its terminals. At intervals of several minutes readings were obtained of total, cathode and anode polarization. At the end of twenty minutes the voltage was raised to 0.8 volt, readings obtained as before, and the process repeated again at 1.4 volts. Table XV shows that the electrode potentials change very little with time, surely not enough to introduce serious errors into decomposition experiments. Table XVI shows the same results for a cell fitted with a small cathode and a large anode. While these results may appear unexpected, still, if the time taken for the electrodes to reach their final potential for any value of impressed electromotive force is considered, the above will not appear extraordinary.

Experiment shows that with cells like those used it takes but ten seconds for an anode polarization of 0.7 volt to build up, and twenty-five seconds for the same polarization to appear at the cathode, both representing final potentials under the conditions imposed. Furthermore, the cathode polarization falls off almost the instant the electrolyzing circuit is broken, but the anode polarization decreases very slowly. Indeed, lifting the anode from the cell, rinsing, drying or even heating[4] it, does not materially alter the slow rate at which the anode potential returns to its value before use.

These observations point to the following conclusions: (*1*) In the case of the anode, polarization is almost entirely due to the oxygen saturated electrolyte around the electrode. The slowness of diffusion of oxygen, the small occlusive power of platinum for oxygen, and the slow decrease of polarization on open circuit, seem to indicate that a very large part of the anode polarization is accounted for by the concentration of oxygen in the solution rather than in the electrode. An extremely thin film of saturated electrolyte, such as is produced at the surface of the anode on closing the circuit, suffices to completely polarize the electrode for the given applied voltage. Since neither diffusion nor occlusion decreases this instantaneous concentration to a great extent, it is to be expected that the anode will show its final value of polarization very soon after pressure is applied to the cell. Continued application of electromotive force merely serves to increase the thickness of the oxygen-saturated film. The value of polarization depends on the maximum and minimum concentrations of oxygen in the electrolyte between the electrodes ($e = R.\,T.\,log.\frac{C}{C'}$, where C is the concentration of oxygen at the anode and C' the concentration of that part of the electrolyte containing the smallest amount of oxygen), so that it does not matter whether the film is one-thousandth of a millimeter thick or thicker, so long as C and C' remain the same. (*2*) At the cathode the concentration

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[4] Transactions Am. Electrochemical Society, 4, 122 (1903).

of the film of hydrogen-saturated electrolyte produced by the first surge of current is diminished by diffusion (large for hydrogen) and by the occlusion of the gas by the platinum electrode. A longer interval is consequently required to build up the cathode potential, and as soon as the building and maintaining force—the impressed electromotive force—is cut off, the concentration is rapidly lowered, a fact in accordance with the rapid decline of cathode potential when the circuit is opened. It is true that platinum will continue to absorb hydrogen over an extended period of time; the continued upward slope of the cathode polarization curves after hydrogen evolution in any of the plates shown confirms that, but it is very evident that the greater part of occlusion occurs in a very short time, to be followed by a period of occlusion where the rate of absorption is so low that the potential of the electrode may be considered practically constant.

CONCLUSIONS.

It conclusion it may be stated that:

a. Decomposition of water can be accomplished at any voltage with platinum electrodes, provided the latter are of the proper size.

b. The oxygen normally present in laboratory reagents is sufficient to produce marked depolarization at the cathode.

c. The single potential of each electrode so depends on that of the other that any change in one, due to disturbing influences, is counteracted by such a change in the other that, below the decomposition point, the sum of the separate electrode polarizations equals the total polarization, and this in turn equals (very nearly) the impressed electromotive force.

d. Any desired current may be passed thru an aqueous solution of sulphuric or hydrochloric acid without causing evolution of gas, provided the electrodes are made large enough.

e. The evolution of gas at the electrodes depends on the total current density minus that part of the current density neutralized by the action of depolarizing agents.

The writer's thanks are due Dr. O. P. Watts for many valuable suggestions received in the above work.

TABLE I.

Electrodes of equal size, one centimeter square.
Electrolysis of normal H_2SO_4.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.005	—1.152	—1.160
0.2	0.0	0.181	1.118	1.296
0.4	0.0	0.390	1.090	1.477
0.6	0.05	0.581	1.090	1.673
0.8	0.07	0.766	1.033	1.798
1.0	0.20	0.960	0.867	1.825
1.2	0.20	1.185	0.671	1.839
1.4	0.20	1.378	0.476	1.853
1.6	0.60	1.556	0.337	1.895
1.7*	1.50	1.626	0.323	1.950
1.9	13.00	1.723	0.309	2.034
2.1	30.00	1.765	0.295	2.061
2.3	57.00	1.793	0.295	2.090

* Evolution of gas at both electrodes.

TABLE II.

Electrodes of equal size, one centimeter square.
Normal H_2SO_4 electrolyte covered with kerosene.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.022	—1.022
0.2	0.0	0.182	0.980	1.176
0.4	0.0	0.378	0.938	1.344
0.6	0.0	0.588	0.840	1.442
0.8	0.0	0.784	0.742	1.512
1.0	0.05	0.994	0.644	1.624
1.2	0.10	1.178	0.532	1.709
1.4	0.15	1.359	0.464	1.709
1.6	0.70	1.527	0.280	1.792
1.7*	0.70	1.597	0.252	1.849
2.0†	8.00	1.738	0.252	1.961
2.2	14.00	1.764	0.252	1.989
2.4	28.00	1.805	0.238	2.044

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE III.

Electrodes of equal size, one centimeter square.
Electrolysis of normal H_2SO_4 in partial vacuum.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.087	—1.087
0.2	0.0	0.180	1.031	1.217
0.4	0.0	0.388	0.989	1.363
0.6	0.0	0.595	0.837	1.432
0.8	0.0	0.789	0.698	1.529
1.0	0.0	0.969	0.657	1.611
1.2	0.0	1.190	0.588	1.750
1.4	0.05	1.370	0.422	1.778
1.6*	0.30	1.522	0.338	1.861
1.8†	1.5	1.633	0.311	1.861
2.0	2.0	1.716	0.280	2.040
2.4	22.0	1.854	0.261	2.082
2.8	65.0	1.854	0.261	2.110

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE IV.

Electrodes of equal size, one centimeter square.
Normal H_2SO_4 saturated with oxygen.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.144	—1.144
0.2	0.0	0.181	1.116	1.311
0.4	0.0	0.375	1.088	1.477
0.6	0.0	0.612	1.061	1.671
0.8	0.1	0.764	1.033	1.783
1.0	0.2	0.986	0.838	1.825
1.2	0.25	1.168	0.643	1.811
1.4	0.3	1.361	0.477	1.811
1.6	0.6	1.530	0.338	1.866
1.7	1.0	1.612	0.338	1.950
2.0	6.0	1.710	0.338	2.006

Oxygen evolved at anode at 1.9 volts E. M. F.

TABLE V.

Cathode = 1 centimeter square. Anode = 1 decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.014	—1.074	—1.088
0.2	0.0	0.181	0.991	1.172
0.4	0.0	0.375	0.908	1.269
0.6	0.4	0.570	0.755	1.325
0.8	..	0.765	0.615	1.380
1.0	0.5	0.986	0.435	1.421
1.1*	..	1.085	0.352	1.449
1.2	..	1.182	0.324	1.546
1.4†	4.0	1.404	0.309	1.687
1.6	15.0	1.516	0.296	1.798
1.7	..	1.516	0.296	1.852
1.8	38.0	1.571	0.282	1.852

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE VI.

Cathode = 1 centimeter square. Anode = 1 decimeter square.
Repetition of No. 5 with same lot of electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.014	—1.116	—1.130
0.2	0.1	0.193	0.977	1.157
0.4	0.2	0.348	0.796	1.157
0.6	0.2	0.598	0.560	1.157
0.8	..	0.806	0.379	1.172
1.0	..	0.986	0.338	1.325
1.1	0.25	1.099	0.324	1.394
1.2*	0.25	1.210	0.324	1.533
1.4	1.5	1.405	0.310	1.713
1.6	19.0	1.501	0.296	1.825
1.8	41.0	1.600	0.296	1.909
2.0†	100.0	1.669	0.296	1.979

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE VII.

Cathode = 1 decimeter square. Anode = 1 centimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.136	—1.136
0.2	0.5	0.181	1.136	1.327
0.4	0.5	0.404	1.136	1.537
0.6	0.5	0.600	1.136	1.703
0.7	0.5	0.698	1.120	1.858
1.0	1.0	0.949	1.104	2.025
1.1†	1.5	1.018	1.062	2.080
1.2	3.0	1.073	1.021	2.109
1.4	10.0	1.241	0.867	2.109
1.6	..	1.505	0.685	2.122
1.8	..	1.637	0.616	2.136
2.0	20.0	....	....	....

† Evolution of oxygen at anode.

TABLE VIII.

Cathode—Wire: area = 14 square millimeters.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.189	—1.189
0.2	0.0	0.195	0.999	1.189
0.4	0.0	0.419	0.755	1.185
0.6	0.0	0.586	0.602	1.185
0.8	0.0	0.795	0.393	1.185
0.9*	0.1	0.879	0.351	1.230
1.0	0.2	0.991	0.345	1.328
1.1	0.25	1.073	0.337	1.411
1.2	0.30	1.130	0.337	1.482
1.4	1.0	1.242	0.337	1.592
1.6	2.0	1.410	0.337	1.732
1.8	3.2	1.492	0.329	1.791
2.0	10.6	1.562	0.309	1.842
2.2	24.0	1.619	0.309	1.899
2.4	42.0	1.673	0.295	1.955

* Evolution of hydrogen at cathode.

TABLE IX.

Cathode = 1 centimeter square. Anode = 1 decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.230	—1.230
0.2	0.0	0.181	1.091	1.286
0.4	0.1	0.396	0.964	1.355
0.6	0.15	0.572	0.811	1.384
0.8	0.15	0.795	0.630	1.411
1.0	0.15	0.991	0.435	1.439
1.1	0.50	0.130	0.365	1.495
1.2*	0.60	0.213	0.359	1.561
1.4	3.0	1.381	0.337	1.737
1.6	19.0	1.520	0.331	1.849
1.8	40.0	1.618	0.331	1.928
2.0†	60.0	1.646	0.337	1.983
2.2	80.0	1.672	0.337	2.010
2.4	120.0	1.701	0.337	2.039

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE X.

Cathode = 50 square centimeters. Anode = 1 decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.231	—1.231
0.2	0.0	0.209	1.118	1.313
0.4	0.2	0.404	1.063	1.468
0.6	1.0	0.600	1.007	1.620
0.8	2.5	0.809	0.979	1.760
1.0	6.0	1.019	0.783	1.788
1.2	8.0	1.186	0.610	1.788
1.4	10.0	1.395	0.420	1.816
1.5*	15.0	1.479	0.350	1.843
1.6	30.0	1.549	0.337	1.899
1.7	40.0	1.604	0.337	1.928
1.8	70.0	1.660	0.328	1.997
2.0†	200.0	1.730	0.328	2.010
2.2	280.0	1.730	0.328	2.039

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE XI.

Electrodes of equal size, one decimeter square.
Normal H_2SO_4 electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.174	—1.174
0.2	0.1	0.196	1.146	1.338
0.4	1.0	0.404	1.119	1.509
0.6	2.5	0.629	1.063	1.703
0.8	3.0	0.782	1.007	1.788
1.0	10.0	0.004	0.797	1.815
1.2	15.0	1.185	0.644	1.843
1.4	20.0	1.352	0.476	1.843
1.6*	25.0	1.549	0.365	1.871
1.7	30.0	1.619	0.337	1.955
1.8	35.0	1.673	0.337	2.025
2.0†	95.0	1.757	0.323	2.065
2.2	200.0	1.813	0.309	2.095

* Evolution of hydrogen at cathode.
† Evolution of oxygen at anode.

TABLE XII.

Electrodes of equal size, one centimeter square.
Normal HCl electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.059	—1.059
0.2	0.0	0.208	0.970	1.198
0.4	0.04	0.403	0.948	1.336
0.6	0.04	0.596	0.879	1.475
0.8	0.05	0.776	0.809	1.586
1.0	0.10	0.984	0.643	1.639
1.2	0.15	1.205	0.435	1.639
1.4*	7.00	1.370	0.338	1.709
1.6†	40.00	1.399	0.338	1.722
1.8	60.00	1.399	0.338	1.722

* Evolution of hydrogen at cathode.
† Evolution of chlorine at anode.

TABLE XIII.

Cathode = 1 centimeter square. Anode = 1 decimeter square. Normal HCl electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.142	—1.142
0.2	0.0	0.199	1.976	1.184
0.4	0.0	0.374	1.851	1.253
0.6	0.0	0.569	1.712	1.281
0.8	0.0	0.804	1.505	1.309
0.9	0.0	0.901	1.422	1.309
1.0	0.5	1.010	1.366	1.364
1.1	1.0	1.093	1.338	1.461
1.2*	2.0	1.219	1.338	1.570
1.4	20.0	1.343	1.333	1.667
1.6	65.0	1.343	1.333	1.667
1.8	90.0	1.343	1.333	1.667
2.2	450.0	1.375	1.311	1.695
2.6†	...	1.375	1.338	1.723

* Evolution of hydrogen at cathode.

† Evolution of chlorine at anode.

TABLE XIV.

Cathode = 1 decimeter square. Anode = 1 centimeter square. Normal HCl electrolyte.

Impressed E. M. F. Volts	Current Milli-amperes	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
0.0	0.0	+0.000	—1.225	—1.225
0.2	0.0	0.180	1.198	1.364
0.4	0.0	0.402	1.170	1.558
0.6	0.2	0.596	1.058	1.640
0.8	2.0	0.804	0.893	1.695
0.9	3.0	0.901	0.795	1.695
1.0	4.0	0.984	0.698	1.695
1.1	4.5	1.094	0.643	1.695
1.2	5.0	1.163	0.518	1.695
1.4	23.0	1.370	0.353	1.723
1.6	112.0	1.436	0.338	1.750
1.8	190.0	1.412	0.338	1.750

Evolution of hydrogen at cathode at 1.5 volts E. M. F.

Evolution of chlorine at anode at 1.58 volts E. M. F.

TABLE XV.

Data on constancy of platinum electrode potentials.
Electrodes of equal size, 1 centimeter square.

Time	Impressed E. M. F. Volts	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
Beginning	0.0	+0.000	—1.185	—1.185
½ min. later	0.2	+0.195	—1.149	—1.338
2 “ “	0.2	+1.195	—1.144	—1.338
6 “ “	0.2	+0.195	—1.135	—1.325
10 “ “	0.2	+0.195	—1.135	—1.325
14 “ “	0.2	+0.195	—1.116	—1.310
20 “ “	0.2	+0.195	—1.116	—1.310
		Impressed voltage was increased.		
½ min. later	0.8	—0.778	—0.977	—1.756
2 “ “	0.8	—0.778	—0.977	—1.756
6 “ “	0.8	—0.778	—0.977	—1.756
10 “ “	0.8	—0.778	—0.977	—1.756
14 “ “	0.8	—0.778	—0.963	—1.742
		Impressed voltage was increased.		
½ min. later	1.4	+1.377	—0.379	—1.756
2 “ “	1.4	+1.377	—0.379	—1.756
4 “ “	1.4	+1.377	—0.379	—1.756
10 “ “	1.4	+1.405	—0.366	—1.756
20 “ “	1.4	+1.390	—0.366	—1.756

TABLE XVI.

Data on constancy of platinum electrode potentials.
Cathode, 1 centimeter square. Anode, 1 decimeter square.

Time	Impressed E. M. F. Volts	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
Beginning	0.0	+0.000	—1.170	—1.170
½ min. later	0.2	0.180	1.073	1.253
5 “ “	0.2	0.180	1.059	1.253
10 “ “	0.2	0.193	1.059	1.253
15 “ “	0.2	0.193	1.059	1.253
20 “ “	0.2	0.193	1.059	1.253
		Impressed voltage was increased.		
½ min. later	0.6	+0.595	—0.795	—1.363
5 “ “	0.6	0.595	0.782	1.363
10 “ “	0.6	0.595	0.782	1.363
15 “ “	0.6	0.595	0.782	1.363
20 “ “	0.6	0.595	0.782	1.363

Impressed voltage was increased.

Time	Impressed E. M. F. Volts	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
½ min. later	1.0	+0.997	—0.477	—1.474
5 “ “	1.0	0.984	0.505	1.502
10 “ “	1.0	0.984	0.505	1.502
15 “ “	1.0	0.987	0.505	1.502
20 “ “	1.0	0.987	0.505	1.502

Impressed voltage was increased.

Time	Impressed E. M. F. Volts	Polarization		
		Total, Volts	Cathode, Volts	Anode, Volts
½ min. later	1.4	+1.386	—0.238	—1.620
5 “ “	1.4	1.386	0.238	1.620
10 “ “	1.4	1.386	0.238	1.620
15 “ “	1.4	1.386	0.238	1.620
20 “ “	1.4	1.386	0.238	1.620

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A MICROSCOPIC STUDY OF ELECTROLYTIC IRON.

By Oliver W. Storey.

The electrolytic refining of iron was first carried out successfully ten years ago by Prof. C. F. Burgess at the Chemical Engineering Laboratories of the University of Wisconsin.[1] Since then, several thousand pounds of iron have been refined. In its manufacture a large variety of forms of cathode deposits has been produced, varying from dense to porous, and from smooth to nodular iron. The work presented in this paper was undertaken to study the different kinds of deposited irons and also to study the effect of heat treatments upon them. The author is indebted to Prof. C. F. Burgess, of the Northern Chemical Engineering Laboratories, for his co-operation in this research.

The refining of iron is carried out at present in stoneware tanks, each containing three sets of anodes, connected in parallel, between which are placed the two cathode sheets, allowing deposition to take place on both sides of the latter. The anodes first used were Swedish bar iron, though later American Ingot Iron has been used as a purer grade of raw material. With a current density of about ten amperes per square foot and an electrolyte consisting of an aqueous solution of iron sulphate and ammonium chloride the deposition proceeds uniformly.

A typical analysis of the refined iron follows:

	Single Refined	Double Refined
Sulphur	0.001%	none
Silicon	0.003	0.013%
Phosphorus	0.020	0.004
Manganese	none	none
Carbon	0.013	0.012
Iron	99.963	99.971
Hydrogen	0.083	0.072

The double refining is accomplished by using an electrodeposited material as anode.

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[1] Burgess and Hambuechen, Tr. Am. Electrochemical Society, 5, 201 (1904).

The electrodeposition of iron presents difficulties not unlike those present in the deposition of various other metals. By varying the factors such as current density, temperature, circulation of solution, composition of electrolyte, gases and impurities in the electrolyte, and thickness of deposit, various kinds of deposits may be obtained.

The microstructure of electrolytic iron has been the subject of a paper presented before this society by Professors C. F. Burgess and O. P. Watts.[2] This described the various kinds of deposits obtained and also the conditions producing these deposits. Attention was also called in this paper to the striking similarity of the structures of electrolytic iron to the structures of certain minerals as formed by nature. This similarity was especially noticeable with manganite, hematite and limonite.

Different types of deposits are shown in Figs. 1, 2 and 3. Fig. 1 shows a fracture of a hard, dense deposit illustrating a characteristic tooth-like growth. These nodular deposits may be separated from the main body of the metal by hitting them a sharp blow with a hammer. Cavities, sometimes one-half inch in depth, are formed. A group of nodules or teeth resulting from the breaking up of an iron cathode are shown in Fig. 4.

The deposit shown in Fig. 2 illustrates the usual fine grained deposit which is more fibrous in nature than that of the nodular iron shown in Fig. 1.

Fig. 3 shows a coarse, porous, crystalline deposit. The dense structures of Figs. 1 and 2 are entirely absent but instead a series of layers of iron is shown. The fine crystals shown at the bottom of the cathode gradually grow into coarse crystals at the top.

All of these deposits show lines parallel to the starting sheet indicating surfaces of cleavage. These cleavage surfaces are produced when some interruption or change in the deposition occurs. In the denser deposits the planes of cleavage are not as apparent as in the porous structure of Fig. 3. In this deposit layers of iron may be easily removed with a pen knife.

That the deposits obtained are of a variable structure is illus-

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[2] A Microscopic Study of Electro Deposits, Tr. Am. Electrochemical Society, 9, 229 (1906).

trated in Fig. 5. Some of the layers are dense and hard as is shown by the slight amount of etching while others are porous and easily etched.

When a metal solidifies from the molten state, the growth of crystals commences from nuclei distributed at random throughout the mass. The individual crystals grow outwards from these nuclei (usually by means of dendrites) until the sides of the mould or other crystals prevent further growth. In this manner the neighboring crystals found in metals solidified from the solid state usually are of different orientation. The growth of a metal when deposited by means of the electric current is different from the above case. The metal is first deposited on a starting sheet and the growth of it can be in only one direction—perpendicular to the surface of the starting sheet.

A microsection of the electrolytic iron shown in Fig. 3 in a plane perpendicular to the starting sheet gave the structure shown in Figs. 6 and 7. Fig. 6 shows the finer crystals at the starting sheet while Fig. 7 illustrates the coarseness of these crystals at the outside of the deposit, which was 5/16-inch (8 mm.) in thickness.

The crystal growth of Fig. 6 presents a peculiar fan-like appearance. The heavy line shown in the photograph is the result of a marked interruption in the deposition. The finer black lines which are about one-half inch apart and parallel to the heavier line are the result of slight interruptions in the deposition. The heavier lines are cleavage planes along which the layers of iron easily separate.

The growth of the crystals is again illustrated in Figs. 8, 9 and 10. Fig. 8 shows the microstructure of the cathode next to the starting sheet and parallel to it. This deposit when resolved under high powers shows a grain structure. Fig. 9 represents Fig. 8 at a higher magnification. The outside of the cathode has a coarse grain structure as illustrated in Fig. 10.

A more common form of deposit is shown in Fig. 11, which is a modified form of the deposit of Fig. 6. The black spots are probably cavities due to gases or other occlusions. The structure of the exterior of this cathode is illustrated in Fig. 12.

The interesting feature of Fig. 12 is the spider web appearance of some of the crystals. Müller,[3] in his work on electrolytic iron, refers to this peculiar structure and shows a web with five sections. The author has been able to find such areas with both five and six sections, the latter being more frequent.

Fig. 13 is a micrograph of a dense though coarse deposit. The crystals in the fractured deposit were plainly visible to the naked eye and were often ⅛ inch in length. No interruptions had occurred in this deposit and the crystals grew to large sizes.

The microstructure of a dense deposit which is not nodular is shown in Fig. 14. The tendency to form well defined crystals is suppressed and only an indication of these crystals is present. The exterior of the cathode deposit shows a well defined granular structure. See Fig. 15.

The microstructure of the dense deposits resulting in the nodules of Fig. 4 and the nodular deposit of Fig. 1 differs from the crystalline deposits previously shown. The polished and etched surface of such a dense section is shown in Fig. 16.

A large nodule formed in the interior of this deposit may be distinctly seen, while a band of less dense deposit is visible at the top of the specimen. The microstructure of this section is seen in Fig. 17 while a part of the dense portion showing the boundary between two nodules is shown in Fig. 18. It was impossible to develop a crystal structure in this iron.

MICROSTRUCTURE OF HEATED ELECTROLYTIC IRON.

In their paper, C. F. Burgess and O. P. Watts,[4] showed that electrolytic iron, upon heating to 1,000° C., assumed the structure of ordinary iron, that is, it became granular. It was desirable to know at what temperature this change took place and what effect the liberation of hydrogen had upon the structure.

Electrolytic iron, as deposited, possesses peculiar properties. It is extremely brittle and dissolves with ease in acids, being more soluble than zinc.[5] The brittleness is probably due to the presence of hydrogen, either occluded or combined with the iron.

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[3] Metallurgie, 1909, p. 145.

[4] A Microscopic Study of Electro Deposits, Tr. Am. Electrochemical Society, 9, 229 (1906).

[5] Burgess and Engle, Tr. Am. Electrochemical Society, 9, 199 (1906).

Upon heating electrolytic iron to between 500° and 600° C., a large amount of hydrogen was given off and the iron became ductile and more resistant to acid attack. Upon examination of the iron after heating for one hour at 600° no apparent change in the crystalline structure had taken place. Specimens heated for one hour at 700°, 800°, 850° and 875°, showed no change which could be detected by the microscope. By heating specimens at 910° to 915° C. for one hour the crystalline structure of the deposited iron had changed completely to the grain structure of ordinary ferrite.

This phenomenon occurs at the A_3 point in iron where a known allotropic transformation from gamma to non-gamma ferrite takes place. A change of the crystal form occurs and explains the cause of the change of the electro-deposited iron to the ordinary grain structure.

In this work the determination of change of structure was made upon a section perpendicular to the cathode surface. The close resemblance of the cathode surface to the ordinary grain structure did not allow a close determination of any change to be made. On the other hand, any difference in structure of the perpendicular surface could be detected.

For the further investigation of this phenomenon two varieties of electrolytic iron were used, fine and coarse. The fine electrolytic iron was dense and finely crystalline. Fig. 19 shows a micrograph of this structure. The coarse material was porous and the structure is shown in Figs. 6 and 7. In one set of experiments the specimens were annealed after heating at a constant temperature in the furnace and in the other were quenched in water.

An electrically heated tube furnace was used. The temperatures were measured by a base metal thermocouple correct to within 2°. The furnace atmosphere was oxidizing and a scale formed on all specimens. A list of experiments with results follows. All specimens were etched with picric acid:

1. Heated at 900° for 15 minutes and quenched.

a. Fine deposit; first changes in structure occur. See Fig. 20. The dense white bands of crystals of Fig. 19 have developed into several large grains while the porous dark bands have separated into fine grains of ferrite as seen in the areas adjacent to the coarse grained white band.

b. Coarse deposit; no noticeable change in structure.

2. Heated at 900° for two hours and quenched.

a. Fine deposit; Fig. 21. A few traces of the old structure remain. The porous areas have been broken up into well defined fine grains while in the denser areas the coarse grains of Fig. 20 have divided into finer grains. The specimen appears to be breaking up into finer grains though Fig. 20 showed some that were coarse.

b. Coarse deposit. Fig. 22. The first breakdown of the crystalline to the granular structure is taking place. The change appears sluggish in comparison to the fine deposit. The entire surface has not changed. As seen in Fig. 22, fine grains are forming but these can only be found where a fine crystal structure had existed and are prominent at the base of these crystals. At the coarse end of the crystals no traces of a grain formation are found.

3. Heated at 910° to 915° for one hour and cooled in furnace. Only the coarse deposit was used.

a. Coarse deposit. See Fig. 23. The crystalline structure has changed entirely to the grain structure. Though traces of the old crystal outlines remain the grain boundaries are apparently not influenced by the crystal boundaries. The grains are several times as large as those obtained with the fine structure of Fig. 21.

4. Heated at 925° for five minutes and quenched.

a. Fine deposit. The entire specimen has become fine grained with few traces of the deposited crystals.

b. Coarse deposit. Fig. 24. The entire specimen has become granular but the outlines and markings of the deposited crystals are but slightly obliterated. The grain size varies over the surface of the specimen. Where the deposited crystals of iron have been small the grains are small and likewise coarse grains are found where the deposit has been coarse. These large grains are shown in Fig. 24. The grain outlines do not follow the crystal outlines but are independent of the previous structure.

5. Heated at 925° for five minutes and cooled in furnace.

a. Fine deposit. The crysalline structure has become granular and the structure is like that obtained in 4a.

b. Coarse deposit. The crystalline structure has changed slightly. The areas at the roots of the deposited crystals have become fine grained while the coarse areas have apparently been unchanged. The resulting structure closely resembles Fig. 22 of 2b.

6. Heated at 950° for five minutes and quenched.

a. Fine deposit. The entire specimen has become fine grained.

b. Coarse deposit. Though the entire specimen is granular the grains vary in size corresponding to the size of the deposited iron crystals.

7. Heated at 950° for fifteen minutes and quenched.

a. Fine deposit. Entire specimen fine grained.

b. Coarse deposit. The structure is not different from that in 6b.

8. Heated at 1,000° for fifteen minutes and quenched.

a. Fine deposit. Fine grained.

b. Coarse deposit. The coarse grains obtained from the coarse crystals at the lower temperatures are breaking up into finer grains.

9. Heated at 1,150° for five minutes and cooled in furnace.

a. Fine deposit. Fig. 25. A fine grained, well defined structure of normal ferrite results.

b. Coarse deposit. Fig. 26. The entire specimen consists of uniform sized grains which are several times larger than those resulting from the fine deposit in 9a.

10. Heated at 1,150° for fifteen minutes and quenched.

a. Fine deposit. Fig. 27. The fine grains do not have as clearly defined boundaries after etching as when annealed from the same temperature. Specimens quenched from the high temperatures show this tendency.

b. Coarse deposit. A grain structure like that of Fig. 26 is produced.

11. Heated at 1,150° for one hour and cooled in furnace.

a. Fine deposit. Fig. 28. After annealing at this high temperature for an hour the fine grains of Fig. 25 have grown slightly but the growth is slow.

b. Coarse deposit. Fig. 29. The grains of Fig. 26 have grown slightly.

12. In this experiment a piece of a dense deposit was heated to near fusion in a platinum crucible. The specimen remained at this high temperature for about five minutes. The resulting structure is shown in Fig. 30. The grains are small and well defined.

The results of these experiments showed that the crystalline structure of electro-deposited iron changed to the usual grain structure at the A_3 point and that the character of the deposited iron determined the rapidity of the recrystallization and also determined the subsequent grain structure.

The experimental work showed that the deposit composed of fine crystals was readily transformed into grains at 900° with a heating period of less than fifteen minutes, while a deposit composed of coarse crystals which had been heat treated with the same sample showed no signs of change. Even with a heat treatment of two hours duration at this temperature the change in structure had only occurred where the crystals were finest.

The above experiments at 900° also show that the time is an important factor. The fine deposit heated for two hours (Fig. 21) showed an almost uniform fine grain structure, while the deposit heated for fifteen minutes (Fig. 20) showed an early stage of the transformation. The coarse deposit when heated at 900° for fifteen minutes showed no change while that heated for two hours showed only a transformation of the smaller crystals.

In experiment 3a where the coarse crystals were heated for one hour at 910° to 915° the transformation was complete, while in experiments 4b and 5b, where the samples were heated for five minutes at 925°, the transformation was barely complete in the one case and partially complete in the second. The discrepancy in 4b and 5b is probably due to different conditions of heating.

The most striking feature was the influence of the crystal size of the deposited iron upon the resulting grains and the stability of the grain size at various temperatures.

This was first noticed in experiments 1a and 2a. In 1a (Fig.

20), the fine deposit, after heating at 900° for 15 minutes, showed large grains in bands where the crystals had previously been dense. But upon heating for two hours at this temperature the large grains were partly divided into smaller ones though not as fine as when heated at 925°.

In experiments 4b where a coarse deposit was heated at 925° for five minutes a peculiar structure resulted. A small grain structure was obtained in the fine crystal areas but in the coarse crystal areas large grains resulted (Fig. 24). At 950° the same structure resulted but at 1,000° the large grains had apparently decreased and the smaller ones had increased in size.

When the coarse crystal specimen had been heated to 1,150° the grains were uniform throughout the specimen (Fig. 26), but these grains were several times larger than those resulting from a similar heat treatment of a fine deposit (Fig. 25).

From the foregoing experiments it is evident that the ferrite grains resulting from the change from the deposited state are influenced by the deposited crystals. The larger these crystals the slower the change to the granular state and the larger the resulting grains. The large grains resulting from a coarse deposit break down at a temperature well above the A_3 point if the time of heating at that temperature is short. With the coarse deposit used and the temperature maintained at the maximum for five minutes the point of breakdown for the large grains is at about 1,000°. That a lower temperature for a longer time will accomplish the same result is evident from experiment 3a, where the grain size differed but slightly over the entire specimen after heating at 910° to 915° for one hour.

This phenomenon is probably best explained by Stead and Carpenter,[6] in their work on the "Crystallizing Properties of Electro-deposited Iron." In their researches they found that when thin strips of electrolytic iron were cooled through the Ar_3 range at any rate short of actually plunging the specimen a coarse crystallization of the iron took place resulting in grains often several millimeters in diameter. They also found that long heating above the Ac_3 point did not result in coarse grains. Their explanation follows:

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[6] Journal of the Iron and Steel Institute, Sept., 1913.

"The refining of the structure caused by prolonged heating in the region of gamma iron can be explained in accordance with well established facts of the genesis and growth of crystals in the following way:—On heating the iron strip which consists of an aggregate of alpha crystals, above Ac_3, a region is entered in which gamma is the stable phase, and provided it is held there sufficiently long, not only the alpha crystals, but their nuclei will be destroyed. When the strip is cooled through Ar_3, and again enters the alpha region, it is, *a priori*, a question whether a large number of alpha nuclei will be formed simultaneously, in which case the crystals that result from them will be both numerous and small, or a small number of nuclei are formed, in which case, provided diffusion can take place with sufficient rapidity, the nuclei will develop into a small number of large crystals, or, of course, any intermediate proportion may be assumed. A reasonable explanation of the fine alpha crystallization resulting from prolonged heating in the gamma region is, therefore, that very numerous alpha nuclei are formed simultaneously on passing through Ar_3, and accordingly the crystals are small. On the other hand, a short heating above Ac_3 may be insufficient completely to destroy the alpha nuclei, and when the strip cools through Ar_3 a certain number will be present which will act as centers of crystallization, so that, if diffusion is operative, large crystals will grow from these centers. This would account for the coarse crystallization that results after a short heating above Ac_3, and it is the explanation which appears to the authors to be reasonable, and to fit in with the observed facts."

In the author's work the electrolytic iron was used in thick sections of from ten to twenty grams in weight instead of strips 0.01 inch or less in thickness. The coarse crystallization obtained is not to be compared with that obtained by Stead and Carpenter though the general nature of the phenomena is the same. Though the specimens were quenched, the rate of cooling was probably slow, due to their weight. The persistence of the large crystals and the formation of the large grains is explained by the persistence of the alpha or non-gamma crystals.

Stead and Carpenter,[7] in their work, showed that the iron used

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[7] Journal of the Iron and Steel Institute, Sept., 1913.

did not coarsen perceptibly upon heating beyond Ar_3. Howe[8] states that he was able to coarsen electrolytic iron somewhat upon heating to 1,300°. These experiments also show that electrolytic iron when heated in the gamma range does not coarsen appreciably at temperatures up to 1,150°.

SUMMARY.

1. No change in structure of electrolytic iron could be determined at temperatures below the A_3 range.
2. A fine deposit is more readily changed to the grain structure than a coarse deposit.
3. With a short heating above the A_3 range the fine deposit is transformed into a fine grain structure while a coarse deposit becomes coarse grained.
4. The coarse grains resulting from a coarse deposit may be broken down into smaller grains by long annealing at the Ac_3 point or by heating to 1,000° or higher.
5. The grain structure resulting from a fine structure is always finer than that resulting from a coarse deposit.
6. The grains of electrolytic iron do not grow appreciably at 1,150°.

MICROSTRUCTURE OF FUSED ELECTROLYTIC IRON.

Three samples of fused electrolytic iron were used in this study, all samples being in the form of small ingots made in a vacuum furnace. Ingot A was obtained through the courtesy of Mr. Arsem, of Schenectady, New York. Ingot B was made by Dr. O. P. Watts, and ingot C by Mr. L. T. Richardson, at the Chemical Engineering Laboratories of the University of Wisconsin. These ingots were halved, polished, and etched and are shown in Figs. 31, 32 and 33.

Fig. 31 shows ingot A. The heat treatment of this sample is not known. By comparison with ingots B and C, whose history is known, it probably was kept in the fused state for a long period and then allowed to cool slowly. The sample shows a coarse grain, as seen in Fig. 31. Some of the grains are from 5 to 7 mm. in diameter. The ingot shows a small pipe and numerous blow

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[8] Bulletin Am. Inst. Min. Eng. No. 84, p. 2821.

holes. It is evident that these blow holes were filled by a reducing gas, probably hydrogen, since the iron surrounding them was bright and untarnished.

Fig. 32 shows ingot B, which was melted in a magnesia crucible. Upon heating the electrolytic iron to above its melting point a violent evolution of gas took place. After two hours of heating at about 1,600° to 1,700° the gas continued to come off at a slow rate. The ingot was then cooled in the furnace, the cooling from the melting temperature to a low red occupying about 15 minutes. The large pipe with the absence of blow holes and the small grains are the striking features of this ingot.

Fig. 33 shows ingot C. The iron was heated to about 1,600° when a violent evolution of gas took place. After ten minutes the ingot was allowed to cool Upon the first freezing of the outside portions of this ingot the interior began to boil, throwing small particles of iron above the surface of the ingot. The result of this violent evolution of gas is evident in the photograph. Not only has a large pipe and cavity with numerous blow holes resulted, but a collar of metal has been formed about the top of the ingot by the ejected metal. The grain size is the same as that of ingot B.

Fig. 34 shows the surface of ingot A after etching with picric acid. The grain is coarse and several grains are apparently merging into each other as is seen by the disappearing boundary lines of some of the grains. A large blow hole is seen in one corner and smaller pits are distinguishable upon the surface.

Fig. 35 is a micrograph of the structure near the surface of the ingot, showing the orientation of the ferrite grains at right angles to it. Here again grain boundaries are disappearing to form larger grains.

The etching of this specimen was continued, by alternating the picric acid with a four percent solution of nitric acid in amyl alcohol. This etching was continued for over two hours and developed the structures shown in Figs. 36 to 40. These micrographs not only show the coarse grains developed with the first etching, but also show the devolopment of a new structure in the interior of these grains. These sub-grains will be called "inner grains" for convenience.

Each grain showed an inner grain structure, though some had developed this structure only slightly. The size of the inner grains varied in different grains.

Fig. 36 shows several grains of ferrite. The inner grains are of the same size in neighboring grains, though varying in the same one. The attack of the etching reagent is more noticeable in the darker grains and the inner grain boundaries are more prominent.

In Fig. 37 the attack has been heavier, and, although the light area does not show an inner grain structure in the micrograph, a close examination of the specimen showed that this structure was present.

A study of the boundaries of the grains and the inner grains showed a marked difference in their appearance. While the boundaries of the grains seemed to be "V" shaped grooves those of the inner grains were merely shallow depressions. Upon etching for a prolonged period the inner grain structure of Figs. 38, 39 and 40 was developed. The shallow troughs were deepened by this prolonged etching until a series of pits developed. The deepening of the inner grain boundaries by these pits is shown in the partly developed inner grains of Figs. 38 and 39.

Two neighboring grains having a differing crystal orientation did not show any continuity of inner grain structure. The boundary between these two grains did not allow any continuance of inner grain boundaries. But in the neighboring grains where the crystal orientation was similar, the inner grains were often continuous. This was especially true with boundary lines which were partly obliterated. In these cases the crystal orientations were similar and the boundary lines were slowly disappearing. A large number of these vanishing boundary lines were present in the specimen. Deep etching developed pits along these vanishing boundary lines while the "V" shaped grooves pitted but slightly. Some of the larger inner grains, when examined under higher magnifications, seemed to be subdivided into two or three smaller grains by shallow trenches which were barely noticeable.

Upon annealing a specimen of this iron at 925° the large grains were partly broken down and the inner grain structure persisted, but not as marked as in the original specimen. Upon annealing at 950° and then at 1,150° the large grains were completely broken down and only traces of the inner grains remained.

The inner grain structure surrounding a blow hole was much finer than the normal size. This is shown in Fig. 40.

The significant facts in connection with this inner grain structure follow:

1. Each ferrite grain has a peculiar inner grain size.
2. The inner grain boundaries are shallow depressions.
3. The development of the inner grain depends upon the crystal orientation of the grain.
4. The boundaries of the grains are more quickly developed than the inner grain boundaries.
5. Two adjacent grains of dissimilar crystal orientation show no continuity through their boundaries of the inner grain boundaries.
6. Two merging grains show a continuity through their boundaries of the inner grain boundaries.
7. Deep etching causes the shallow depressions to become pitted.
8. Several annealings above the Ac_3 point were required to destroy the inner grain structure.

From these observations the following explanation of this peculiar structure is offered. The inner grains are probably groups of similarly oriented iron crystals. The orientation in all of these groups is alike throughout the ferrite grain. In slowly cooling from the molten state large gamma grains are formed. In changing from the gamma state to the non-gamma state the grain size remains the same. Stead and Carpenter's[10] explanation previously quoted states that a fine grain structure is due to a large number of non-gamma nuclei.

If we consider that, owing to the large gamma grains, a large number of non-gamma nuclei were formed in each gamma grain and that each nucleus was similarly oriented owing to similarly oriented gamma crystals, we can readily see that the ferrite grains would be composed of a large number of groups of similarly oriented crystals.

These groups of crystals would constitute the inner grains. Each nucleus would grow until it met a neighboring group. In

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[10] Journal of the Iron and Steel Institute, Sept., 1913.

this case the crystals would be similarly oriented in the neighboring groups and the boundaries would consist of more or less imperfect and smaller crystals, but of like orientation. In etching, this boundary would etch more rapidly and would cause a depression to be formed resulting in the inner grain boundaries. That the boundaries consist of crystals whose orientation is the same as those of the inner grains is probably correct, since the rate of etching of the boundary is proportional to the rate of etching of the entire grain surface. That is, those grains coloring quickly when etched, owing to their crystal orientation, show the inner grain structure first. This is shown in Figs. 36 and 37.

Humfrey,[11] in his work on "The Intercrystalline Fracture of Iron and Steel," developed a somewhat similar structure by heating a polished strip of Swedish Iron in a vacuum furnace. The etching reagent was CO_2, a slight amount of which was given off by the Mabor slabs supporting the specimen. The section of the specimen heated to the Ar_2 to Ar_3 region showed ferrite grains, some of which showed an inner network of fine lines. The section heated to between the Ar_1 to Ar_2 limits showed iron grains with a network of etching figures closely resembling the inner grains. The boundaries of the grains were also "V" shaped grooves, as were those obtained by the author in his work. The similarity between the two is striking, although the author worked with grains many times larger than those of Mr. Humfrey.

Upon annealing a section of Ingot A, at 950° for one hour, the structure shown in Fig. 41 was obtained. Areas of fine grains intermingled with larger grains resulted. Upon annealing at 1,150° for three hours larger grains were again formed. The boundaries of these grains after this heat treatment again showed a tendency to be discontinuous as in the original specimen. Deep etching showed a few traces of the original inner grain structure.

The microstructure of Ingot B is shown in Fig. 42. The grains are small and the iron appears unclean, small dots appearing over the surface, probably due to remaining gases. A large number of these fine inclusions appear in the grain boundaries. The grains are also covered with a network of fine lines.

Upon annealing Ingot B at 950° for one-half hour the normal

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[11] Carnegie Scholarship Memoirs, IV, p. 80.

ferrite structure of Fig. 43 was obtained. The fine network still appears in the ferrite grains while the inclusions seem to have almost disappeared with the exception of few spots. When annealed at 1,050° for 15 minutes the structure of Fig. 44 was obtained. The ferrite grains of Fig. 43 have grown. The network is still visible while few inclusions remain. When annealed at 1,150° for three hours the structure, shown in Fig. 45, resembles the original structure (Fig. 42). The grains are slightly coarser but the inclusions are segregated in the grain boundaries. A fine network covers the grains.

The structure of Ingot C did not differ materially from that of Ingot B (Fig. 42). The amount of inclusions was greatly increased. The grain size was the same and a network of fine lines in the grains was also present.

ROLLED ELECTROLYTIC IRON.

Several cathodes of electrolytic iron were heated and rolled into standard gauge sheets. A microscopic examination showed a structure of clean ferrite. (Fig. 46).

FORGED ELECTROLYTIC IRON.

In the investigation of the properties of iron alloys electrolytic iron was used as a source of pure iron. In this work rods of pure forged electrolytic iron served as a standard for comparison. The iron was melted in a magnesia crucible in a carbon resistor furnace. The ingot obtained was forged into a rod of the desired size. The microstructure of such a forged rod is shown in Fig. 47. The structure consists of fine grained ferrite with a minimum of impurities.

Under some conditions of melting carbon was absorbed from the CO atmosphere in the crucible and a low carbon steel resulted. A microsection of a forged rod containing a small percentage of absorbed carbon is shown in Fig. 48.

Chemical Engineering Laboratories,
University of Wisconsin.

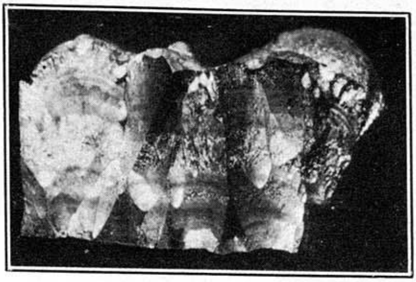

FIG. 1. × 3

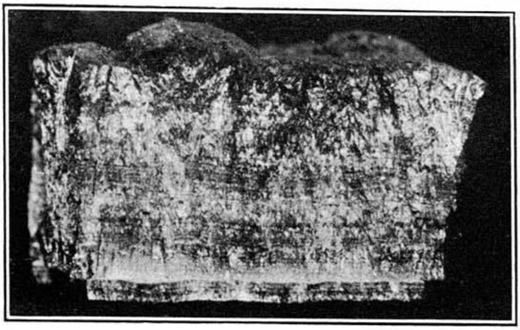

FIG. 2. × 3

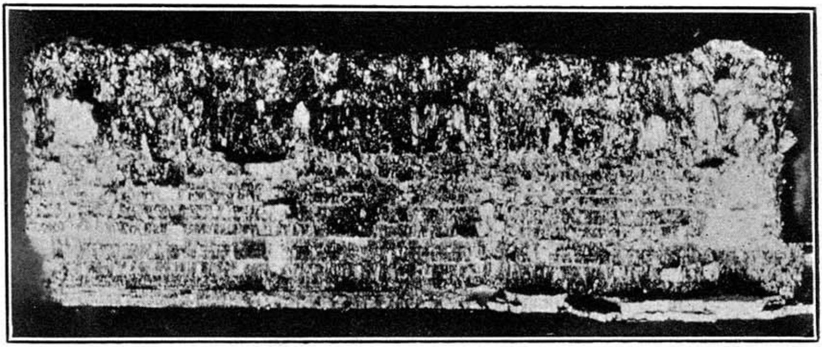

FIG. 3. × 4

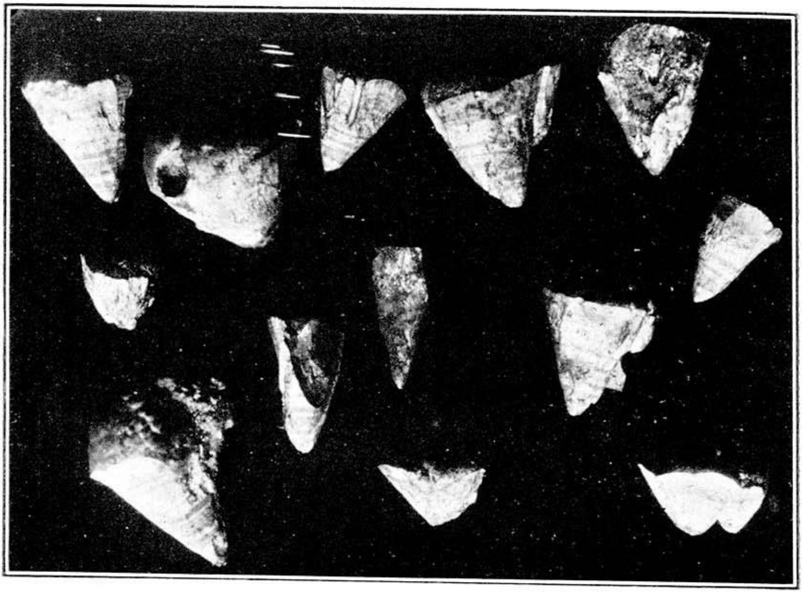

FIG. 4. × 1½

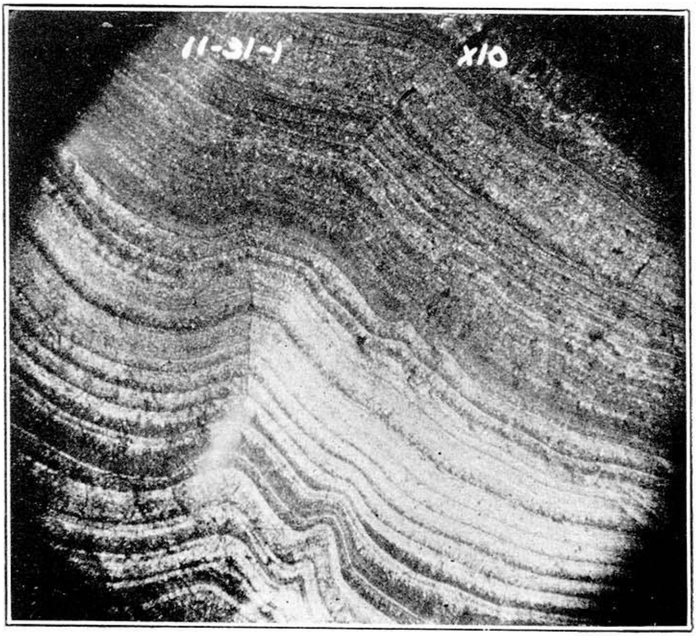

FIG. 5. × 10

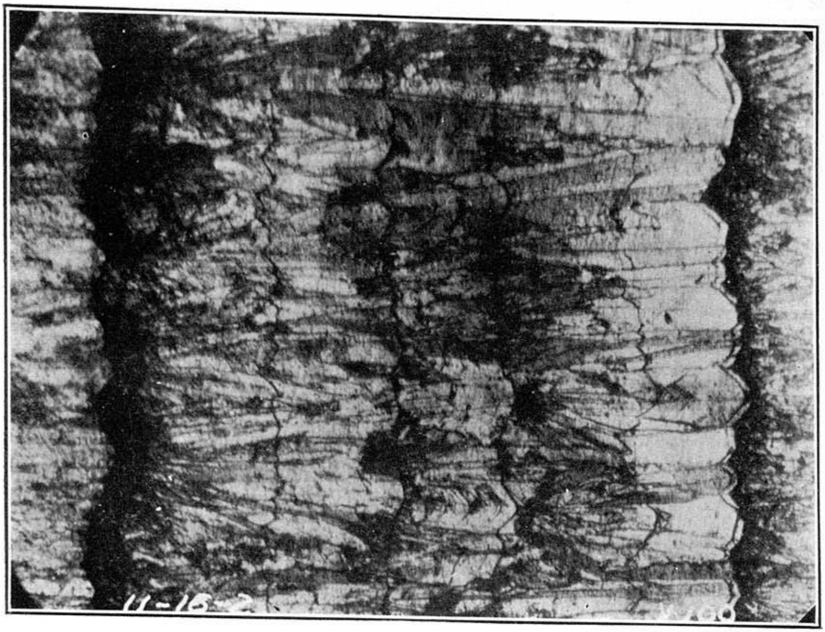

FIG. 6. × 100

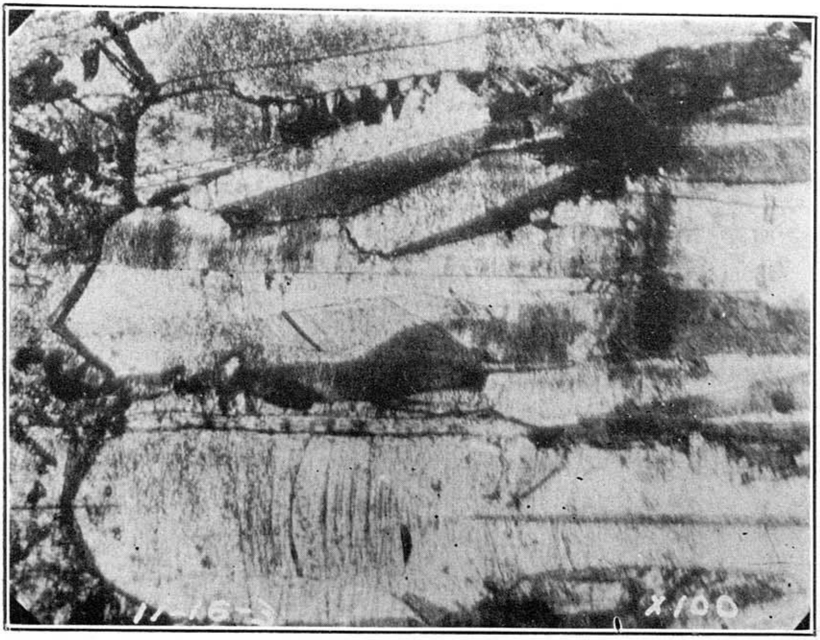

FIG. 7. × 100

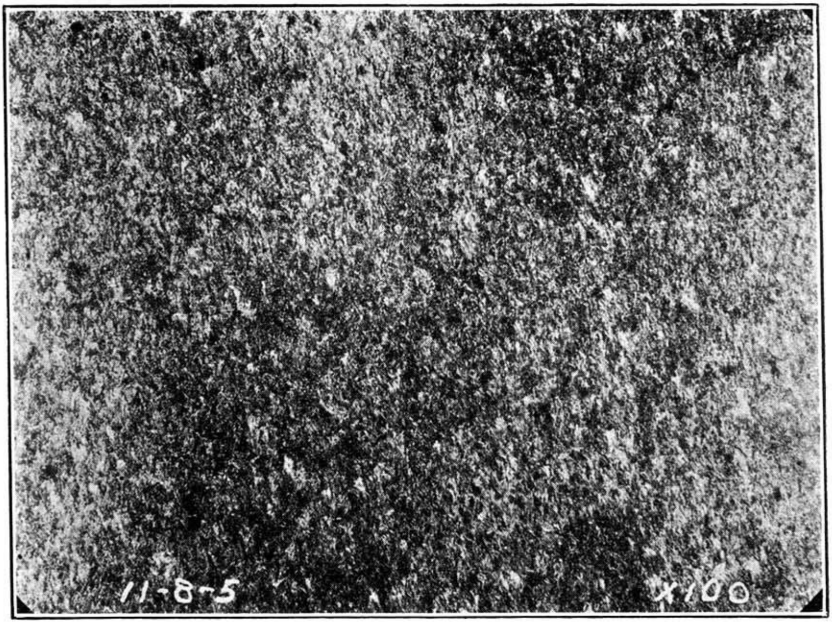

FIG. 8. × 100

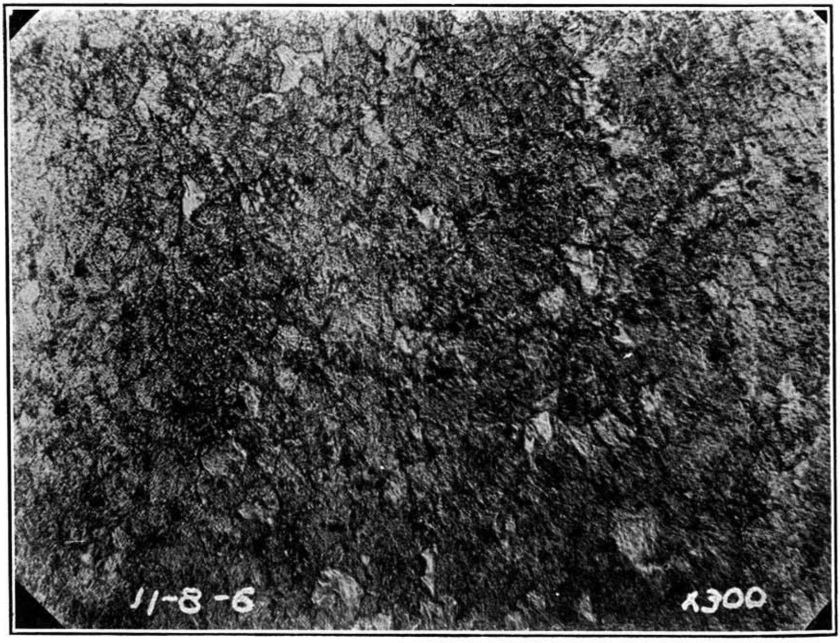

FIG. 9. × 300

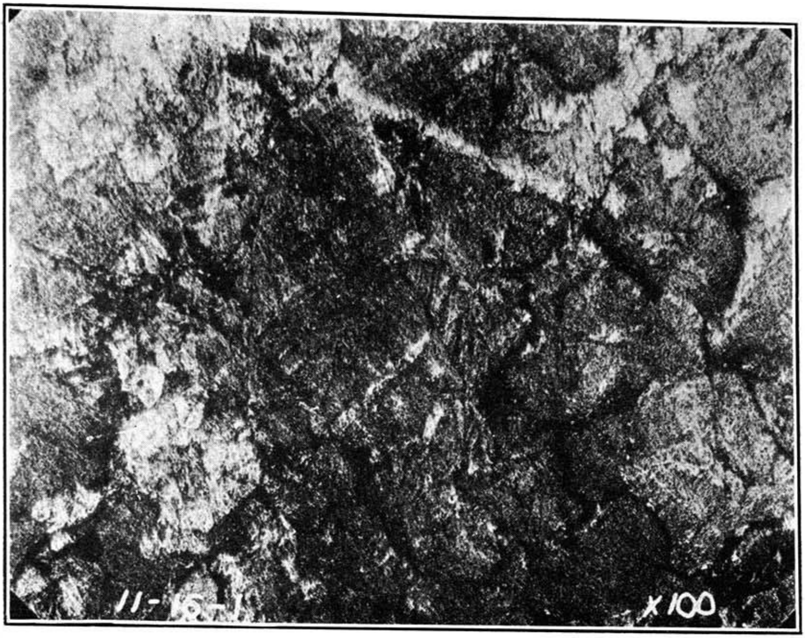

FIG. 10. × 100

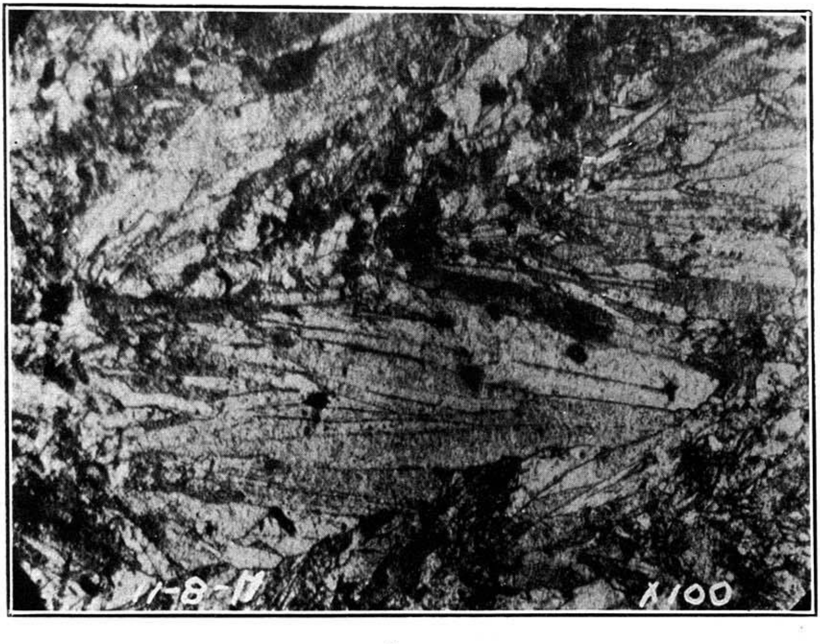

FIG. 11. × 100

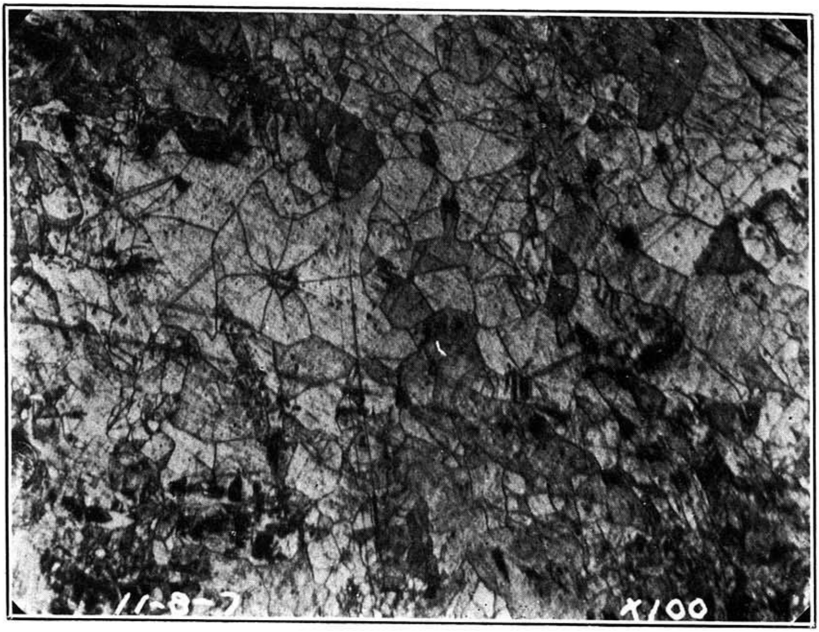

FIG. 12. × 100

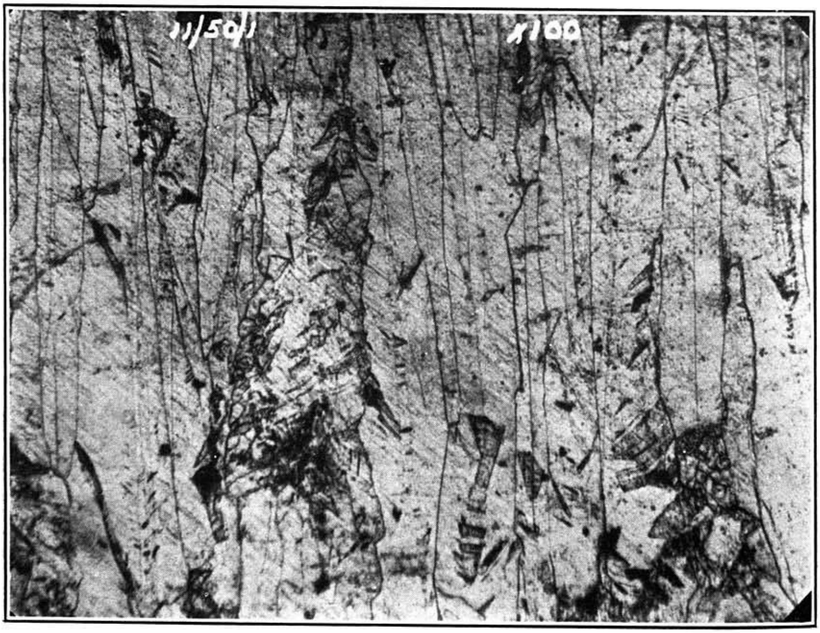

FIG. 13. × 100

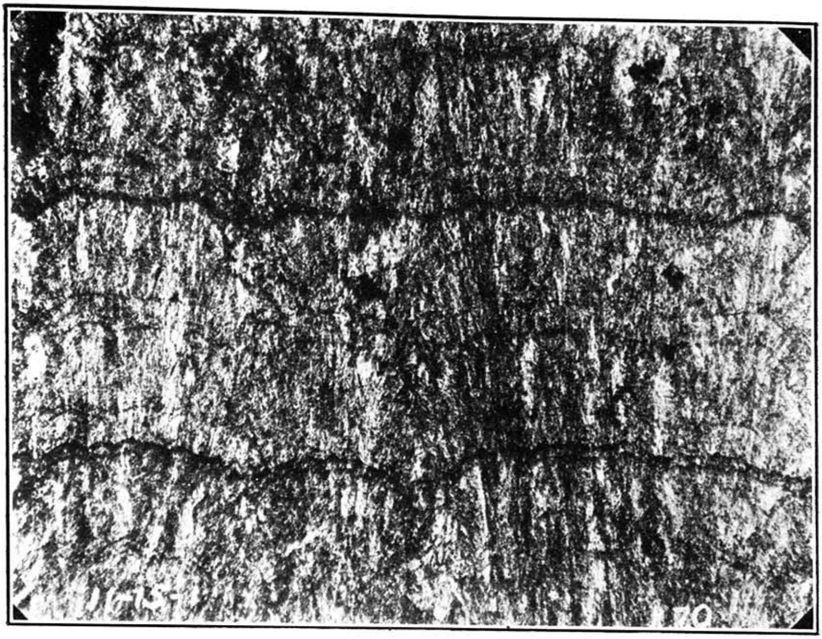

FIG. 14. × 70

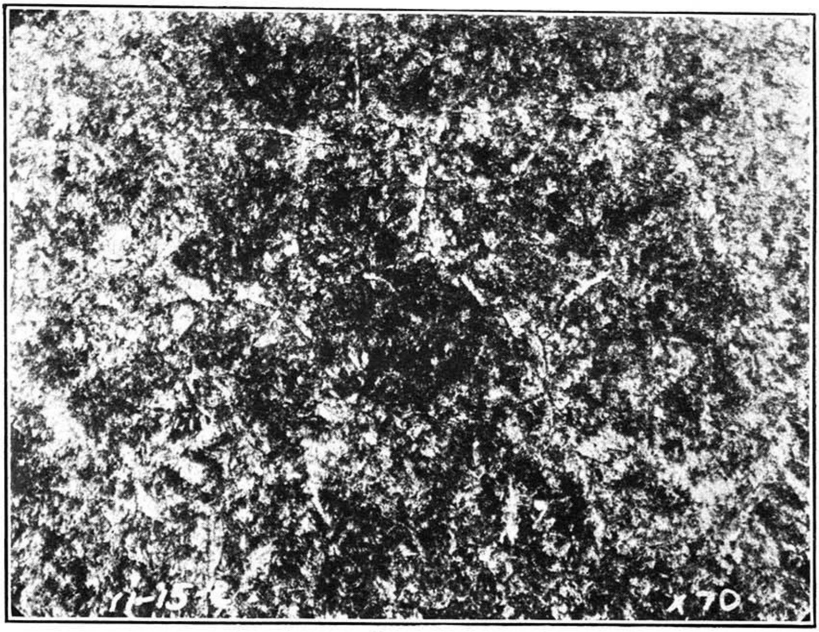

FIG. 15. × 70

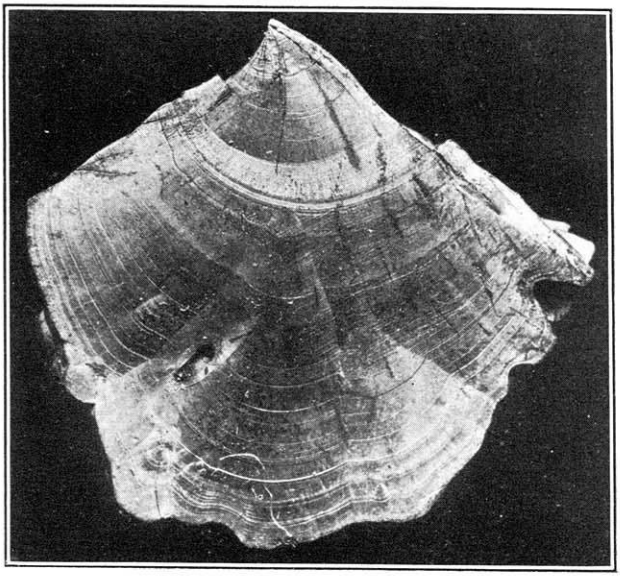

FIG. 16. × 4

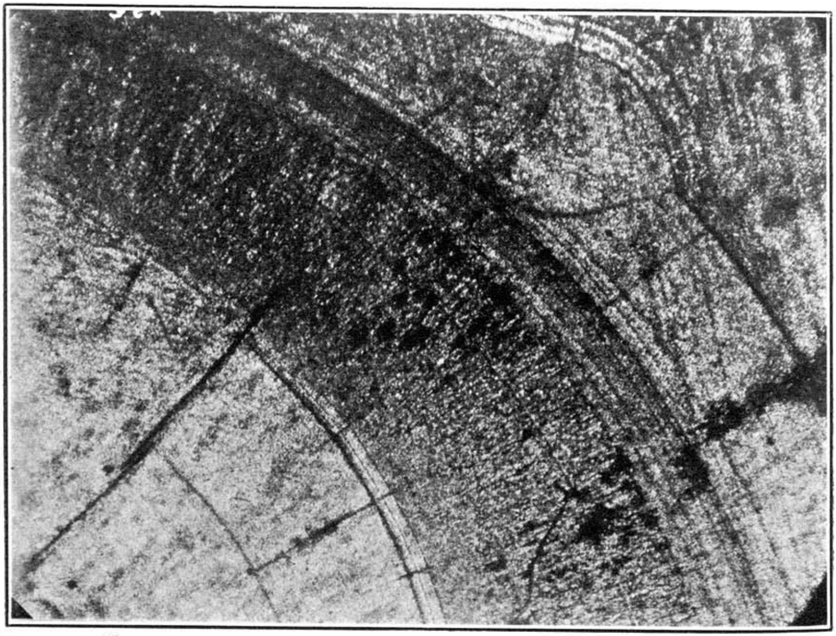

FIG. 17. × 25

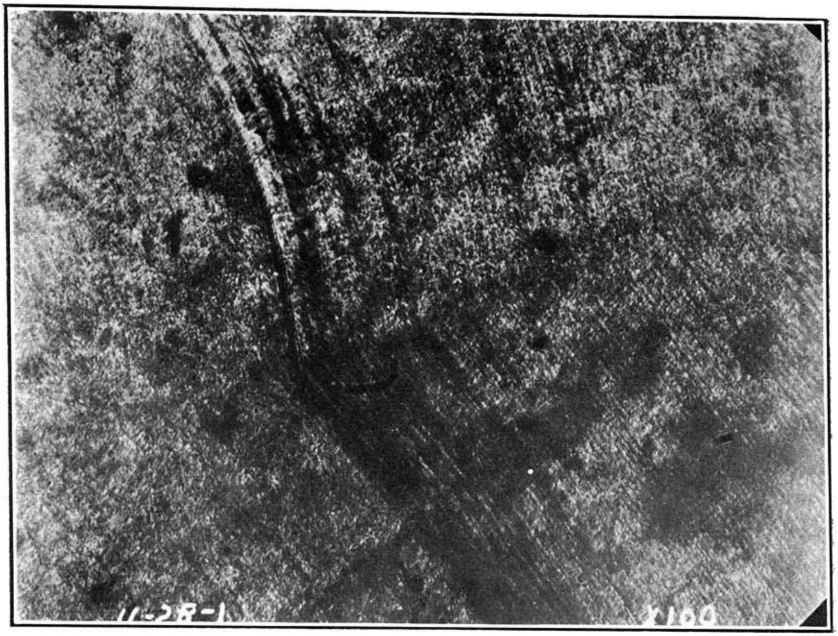

FIG. 18. × 100

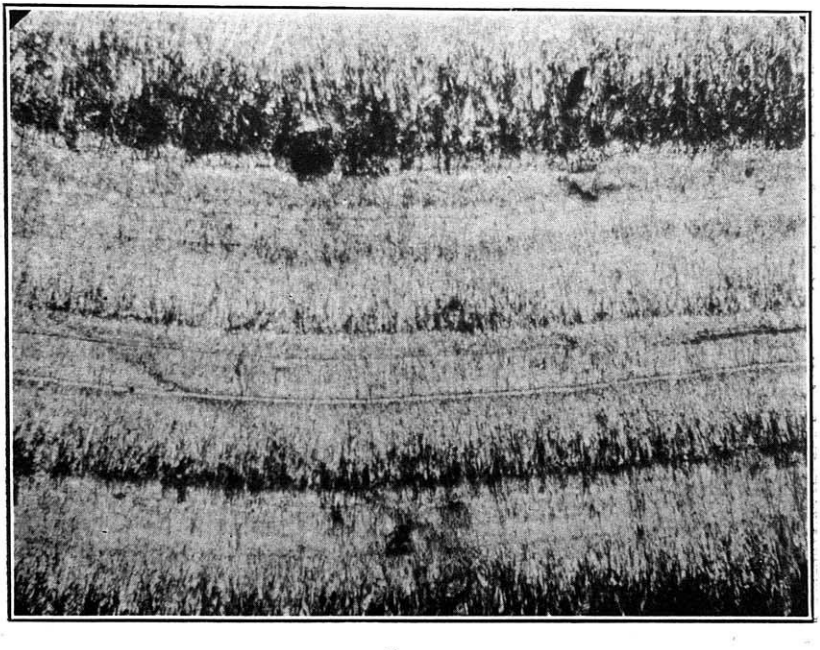

FIG. 19. × 100

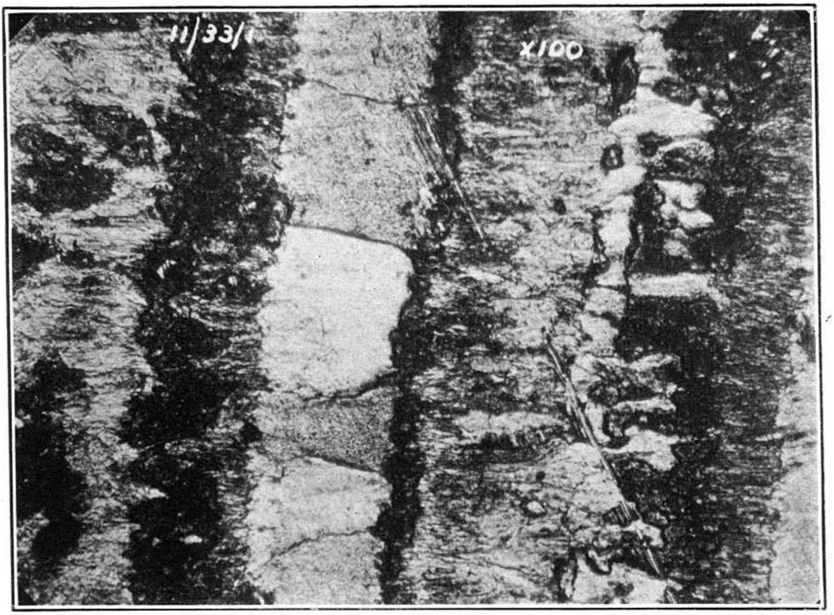

FIG. 20. × 100

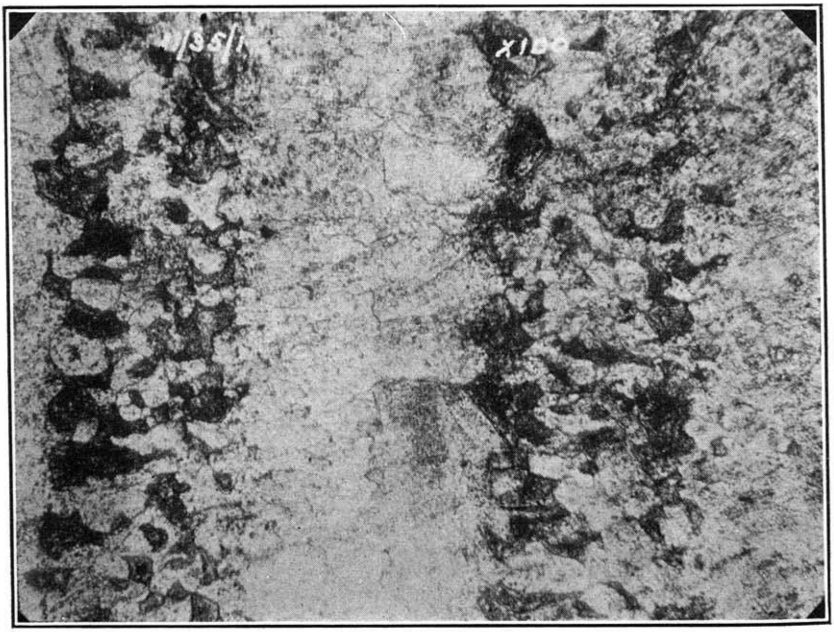

FIG. 21. × 100

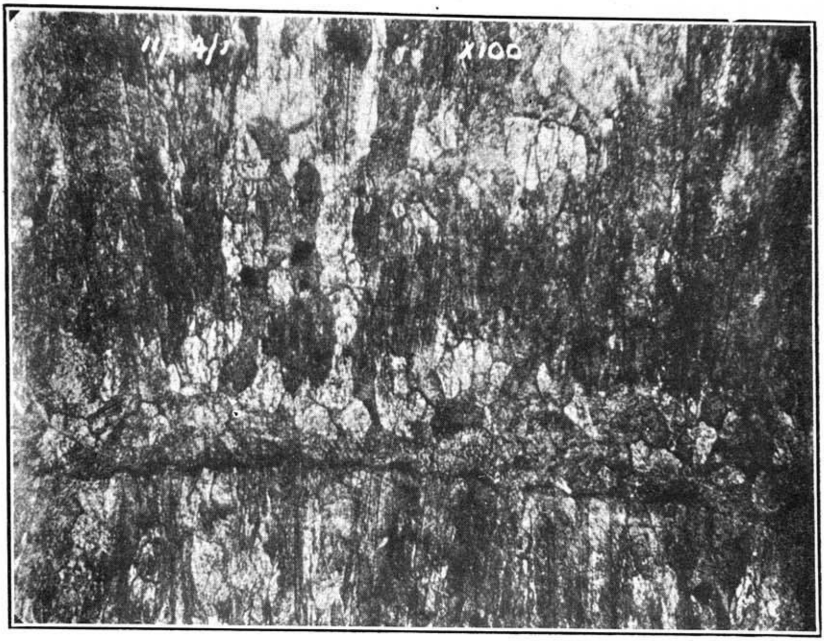

FIG. 22. × 100

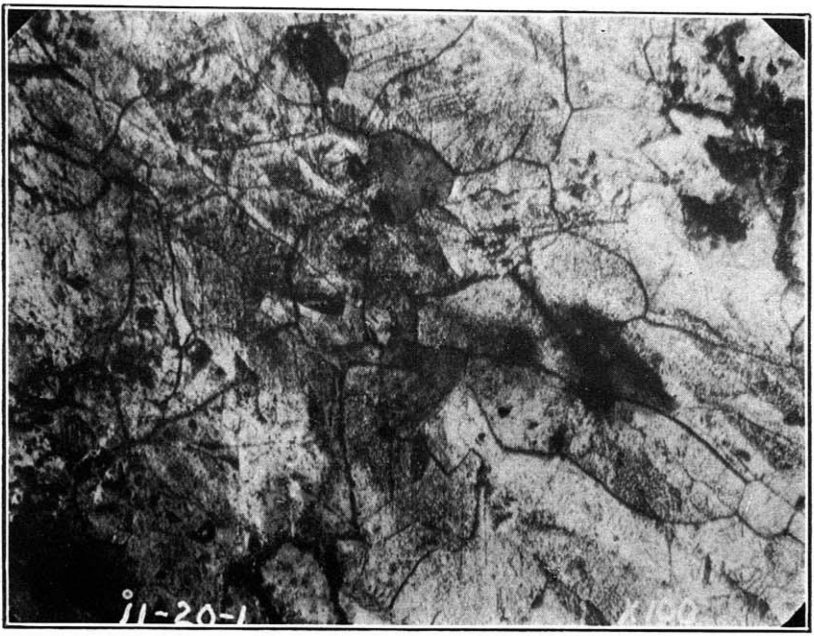

FIG. 23. × 100

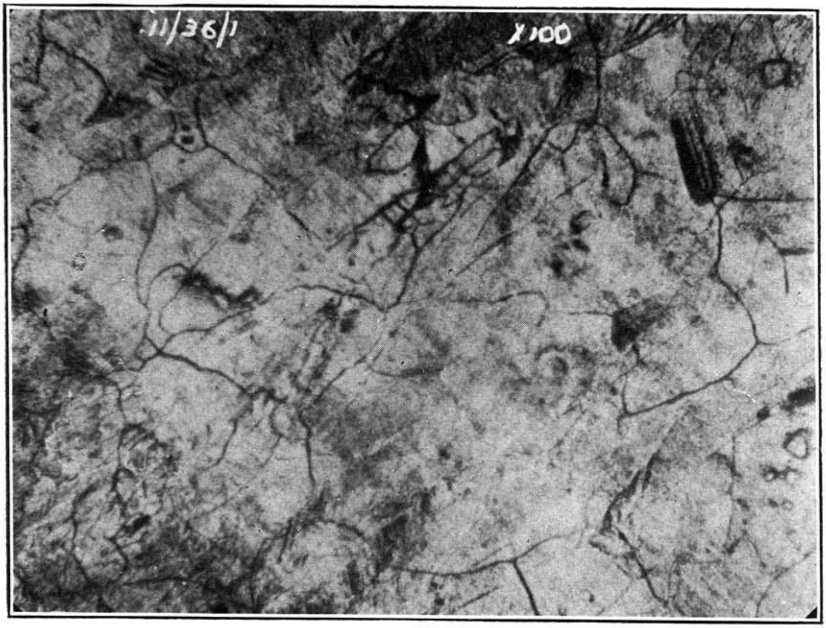

FIG. 24. × 100

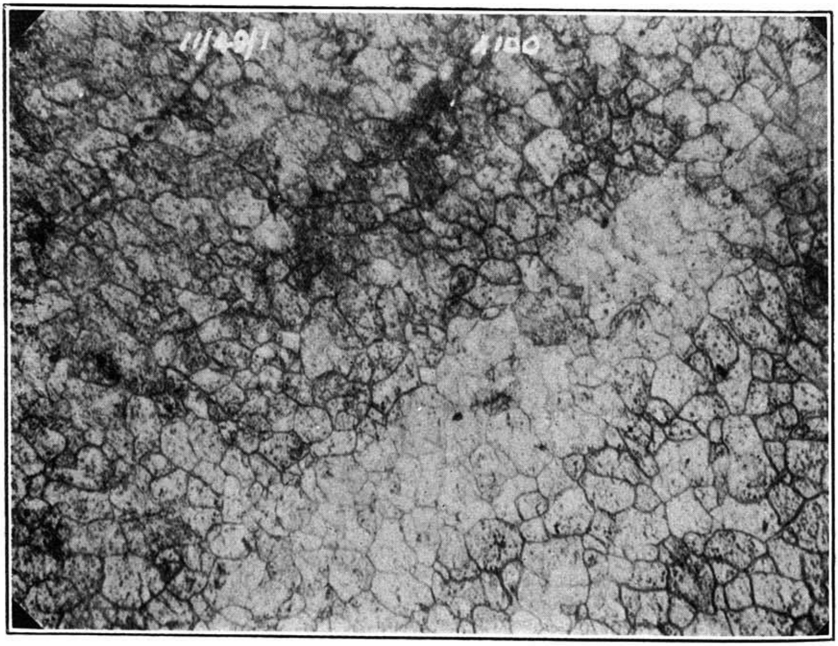

FIG. 25. × 100

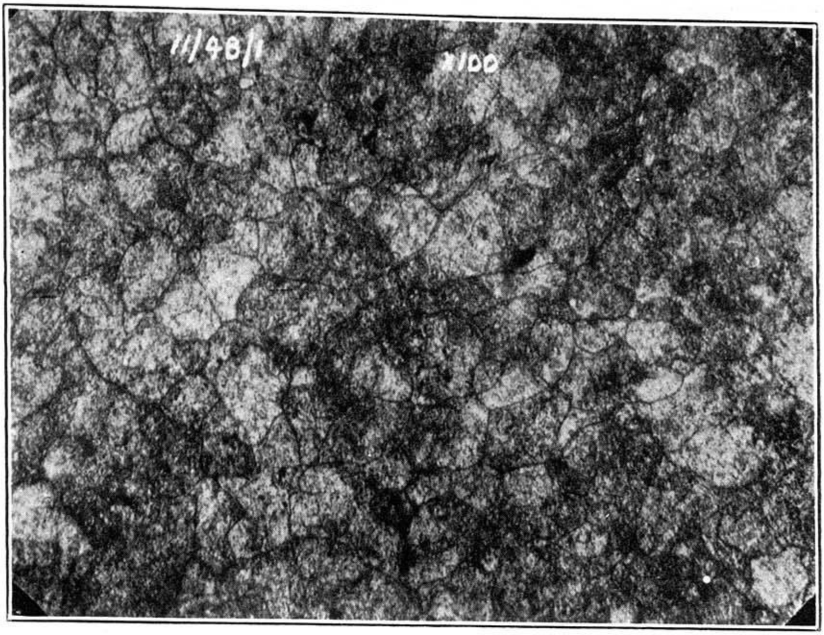

FIG. 26. × 100

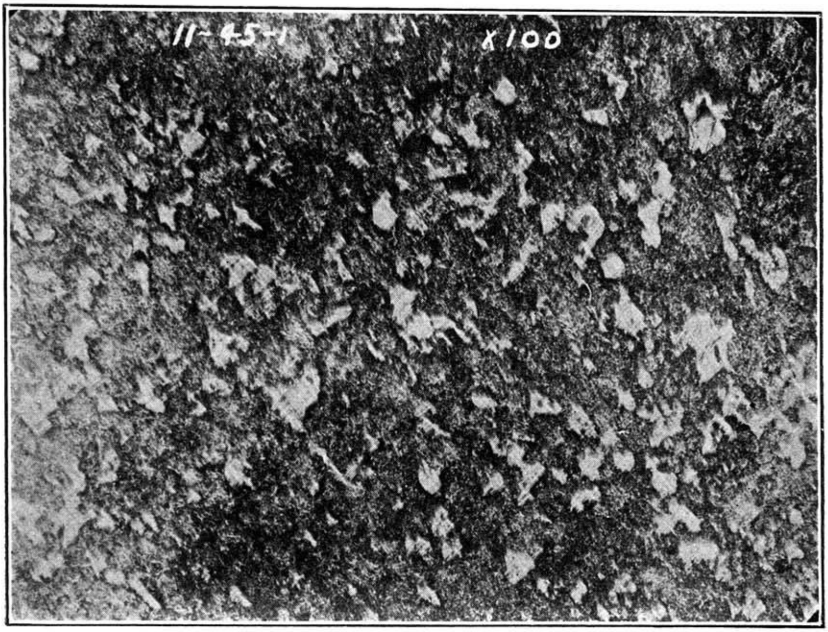

FIG. 27. × 100

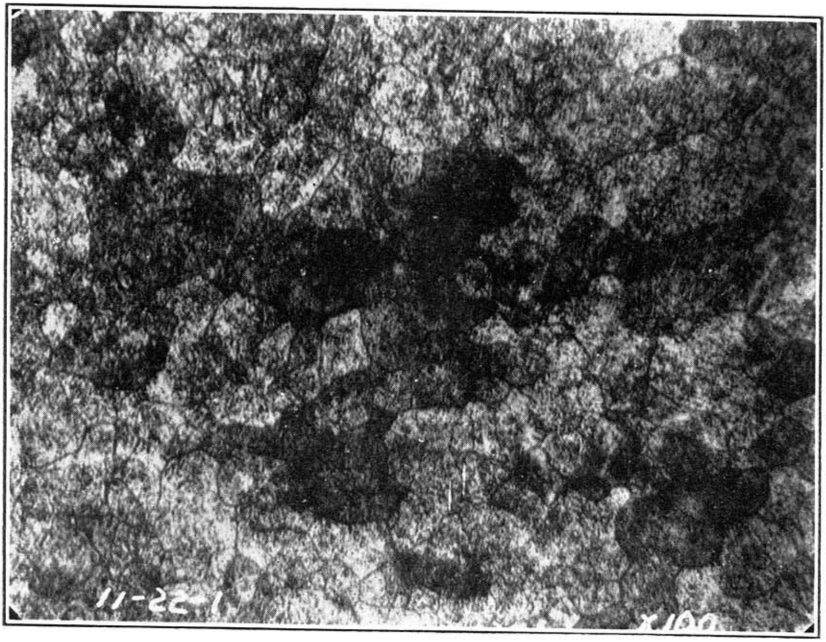

FIG. 28. × 100

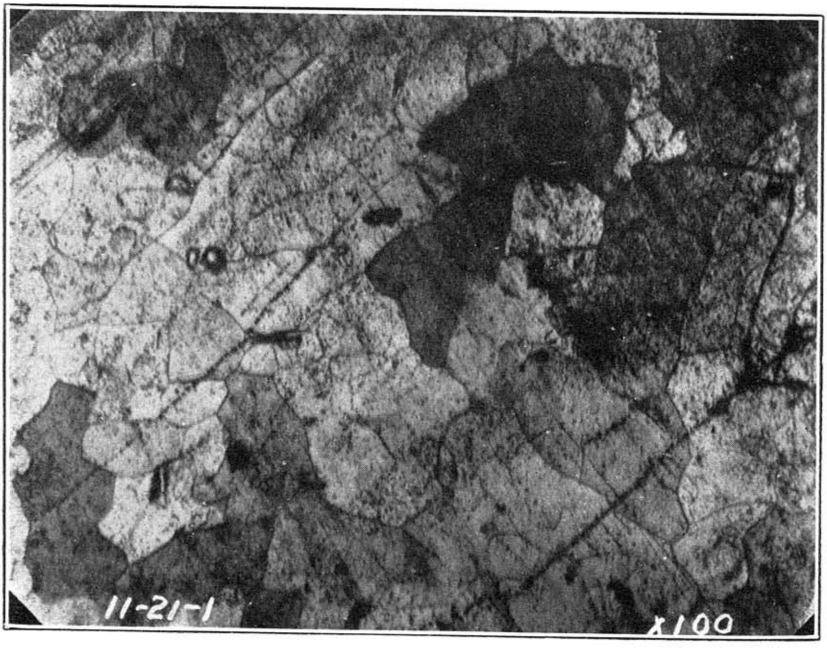

FIG. 29. × 100

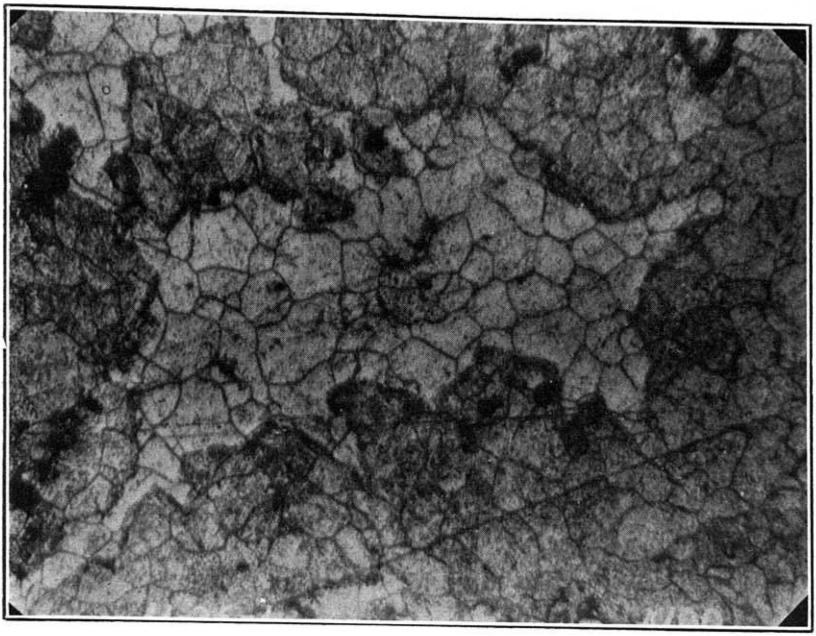

FIG. 30. × 100

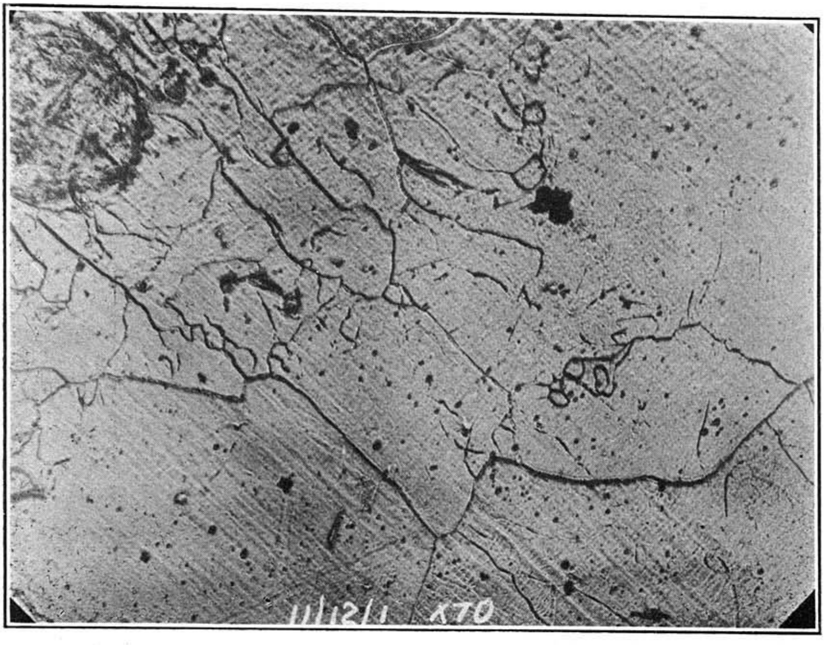

FIG. 34. × 70

FIG. 31. × 2

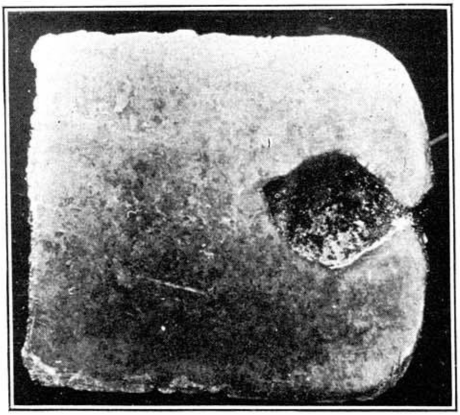

FIG. 32. × 2

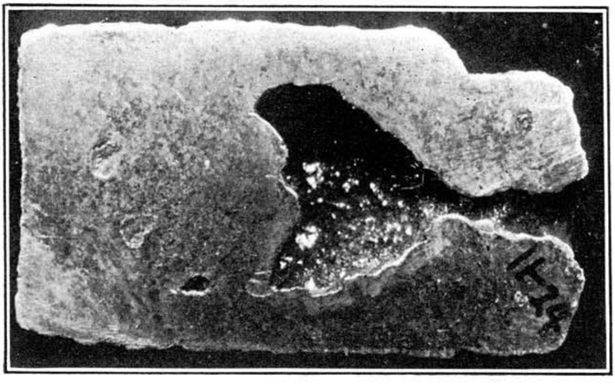

FIG. 33. × 2

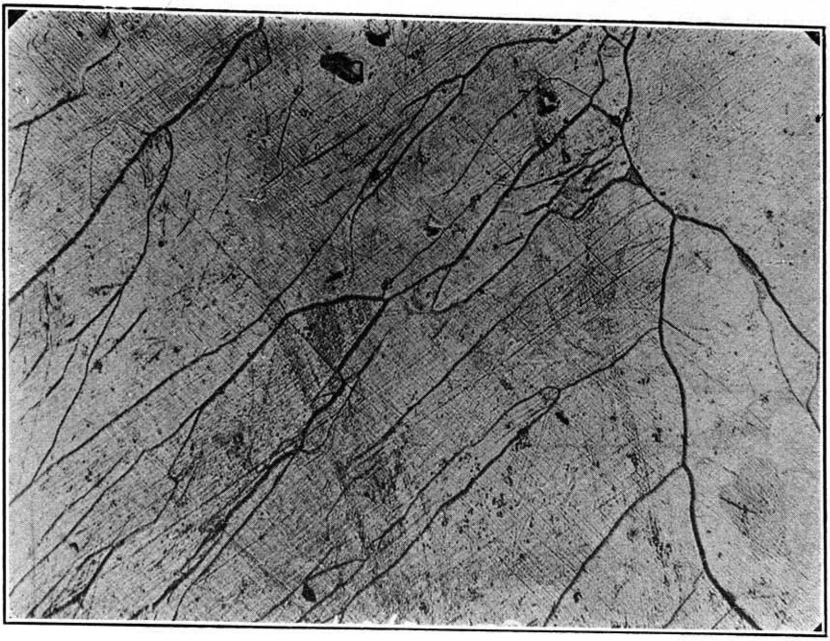

FIG. 35. × 70

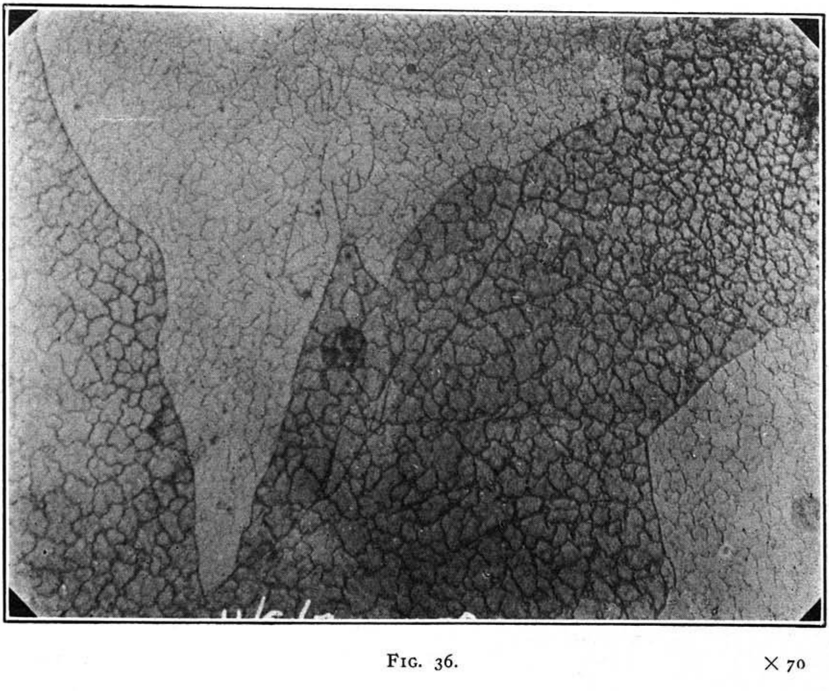

FIG. 36. × 70

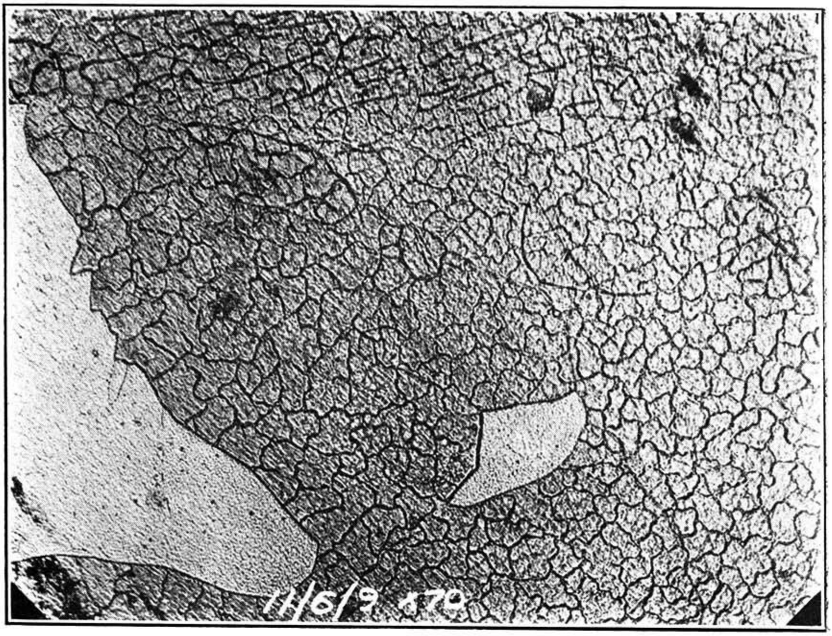

FIG. 37. × 70

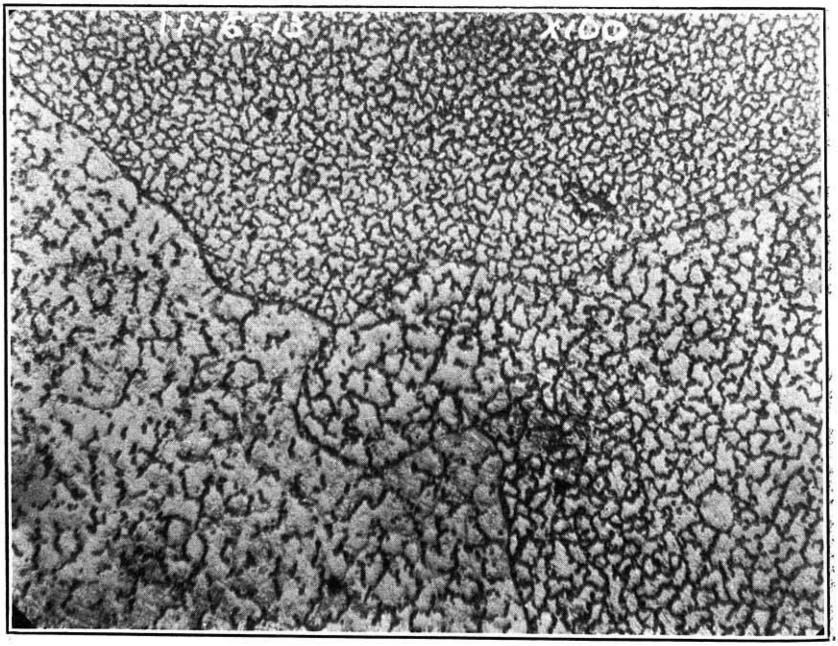

FIG. 38. × 100.

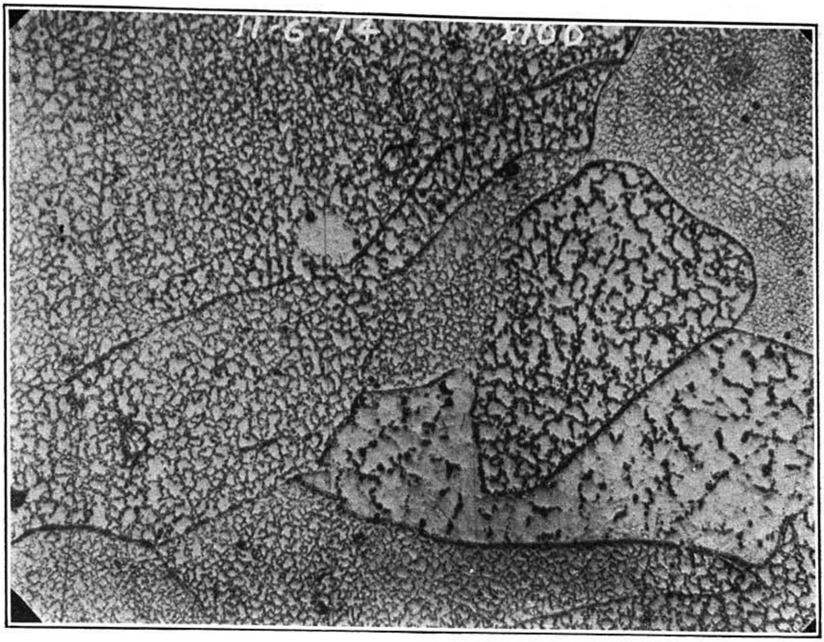

FIG. 39. × 100

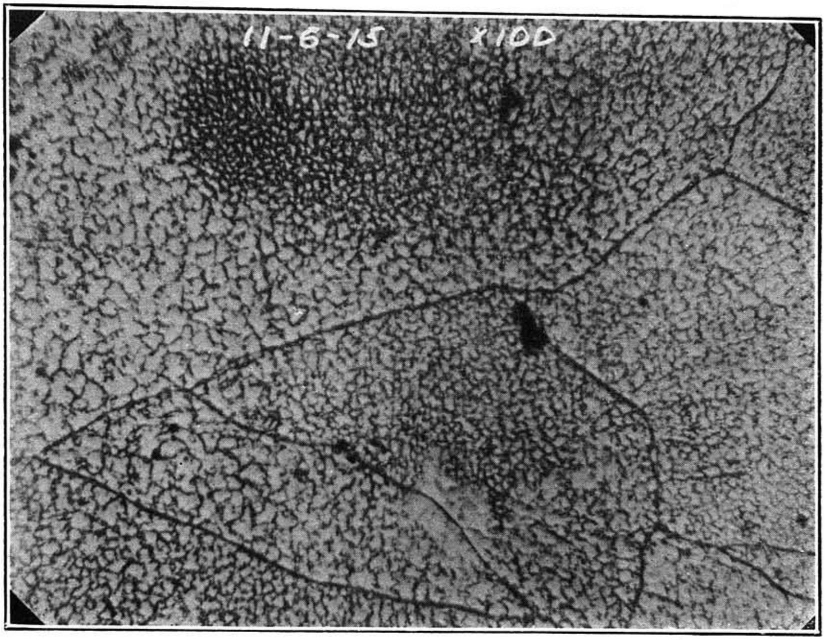

FIG. 40. × 100

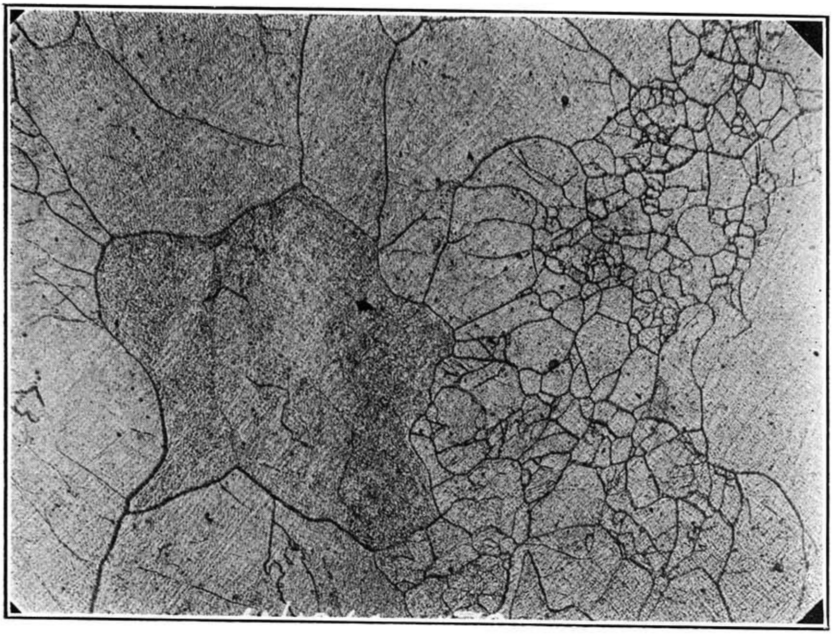

FIG. 41. × 70

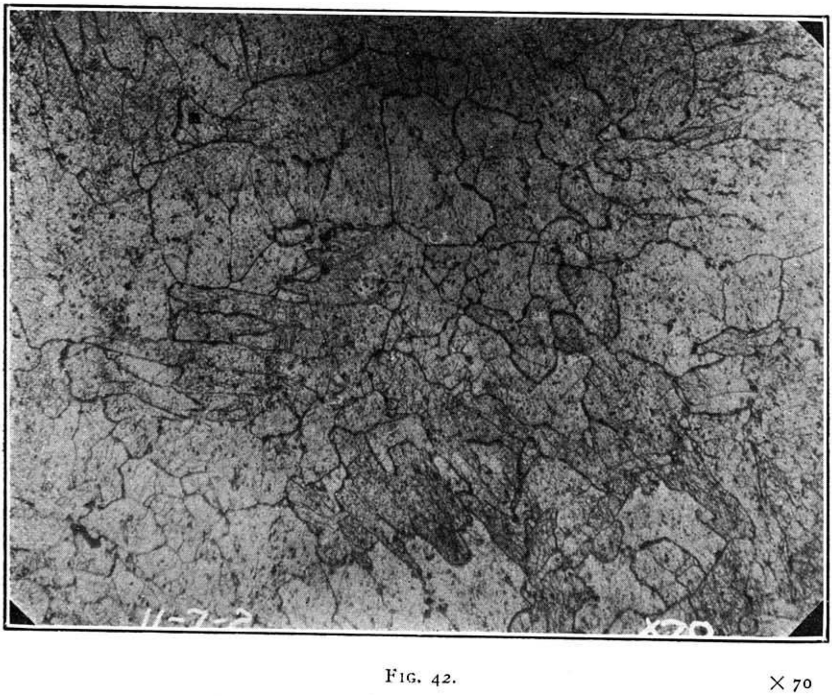

FIG. 42. × 70

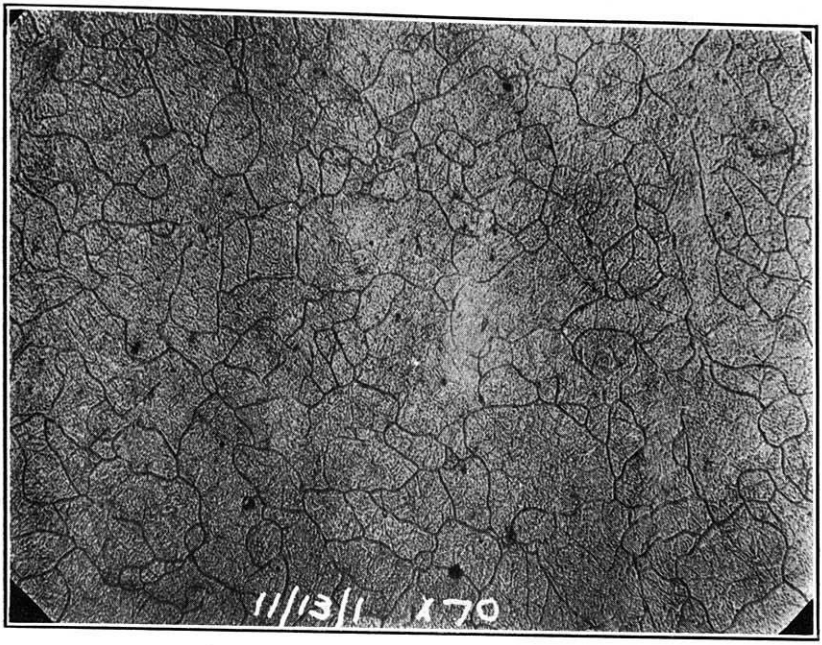

FIG. 43. × 70

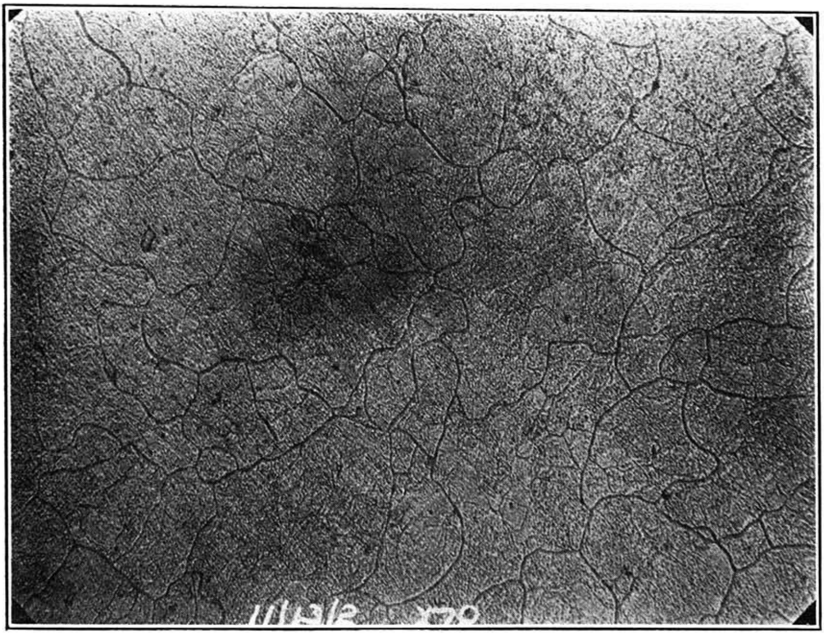

FIG. 44. × 70

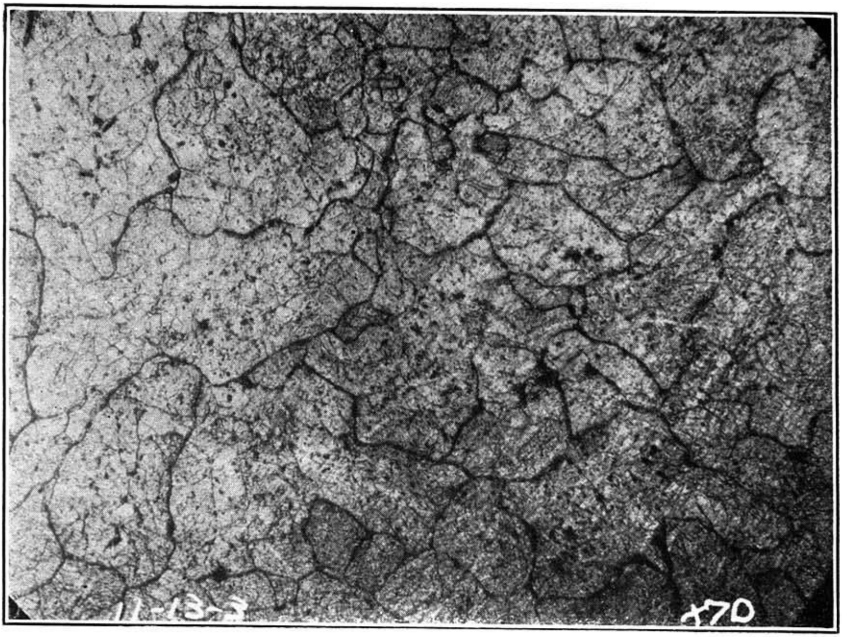

FIG. 45. × 70

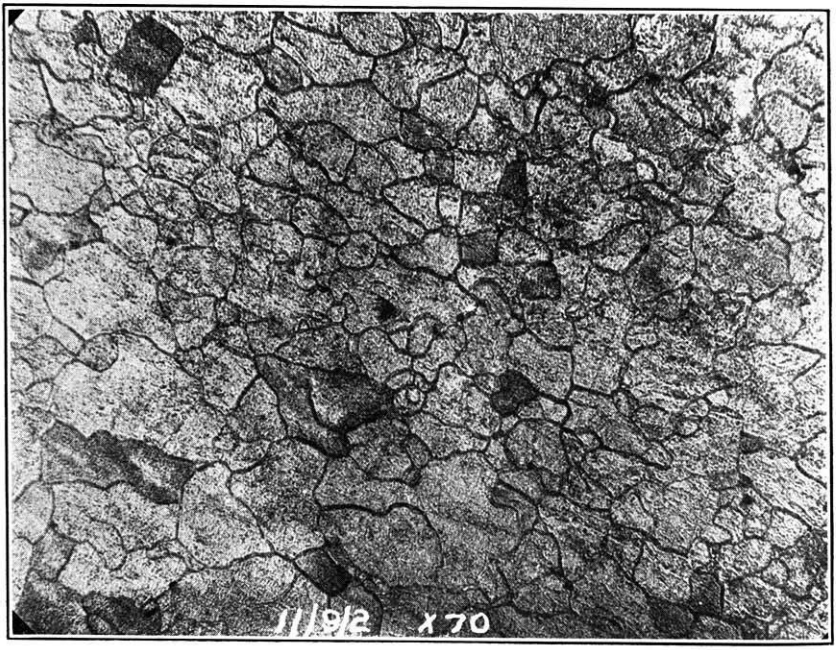

FIG. 46. × 70

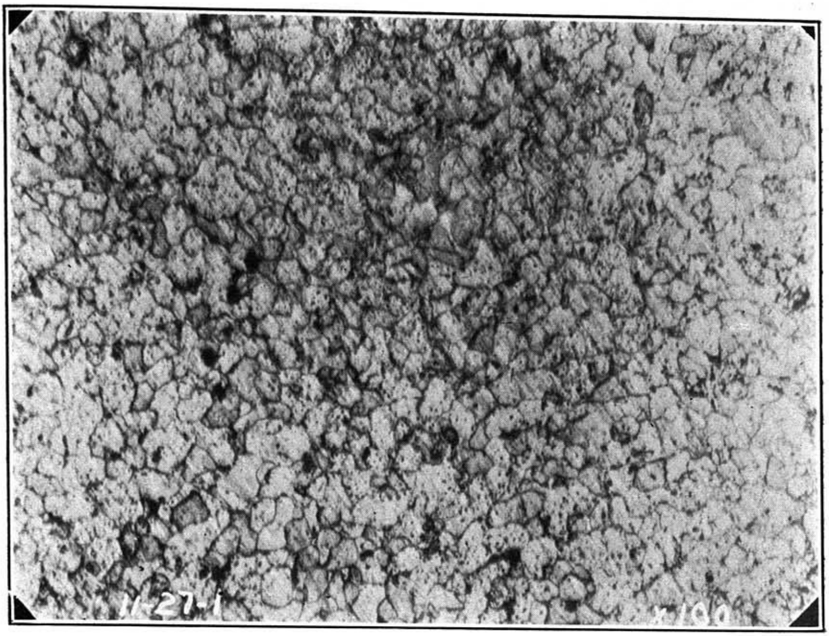

FIG. 47. × 100

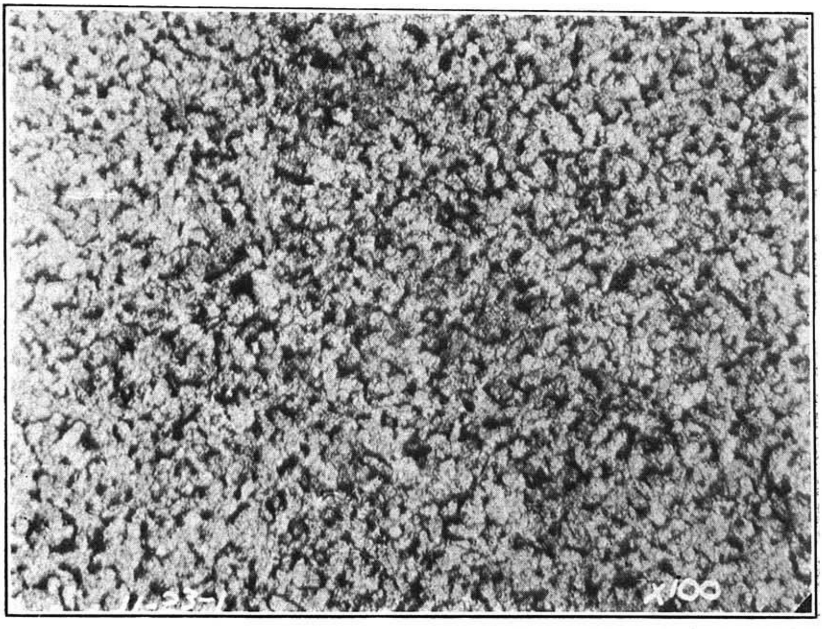

FIG. 48. × 100

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A Study of the Annealing Process for Malleable Castings

BY OLIVER W. STOREY.

This article gives the results of experimental work carried out by Mr. E. L. Leasman under the author's direction at the Chemical Engineering Laboratories of the University of Wisconsin. Although these experiments were preliminary in nature as a basis for extended work, interesting results were obtained.

Malleable cast iron is a product of importance. The annual production of the United States is over 1,000,000 tons. And yet, in such an important industry scientific progress has been slow. Each malleable iron plant makes its product under different conditions, and, as a result no two products are exactly alike except that all usually have to meet standard specifications.

The lack of scientific knowledge of this industry is made evident by the sparsity of the literature. The only book on this industry known to the writer is Richard Moldenke's recent work, "The Production of Malleable Castings." In the preface he states, "of the closely held secret processes of the great iron industry none can rank with the production of Malleable."

The first record of the process is by Reaumur, in 1722. It is probable that the malleablizing process was practiced much earlier, but, no doubt, it was like so many of the earlier industries, and was a secret which was handed down from father to son.

The pioneer manufacturer in this country was Seth Boyden, of Newark, N. J., who, although he did not discover the underlying principles involved, recorded his experiments. These are the first we have and he deserves special credit since they were made at a time when scientific experimentation on industrial problems was frowned upon.

Malleable iron occupies a position between ordinary cast iron and cast steel. It has a higher tensile strength than cast iron, but not as high as that of cast steel, while its resilience is superior to either.

The method of producing malleable castings is fairly uniform throughout the country. The white iron castings are packed in rolling mill scale in rectangular containers. These containers, either three or four high, are carefully luted up to exclude currents of air, placed in the ovens and heated to the desired temperature, being kept at the high point at least sixty hours. The total time of the annealing process is a week from one time of "lighting-up" to the next time.

The experimental work was carried out to determine the effect of the following variables upon the annealing process.

1. Packing materials.
2. Temperature of annealing.
3. Time of annealing.
4. Rate of cooling.

This was undertaken as a metallographic problem. All specimens were studied with the microscope which showed the structural changes.

In making malleable cast iron, white cast iron is used for the hard castings. This white iron must analyze to within certain limits to insure proper annealing. It is then annealed at the proper temperature, usually between 750° and 900° C., depending upon the practice, for about 60 hours, after which it cools slowly.

The structure of such a white cast iron is shown in Fig. 1. The two constituents shown are the white cementite and black pearlite, which is an eutectoid of ferrite and cementite. The cementite or iron carbide, Fe_3C, is present in two forms; first, as excess, and second, associated with ferrite as pearlite.

After being annealed at the proper temperature and slowly cooled the interior structure is usually that of Fig. 2, ferrite and temper carbon, with an outer shell that may vary from a pure iron to a high carbon steel. Fig. 3 is the fracture of a test lug, showing the black heart with an outer bright steel rim.

It is evident that the formation of the malleable structure of ferrite and temper carbon is due to the breakdown of the iron carbide into its elements, iron and carbon, at the annealing temperature, according to the following equation:

$$Fe_3C + \text{heat} = 3Fe + C$$

This reaction explains the formation of the black heart but not the rim structure. A different condition is necessary to produce a pearlite shell than to produce one of pure ferrite. Three different rims are shown in

Figs. 4, 5 and 6. Fig. 4 is the rim structure of the fracture shown in Fig. 3, and shows a medium carbon steel area covered by a thin skin of ferrite. Fig. 5 shows an outer rim of nearly pure pearlite, while Fig. 6 shows one of pure ferrite.

The four variables mentioned determine the structure of the casting. The packing materials will affect the rim, while the time and temperature of annealing and rate of cooling will determine the interior structure, with only a minor effect upon the rim.

The white iron used for the experiments was kindly furnished by the Beaver Dam Malleable Iron Company. The material was in the shape of test bars ¾ x ¾ x 10 inches. Mr. W. G. Grimer, chemist for the above company, furnished the following analysis with the bars:

Total (combined) carbon...	2.60 to 2.70%
Silicon	0.65 “ 0.70%
Sulphur	0.055 “ 0.060%
Phosphorous	0.140%
Manganese	0.27%

Fig. 1 is a micrograph of the white iron used. The structure shows a high percentage of pearlite owing to the low percentage of carbon resulting from steel additions to the melt.

The annealing furnaces used for these experiments consisted of two muffles electrically heated by resistance wire. A low voltage regulating transformer gave absolute temperature control.

All thermocouples used were calibrated frequently against a standard platinum, platinum-rhodium couple.

In order to carry on a larger number of experiments in this preliminary work a number of small containers were made. Several could be used in the furnace at the same time. These containers were made of 1½-inch pipe, cut long enough to take specimens 2 inches in length. They were then luted with fire clay except where caps and nipples were used. The serious objection to these small containers was that the oxygen of the air usually had access to the specimen.

Effect of Packing Materials

The first variable to be studied was the packing material. It had been noticed that certain specimens of commercial malleable iron had an enveloping skin of steel (Fig. 5), others pure carbonless iron (Fig. 6), while others showed an intermediate structure (Fig. 4). It was thought that the packing material would determine the structure of the outer shell.

A large number of packing materials were used, including lime, sand, alundum, rolling mill scale, resistor carbon, manganese dioxide, cement, fine and coarse fire clay, iron oxide, alumina, fine graphite and carborundum.

The results obtained by the use of these various materials showed that their physical and chemical constitution influenced the skin structure of the annealed casting. The packing material had no apparent effect upon the interior in the American "black heart" practice.

The chemical composition of the packing material was a factor that partly determined the nature of the outer portion of the annealed casting. With the materials which were stable at the annealing temperature the structure was uniformly a layer of ferrite. With oxidizing materials a deep layer of ferrite was formed. It is probable that enough oxygen was liberated to decarbonize to a greater depth.

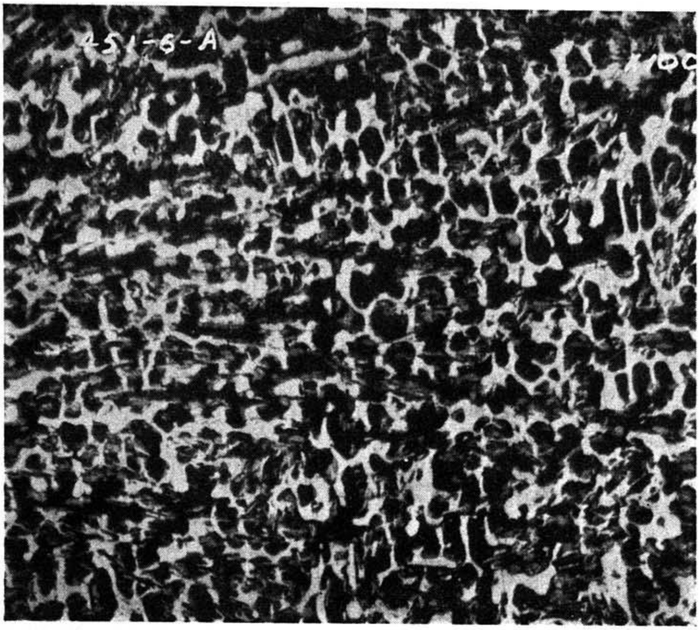

FIG. 1—MICROPHOTOGRAPH × 100

With carbon, charcoal, graphite and case carbonizing materials, a skin structure was formed which varied from a low-carbon to a high-carbon steel.

The physical structure of the packing materials also affected the malleable skin structure. Materials which were loose and porous and allowed a free circulation of the air showed a ferrite exterior. Without the oxygen of the air the structure of the exterior portion did not differ from the interior. This was best illustrated by the following experiments.

Brass turnings were used as a packing material in one of the containers. The brass fused at the annealing temperature and completely inclosed the specimen, preventing the oxygen from coming in contact with the exterior of it. Although a normal malleable structure was formed in the other specimens annealed in the same heat, the temper carbon extended to the brass coating which had formed on the specimen.

That the chemical composition of inert packing materials has little effect on the rim structure is evident from samples of commercial iron. Specimens from various plants using mill scale as a packing material showed a rim structure varying from pure ferrite to a high carbon steel. It is probable that the atmosphere of the furnace and the looseness of the packing rather than the chemical action of the scale determined the rim structure.

The experiments were not carried far enough to determine under what conditions the various degrees of carbonization could be obtained. Even if results were obtained these could hardly be comparable with those obtained in malleable practice. The atmosphere of the experimental furnace was highly oxidizing as compared with that of the commercial furnace. The small containers also allowed a quicker penetration of oxygen than those used in commercial practice. The probable exception was in the use of unusual materials such as case carbonizing mixtures.

But with materials such as mill scale, sand, clay, cinders, ashes, etc., the exterior structure will depend upon the composition of the atmosphere in the furnace, upon the annealing temperature, the method of packing, and the rate of cooling.

The writer recalls one malleable plant where scale is regularly used when the furnaces are running at the normal rate. But when a rush comes anything within reach is used as a packing material, usually ashes and cinders. No difference in structure is apparent between the two malleable products.

In another plant brick dust is replacing scale with no apparent change in structure. Large castings are annealed by merely heating in a muffle, care being taken to prevent excessive oxidation. The structure is the same in all cases, consisting of an exterior layer of ferrite, or pearlite, or both, and an interior of temper carbon and ferrite.

The skin structure, when a neutral atmosphere is used, does not differ from the interior since the breakdown is the same throughout the specimen. This was shown by the specimen annealed in brass. This shows that a slightly oxidizing action is necessary to secure a steel rim and that either a too highly oxidizing or a neutral atmosphere will give a ferrite or a ferrite and temper carbon rim, respectively.

The rate of cooling also has a slight effect upon the skin structure. A slow rate of cooling tends to result in a ferrite rim. This will be discussed later.

Where a case carbonizing mixture was used as the packing material the rim resembled the original iron (Fig. 11), since some of the excess cementite remained undecomposed. This structure will also be discussed later.

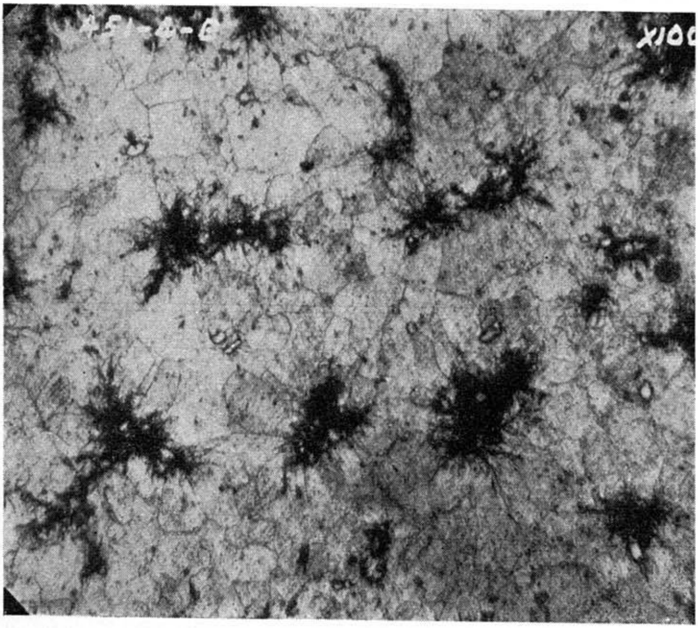

FIG. 2—MICROPHOTOGRAPH × 100

A peculiar rim is shown in Fig. 12. Here two steely strata are seen with a ferrite structure between them. Only one specimen showed such a structure.

The following conclusions may be drawn:

1. The packing material does not influence the interior of "black heart" malleable cast iron.
2. The ordinary packing materials do not directly affect the skin structure of malleable cast iron.
3. A loose packing material allowing a free circulation of oxidizing gases will result in a carbonless rim.

4. A slightly oxidizing atmosphere will result in a steely rim.

5. A neutral atmosphere will result in a rim having the same structure as the interior of the iron.

6. A slow rate of cooling will tend to result in a rim of ferrite.

Effect of Temperature of Annealing

A number of experiments were run to determine the most effective annealing temperature for iron of the analysis given, where the time of annealing was 50 hours and the cooling to 250° C. took 50 hours.

Experiment No.	*Annealing Temperature Deg. C.*
4	815°
5	760°
6	700°
7	730°
9	840°
10	790°–800°

Results

The specimens annealed at 700° were too hard to saw though slightly malleableized.

The specimens annealed at 730° were sawed with difficulty. Upon examination with the microscope the structure had broken down slightly.

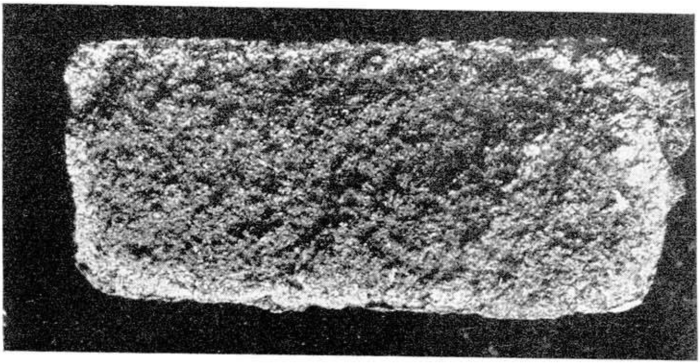

FIG. 3—MICROPHOTOGRAPH × 2½

The specimens annealed at 760° showed a partial breakdown of the cementite, as shown in Fig. 7.

Specimens annealed in experiments 4 and 10 showed but a partial decomposition of the cementite.

Upon annealing at 840° the carbide was almost entirely broken down (Fig. 8).

In one experiment the temperature was kept at 535° to 650° C. for 120 hours, but these specimens were too hard to saw.

In the first experiments an annealing temperature of 870° to 900° was maintained for 50 hours, and this resulted in a complete breakdown of the cementite. (Fig. 6.)

The effect of the temperature is an important factor. Not only does the time of the anneal, but also the quality of the resulting product depend upon the temperature. It is possible to cut down the time of the anneal by raising the temperature, but woe befalls those who do it. A poor product results. The lower the temperature of the anneal the better the product. The balance must be found between the increased value of the improved product and the high cost of the longer anneal.

Figs. 2, 6, 7 and 8 are micrographs of structures of malleable iron annealed at varying temperatures. Fig. 7 shows the result of annealing at 760°. The micrograph shows areas of cementite in a background of ferrite with a few particles of temper carbon. The dendritic structure of the cementite is visible. This shows that the cementite in the pearlite suffers the first breakdown and that the excess cementite is the last to dissociate.

By annealing at 840° the structure of Fig. 8 was obtained. Small particles of undecomposed carbide are still visible though the specimen is composed mainly of ferrite and temper carbon.

Fig. 2 is a micrograph of some commercial iron and shows small areas of cementite. Most commercial malleable iron shows such areas, indicating that the annealing was not entirely completed.

In Fig. 6 the structure is entirely ferrite and temper carbon, indicating that the breakdown at 870° was complete.

Conclusions

1. With an annealing time of 50 hours the white iron furnished required an annealing temperature of 860° to secure a complete breakdown of the cementite.
2. Annealing at 740–760° for 50 hours resulted in a partial breakdown. By continuing the heat to double the above time it is probable that a complete breakdown could have been secured.
3. No decomposition could be observed in specimens annealed below 670°.

The Effect of Rates of Cooling from the Annealing Temperature to 250° C.

In all malleable iron work one of the most important factors is the rate of cooling. In the anneal the cooling is slow, usually requiring from 40 to 60 hours.

If the cooling is too fast a hard, brittle, steely structure results.

In this research the result of the different rates of cooling was noticed in the first three experiments. When the rate was slow, that is, the drop from 900° to 670° required 38 hours, the interior of the specimen showed an excellent malleable structure, ferrite and temper carbon. (Fig. 6). When the same drop in temperature required but 22 hours, the resulting interior structure showed ferrite, temper carbon and areas of pearlite. (Fig. 9.) When the time occupied but 15 hours the interior showed pearlite, temper carbon, and a small amount of ferrite. (Fig. 10).

From these data it was evident that the structure of the resulting anneal was dependent upon the rate of cooling. It was not only desirable to determine the most suitable rate of cooling, but also to obtain the critical range through which this cooling had to be slowest.

The A_1 temperature, 700°, was regarded as the critical point. At this point the transformation of austenite into pearlite occurs. The experiments were run so that the critical range was above 670°, allowing for a lag of 30°.

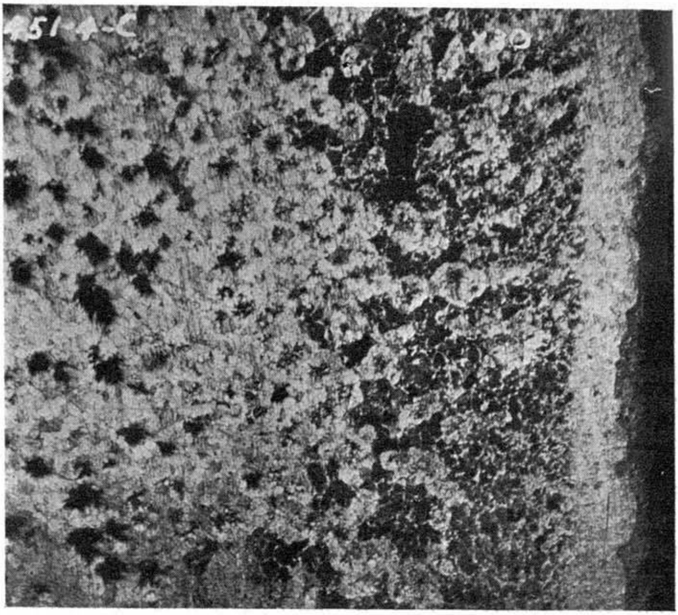

FIG. 4—MICROPHOTOGRAPH × 30

In experiment No. 11, the first of this series, the furnace burned out and the time of cooling was rapid, requiring 14 hours to drop from 870° to 250°. All specimens showed an interior of high-carbon steel and temper carbon similar to that of Fig. 10.

In experiments No. 12 to No. 16 the time of cooling from 870° to 750°, 750° to 670°, and 670° to 250° was varied.

From these experiments one conclusion was drawn. The rate of cooling from 670° to 250° had little, if any, influence on the structure. Though the evidence was inconclusive the work done so far indicated that the rate of cooling from 840° to 730° determined the resulting structure and was the critical range.

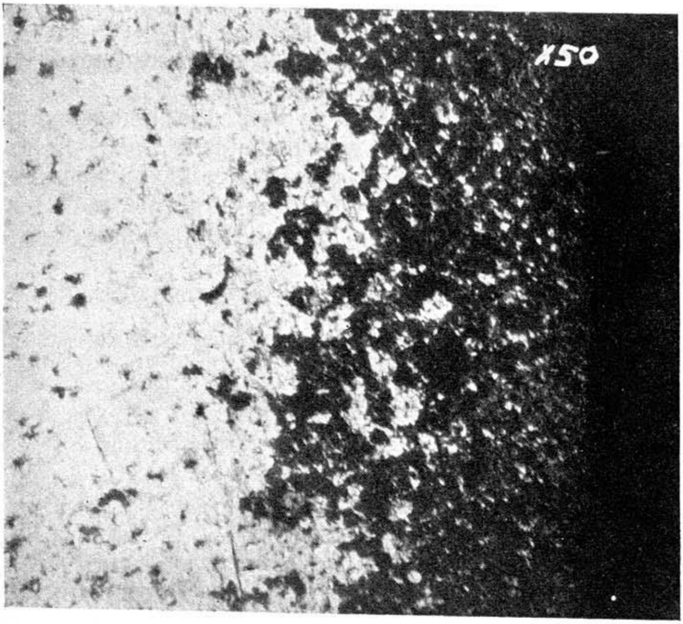

FIG. 5—MICROPHOTOGRAPH × 50

When the malleable iron made in these experiments was reheated for 10 minutes the carbon did not go into solution below 800° and form a steel with air cooling. A slight amount of carbon went into solution when heated for 1 hour at 800°. If the malleable iron was heated at 850° enough carbon went into solution in a few minutes to form a high-carbon steel. This experiment showed that the carbon could not precipitate out entirely above 800°, and that the critical range was below that temperature.

Specimens which had been heated to 900° and consisted of pearlite and temper carbon were annealed at 700° for various periods of time and cooled in the air. When heated to 700° for one-half hour part of the pearlite was decomposed and a narrow band of ferrite surrounded each particle of temper carbon. When heated for 2 hours about one-half of the pearlite was decomposed and the temperature resembled Fig. 10, though the outlines were not as definite. By heating the specimen for 5 hours at this temperature all of the pearlite was decomposed and structure again consisted of ferrite and temper carbon. This experiment would seem to show that the final breakdown of the cementite may occur above the Ar_1 point. At the present time the effect of heating at temperatures above and below 700° has not been studied.

It was noticed that particles of undecomposed excess cementite remained unchanged throughout these heat treatments showing that it was stable in comparison with the dissolved cementite.

If the temperature necessary to entirely decompose the iron, iron-carbide solution was below 800°, and if the reaction was negligible below 670° it was evident that a good structure could be obtained by holding the specimens at the critical temperature upon cooling for the correct length of time and then cooling at a quick rate. It was also evident that a good structure could be obtained by annealing at this critical temperature and cooling rapidly. This was done, and although the time required was longer, owing to the lower temperature, a good structure resulted.

The temperature of the final precipitation of carbon is probably dependent principally upon the silicon and manganese content of the iron. The lower the silicon content the lower the temperature at which the iron carbide is stable.* The proportion of these elements will determine the critical range of the iron.

Conclusions

1. A fast rate of cooling after annealing results in a steely structure.
2. The critical cooling range is between 740° and 830°.
3. If the rate of cooling is sufficiently slow in the critical range all of the carbon in the undecomposed austenite will be precipitated in that range.
4. If the carbon is entirely precipitated in the critical range the rate of cooling below 700° has little effect upon the iron.
5. Very slow cooling will result in a ferrite rim.

Time of Annealing

A number of experiments were run to determine the correct time of annealing at various temperatures.

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*Charpy and Cornu. Compt. rend. 157, 901.

The results showed that a malleable structure was obtained in 36 hours at 870°. By raising the temperature to 985° the time was cut to 18 hours, while at 740° the necessary time was more than 70 hours.

Though the short, high temperature anneal looks attractive it is not practicable owing to several reasons. It soon ruins the furnace, burns the saggers, and results in a poor grade of malleable iron. The lower the temperature of anneal the cheaper the upkeep of the furnace and the better the iron. Though the best product results from the 740° anneal, this low temperature is usually prohibitive where cost must be considered, owing to the length of time.

Reactions In the Annealing Process

A metallographic study of the specimens showed the successive reactions occurring in the process. The following data are significant in determining the reactions resulting in the malleable iron structure:

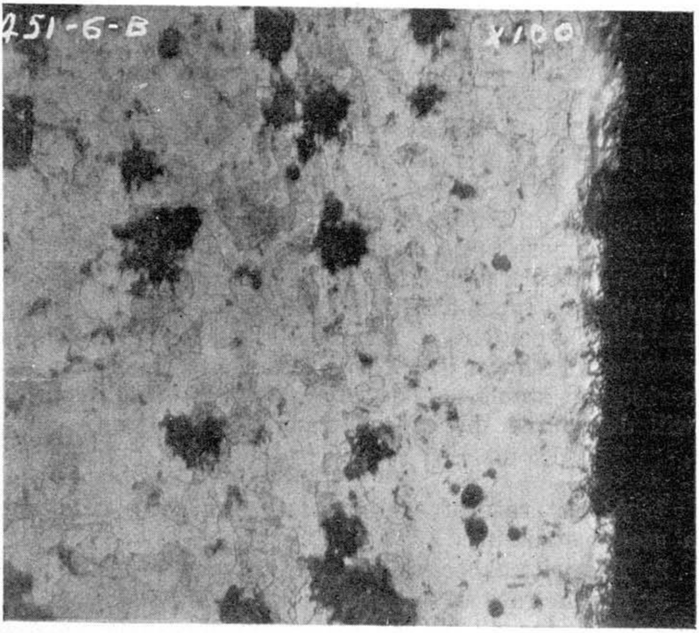

FIG. 6—MICROPHOTOGRAPH × 100

1. When the malleable iron was heated for too short a time or at too low a temperature and slowly cooled the structure consisted of ferrite, cementite and temper carbon. (Fig. 7.)

2. By increasing the time at the maximum temperature or increasing the temperature the cementite areas

were almost (Fig. 8) or entirely eliminated. (Fig. 6.) The structure then consisted of ferrite and temper carbon.

3. By annealing at the proper temperature to insure the breakdown of all of the excess cementite, but cooling rapidly from this temperature, the structure of Fig. 10 resulted. This consists of temper carbon surrounded by ferrite, in turn enveloped by pearlite.

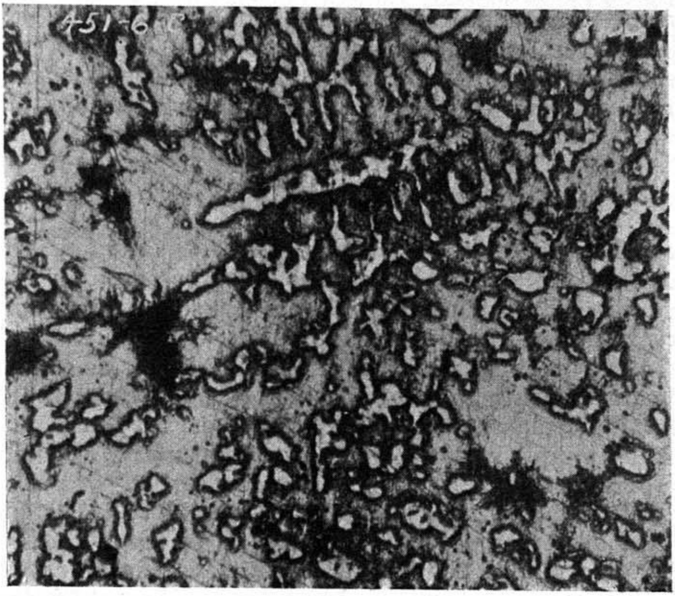

FIG. 7—MICROPHOTOGRAPH × 100

4. When the rate of cooling was slower than in No. 3 the structure of Fig. 9 resulted. This is similar to Fig. 10, but the pearlite areas are much smaller.

5. By annealing at too low a temperature and cooling rapidly the specimen consisted of areas of excess cementite surrounded by pearlite and small particles of temper carbon surrounded by ferrite.

6. When the malleable iron was reheated to about 800° the temper carbon started to go into solution.

7. It was possible to secure a complete decomposition of the dissolved cementite at 700°.

From these data the mechanism of the formation of the malleable structure could be deduced.

The white iron consisted of cementite and pearlite. When heated to the annealing temperature this pearlite went into solid solution as austenite.

It is a question whether the breakdown of the cementite occurs directly from the excess cementite or whether it occurs from the iron carbide dissolved as austenite. Though the research did not result in any definite conclusions, it seemed to indicate that the excess cementite did not break down directly, but that it first went into solution as austenite, from which the carbon was precipitated.

If the excess cementite of the white iron broke down directly the reaction should show some free graphite scattered in areas of cementite, since the decomposition would proceed uniformly throughout the carbide particles. Instead of a uniform breakdown and the scattered formation of temper carbon these cementite areas grow smaller as though they were being gradually dissolved, while the temper carbon forms in large patches. There is no indication of a direct decomposition of the excess cementite.

If the cementite in the austenite decomposes and deposits the temper carbon the ferrite liberated will dissolve the excess cementite. The presence of the nucleus of temper carbon probably causes a more rapid breakdown of the dissolved carbide.

In the specimens examined in which excess cementite remained owing to imperfect annealing, it was found that the cementite adjoining temper carbon areas was usually much smaller than that farthest away. Usually the area directly about the temper carbon was free from cementite. This would be the result if the carbide in the austenite decomposed. Owing to the liberation of the ferrite at the temper carbon the concentration of this consituent would be greatest there and the excess cementite in the immediate vicinity would be more quickly dissolved than that farther away.

The stability of the excess cementite in the white cast iron is shown again in Fig. 11. This specimen was annealed in a case-carbonizing mixture and the exterior portion retained the greater part of the excess cementite. Temper carbon and ferrite were also present in this rim. The interior showed a good malleable structure. In this case it is probable that the carbon necessary to replenish the austenite due to the decomposition of the dissolved carbide was obtained from the carbonaceous gases of the case-carbonizing mixture instead of from the cementite areas. The temper carbon in this rim was not surrounded by ferrite, but was scattered throughout the cementite areas, showing that the latter was more resistant than the gases to the dissolving action of the ferrite liberated at the temper carbon.

The decomposition of the iron carbide in the austenite is not complete at the annealing temperature, but is probably complete at 700°. By cooling quickly from the annealing temperature the specimen consists of nearly pure pearlite and temper carbon, or, if a piece of good malleable, consisting of ferrite and temper carbon, is heated to the annealing temperature, part of the carbon is quickly redissolved to form pearlite. By then annealing at 700° all of the carbon may be reprecipitated.

This pearlite formation shows that the stability of the cementite dissolved in the austenite is a function of the temperature, which is determined more or less by the silicon and manganese ratio. The lower the temperature the less stable the iron carbide. The determination of the limiting temperature or where the cementite is completely unstable was not made, but is probably close to the eutectoid temperature, about 725° to 775°. By cooling slowly through this temperature range the iron carbide may be entirely decomposed and ferrite and temper carbon obtained.

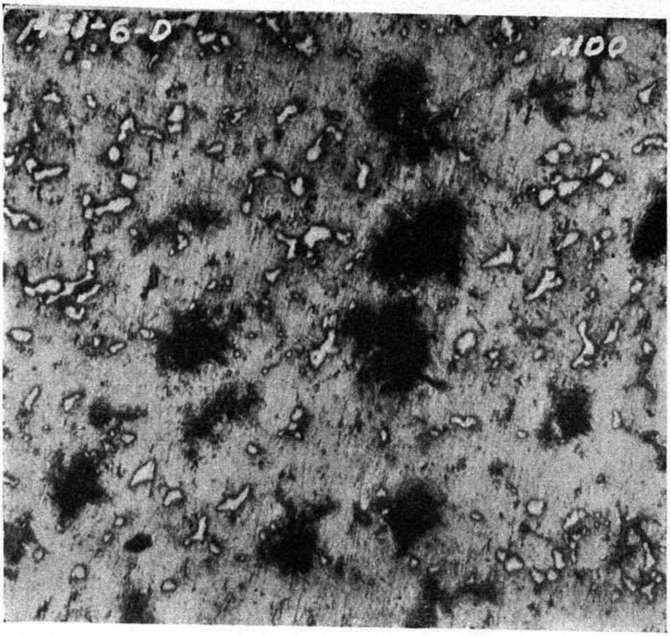

FIG. 8—MICROPHOTOGRAPH × 100

Since the cementite is unstable below this temperature the breakdown of the iron carbide may be possible below the Ar_1 point, but the reaction is slower since it is at a low temperature and the carbide is not in solution. Therefore, if the rate of cooling is slow until 650° or 700° is reached, the cooling may be more rapid to the room temperatures. This is corroborated by the experimental evidence.

Where the cooling from the annealing temperature is too fast the iron carbide forms pearlite. (See Figs. 9 and 10.) Since the austenite about the temper carbon particles is richer in ferrite the rejection of ferrite takes place here and the pearlite forms furthest from the carbon.

The structure of the rim is also dependent upon the rate of cooling. If the carbon is oxidized from the surface to an extent which will result in a medium to a high-carbon steel, as shown in Fig. 5, and the rate of cooling is slow enough to prevent any pearlitic formation in the interior of the specimen, the cementite in the rim will probably be stable owing to the absence of carbon nuclei. If the rate of cooling is too slow even this cementite will decompose forming a lower carbon steel or a pure iron skin, as shown in Fig. 6. Areas of such partly decomposed pearlite are shown in Fig. 12.

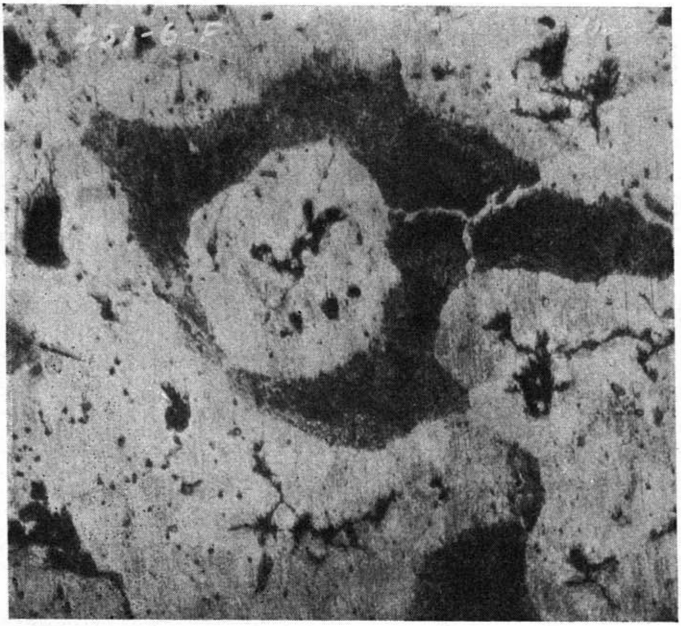

FIG. 9—MICROPHOTOGRAPH × 100

The skin effect has been a much discussed problem. Several different explanations of the disappearance of the carbon, or the decarbonization of the rim of malleable iron, have been offered. Some hold that the carbon migrates to the interior and remains in the casting, while others claim that the carbon migrates out and disappears entirely from the casting. It is obvious that if the carbon migrates out and leaves the iron at the temperature used for annealing, it must do so in the form of a gas. An analysis of the gases formed during the annealing would indicate their nature.

In the hardening and annealing of steels care must be used so that the surface does not become decarbonized. Experience shows how easily and quickly the surface carbon is oxidized. This surface decarbonization is not alone a result of the action of oxygen according to the following reaction:

$$2Fe_3C + O_2 = 6Fe + 2CO$$

$$2CO + O_2 = 2CO_2 \text{ (with excess oxygen).}$$

The surface reaction may also be the result of the action of CO_2 on the iron carbide.

$$\begin{aligned} Fe_3C + CO_2 &= 3Fe + 2CO \\ 2CO + O_2 &= 2CO_2 \\ Fe_3C + CO_2 &= 3Fe + 2CO\text{, etc.} \end{aligned}$$

The amount of decarbonization is therefore dependent upon the presence of oxygen and carbon dioxide.

This reaction may be applied to the annealing process. Since the castings are somewhat inaccessible to the furnace gases the reactions and the rim decarbonization are slow. Where the furnace gases have a large excess of oxygen the reaction is more rapid than where less is used. The slower the oxidation the more steely the rim.

Even with a carbon packing it would be impossible to obtain a steel rim at certain low temperatures owing to the equilibrium relations between CO_2 and CO. This equilibrium calls for more CO_2 at the lower temperatures, and for this reason a casting annealed at a lower temperature, 700–800°, would probably have a more decarbonized rim than one annealed at above 800°. Where a carbon monoxide atmosphere is maintained as in the case of the specimen annealed in a case-carbonizing mixture, no surface oxidation results.

Some experiments were run to determine the gases resulting from the annealing operation. The reducing nature of the gas was shown in a preliminary experiment where a specimen was annealed in cupric oxide. The oxide was reduced, resulting in a mass of metallic copper. Samples of gas, which were being given off by specimens, were then taken and analyzed.

The following gas was taken from a sample being annealed at 870°.

	Per Cent
Carbon dioxide	13.2
Hydrocarbons	0.0
Oxygen	8.8
Carbon monoxide	26.8
By difference, Nitrogen	51.2

A second sample was taken from one annealing at 980°.

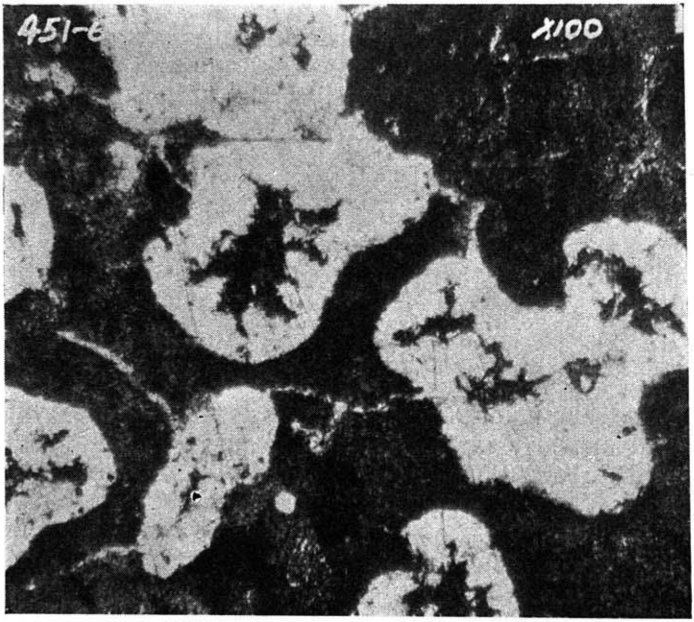

FIG. 10—MICROPHOTOGRAPH × 100

	Per Cent
Carbon dioxide	4.6
Hydrocarbons	0.0
Oxygen	3.4
Carbon monoxide	71.2
By difference, Nitrogen	20.2

The above analyses show that the carbon is removed from the casting as a gas, the composition of the gas depending upon the temperature and oxygen present.

General Summary and Conclusions

1. This research has resulted in the affirmation of some of the established laws in the annealing of malleable cast iron, namely:

   (a) That the packing material does not affect the interior structure.

   (b) Slow cooling is necessary to obtain good malleable.

(c) A low temperature anneal gives a much better grade of product than the high-temperature malleable.

2. The conditions influencing the rim structure have been investigated.

3. The result of too rapid cooling has been studied, and is shown to result in a steely structure.

4. The breakdown of the iron carbide has been studied, and though present results are not final all seem to show that cementite does not break down directly, but decomposes from the solid solution or austenitic condition. This breakdown may be compared to the electrolysis or decomposition of a salt. While it would be difficult to decompose a salt in the dry state it is a simple matter to cause decomposition when dissolved in water. The ionic theory calls for a dissociation into ions when such a salt is dissolved in water.

Cannot the case of the decomposition of iron carbide be compared to the decomposition or dissociation of a salt? The analogy is not perfect, but a comparison can be made.

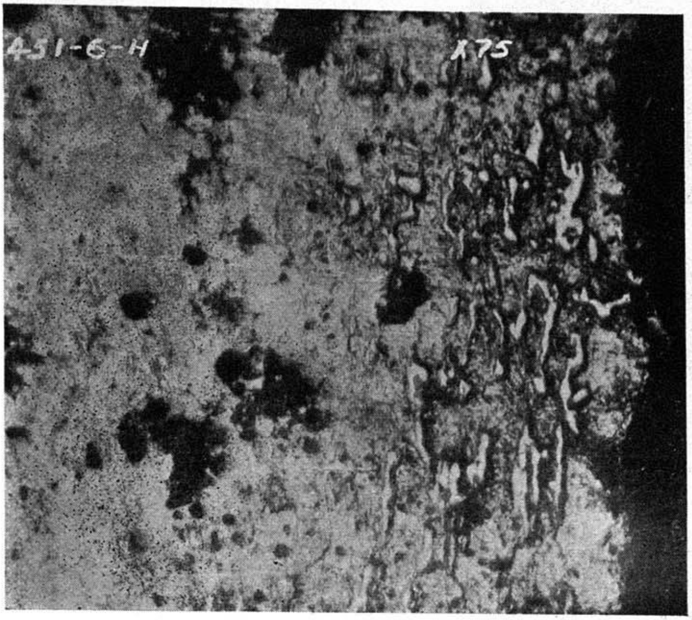

FIG. 11—MICROPHOTOGRAPH × 75

5. The decomposition of the iron carbide is complete above the Ar_1 point of the iron-carbon diagram. Whether iron carbide is unstable below the Ar_1 point has not been determined.

6. The decomposition of the iron carbide is not complete at the annealing temperature, but is complete in a range of temperature just above the Ar_1 point, as given in No. 5.

The author wishes to express his appreciation of the thorough experimental work done by Mr. Leasman, and of the valuable assistance given by the Northern Chemical Engineering Laboratories in the preparation of this paper.

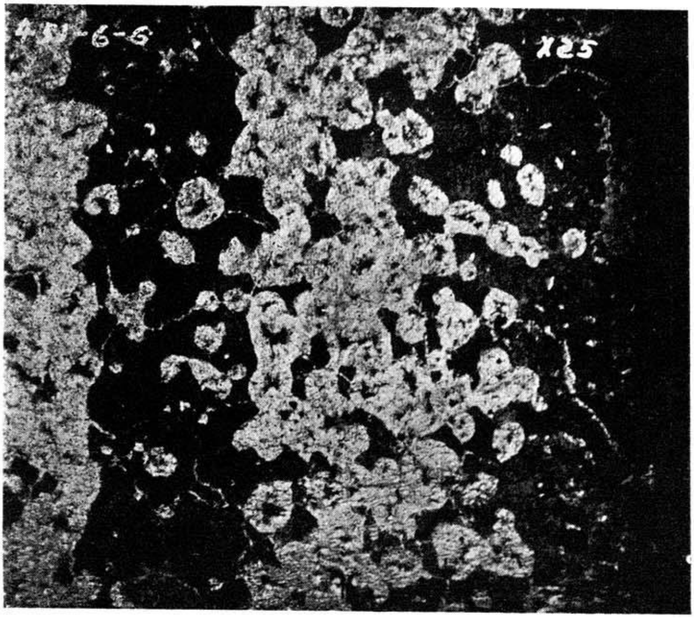

FIG. 12—MICROPHOTOGRAPH × 25

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3/

A STUDY OF THE ANNEALING PROCESS FOR MALLEABLE CASTINGS.

By E. L. Leasman, Boscobel, Wis.

Introduction.

The present development of the malleable casting industry has reached enormous proportions, approximating a million tons per annum. The technique of the industry, however, has advanced but little.

The first record we have is by Reaumur, in 1722. Without doubt, however, the malleableizing process was practiced much earlier, the secret being handed down from father to son.

Seth Boyden, of Newark, N. J., was the pioneer manufacturer in this country. Although he did not discover the underlying principles involved, yet his recorded experiments are the first we have, and he deserves special credit inasmuch as they were made at a time when scientific experimentation on industrial problems was frowned upon.

Malleable cast iron occupies a position between ordinary cast iron and cast steel. It has a higher tensile strength than cast iron, but not as high as that of cast steel, while its resilience is superior to either.

The method of producing malleable castings is fairly uniform throughout the country. The white iron castings are packed in rolling mill scale in rectangular iron containers. These containers, either three or four high, are carefully luted up to exclude currents of air, placed in the ovens, and heated up to the desired temperature, keeping them at the high point at least sixty hours. The total time of the annealing process is a week from one time of "lighting-up" to the next time.

The Metallography of White Cast Iron.

The white cast iron (hard casting) used in the production of malleable castings must have the proper composition for the work at issue, and must be properly melted. The accompanying three illustrations give the characteristic microstructures.

Fig. 1 shows a typical white cast iron structure. The white areas represent the iron carbide, or cementite, which was not attacked by the etching reagent, picric acid. The dark areas are pearlite and are composed of plates of cementite and ferrite. The general structure of Figs. 2 and 3 is the same, but there being more white areas in Fig. 2 shows that a larger percentage is present.

Fig. 1 was taken from a sample which contained steel scrap in the charge. It shows a different structure than that of the other two samples; the areas of pearlite being round in form. Also, the white areas are not as prominent, showing that there was not as much carbon present. This is to be expected, as steel scrap is generally added to the iron melt to cut down the percentage of carbon in the resulting white iron casting.

The analysis of the hard castings would run about as follows:

Total carbon (all combined)	2.75 to 3.25
Silicon	0.50 to 1.00
Sulphur	below 0.08
Phosphorus	below 0.225
Manganese	0.15 to 0.40

Cast iron is a complex alloy of iron with carbon and the other elements above listed. The state of the carbon is of the most importance and the other elements are secondary and influence the state of the carbon. Carbon is associated with iron in three different states, namely: as a definite carbide known as cementite, with the formula Fe_3C; as free carbon or graphite; and as a solid solution of carbon or combined carbon (carbide) in iron.

Of the secondary elements, silicon exerts the greatest influence on the state of the carbon, and tends to form graphitic carbon. Sulphur and manganese tend to form combined carbon. In the casting of white iron, the silicon content is so controlled that its influence during the cooling of the casting will not be great enough to precipitate out the carbon as free graphite, but allow it to remain in the combined form as iron carbide.

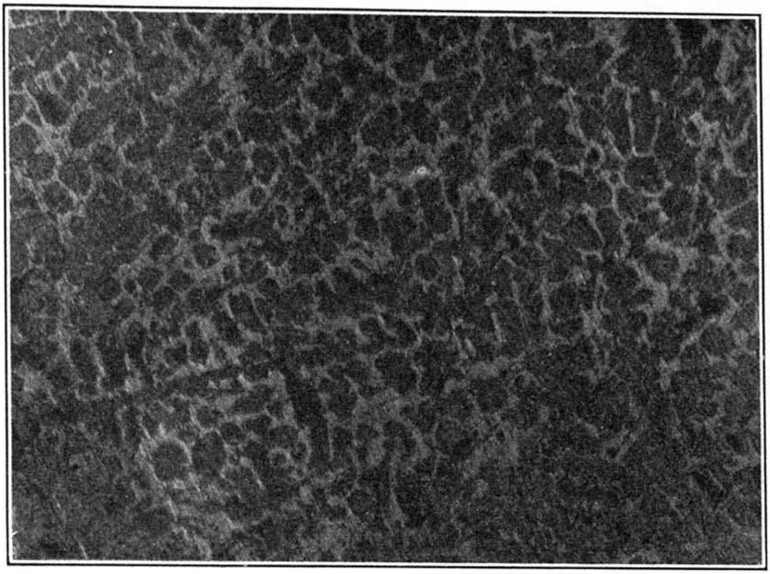

FIG. 1.

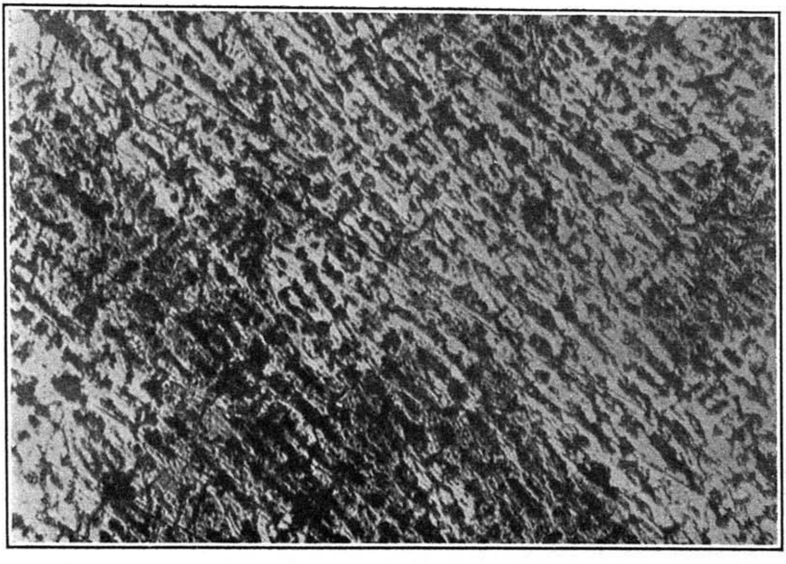

FIG. 2.

EFFECT OF HEAT TREATMENT.

When white iron is heated sufficiently, the cementite, both the excess and that present in the eutectoid, is broken down into its constituents of iron and carbon, according to the reaction,

$$Fe_3C=3Fe+C$$

This change may result from a high heat for a short period of time, or from a lower heat for a longer period of time.

The temperature and time necessary to effect this change depends upon the composition of the white iron. The three elements which will determine these effects are: silicon, manganese and sulphur. The silicon will tend to lower the temperature since this element prevents the formation of combined carbon. By increasing the manganese content, the temperature must be raised since it tends to keep the carbon in the combined form. Sulphur also has the tendency to exert the same influence.

Not only must the temperature be high enough and the time long enough to break down the cementite in the white iron, but the material must be cooled slowly or a steely structure will result.

When cast iron is properly malleableized, the carbide is entirely broken down into its elements, and the carbon is precipitated out as globules of amorphous carbon, surrounded by pure ferrite. Carbon in this form is known as temper carbon and does not occur in flakes as in gray cast iron.

Fig. 4 shows the interior structure of malleable cast iron. The white field is ferrite and the dark spots are particles of temper carbon.

THE PURPOSE OF THIS STUDY.

As the data available in connection with the annealing process for making malleable castings are so meagre, the investigation to be detailed in what follows was undertaken. Four lines of study were mapped out, as follows:

1. The effect of different packing materials.
2. The effects of different annealing temperatures.
3. The effects of different times of annealing.
4. The effect of different times of cooling.

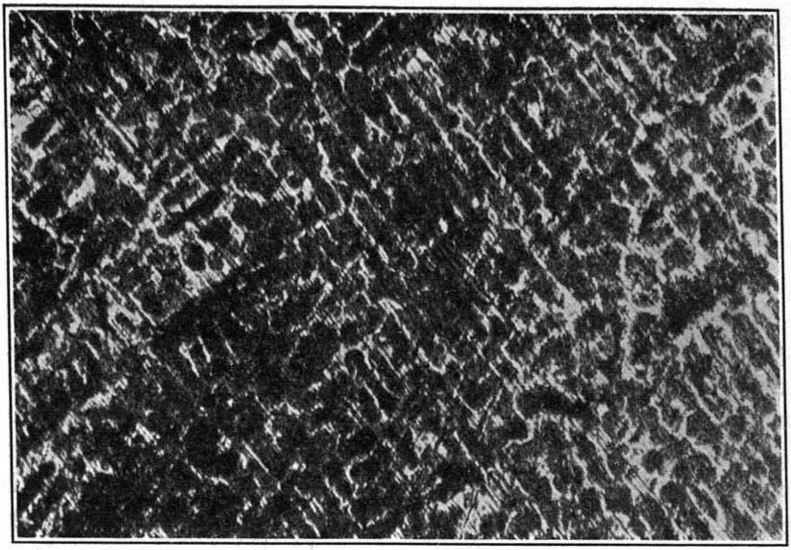

FIG. 3.

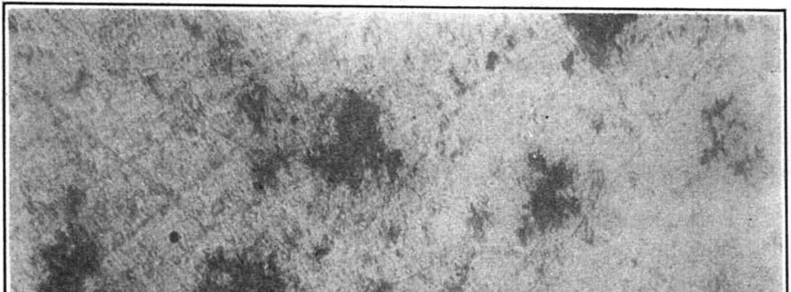

FIG. 4.

There may be said to be five variables entering into the annealing process, namely:

1. Packing materials used.
2. Time of bringing up the oven to maximum temperature desired.
3. Temperature of annealing.
4. Time of annealing.
5. Time of cooling.

Since the second variable is dependent entirely upon the type of oven used, and since it is well known that the rate of heating up the oven does not affect the resulting castings, this variable will not enter into the investigation at all. By arranging matters so that three variables out of the four are kept constant for each series of experiments, the other variable could be studied. The result should be of value as indicating the best conditions for proper annealing, as well as giving an abundance of data on the influence of the several variables.

MATERIALS USED.

The white iron used for these tests was in the shape of test bars $\frac{3}{4}$ x $\frac{3}{4}$ x 10 ins., and were courteously furnished by the Beaver Dam Malleable Iron Company. Mr. W. G. Grimer, their chemist, furnished the following analysis with the bars:

Total (combined) carbon	2.60 to 2.70
Silicon	0.65 to 0.70
Sulphur	0.55 to 0.60
Phosphorus	0.140
Manganese	0.27

The packing material consisted of the usual rolling mill scale and a variety of other materials, as given in the tests themselves.

The containers for holding the specimens (broken from the test bars) were made of 1½ in. pipe, cut to length to take specimens about 2 ins. long. These containers were luted up with fire clay, except where caps and nipples were used. The latter are noted in the experiments as "Special Boxes."

The two muffles used were of the electric type. They were built by the author in the Chemical Engineering Laboratory of the University of Wisconsin, and consisted of muffles heated electrically by resistance wires.

The pyrometers were couples supplied by the laboratory and standardized against regular platinum—Pt. Rhodium couples.

One of the electric muffles was controlled by means of a lamp bank in series with the furnace, and was supplied with current from a 110-volt alternation current circuit. The other furnace was on a 220-volt alternating current circuit, and the pressure was regulated by means of a low voltage transformer. The current was regulated by means of a lamp bank in series with the primary coil of the transformer.

THE EFFECT OF VARIOUS PACKING MATERIALS.

Experiment No. 1.

No. 1. Packed in lime. Fairly heavy scale on specimen; packing adherent but easily removed.

No. 2. Packed in sand. Fairly heavy scale on specimen, with sand adherent and colored red.

No. 3. Packed in alundum. Specimen surrounded with a hard shell, which was easily removed, and left the specimen clean and colored red.

No. 4. Packed in rolling mill scale. Fairly heavy, tenacious scale; packing adherent.

No. 5. Packed in resister carbon. Packing not adherent to specimen, which had a blue and red color.

No. 6. Packed in manganese dioxide. Specimen and container heavily attacked; specimen covered with a shell about $\frac{1}{16}$ in. thick, which was easily removed and left the specimen clean and blue in color.

No. 7. Packed in neat cement. Packing disintegrated and not adherent.

No. 8. No packing. Heavy, tenacious scale formed.

Experiment No. 2.

No. 9. Packed in coarse fire clay. Fairly heavy scale; packing adherent.

No. 10. Packed in fine rolling mill scale. Heavy scale.

No. 11. Packed in pure iron oxide. Fairly heavy scale; packing adherent and brown in color.

No. 12. Packed in fine graphite. Specimen clean; packing hard.

No. 13. Packed in alumina. Fairly heavy scale; packing adherent.

No. 14. Packed in chromite. Heavy scale; packing adherent.

No. 15. Packed in brass turnings. Packing fused and adherent.

No. 16. No packing. Specimen at end of furnace. Coated with heavy black scale.

Experiment No. 3.

No. 16. Packed in Portland cement. Fairly heavy scale; packing tenaciously adherent.

No. 17. Packed in bauxite. Heavy scale easily removed; packing adherent.

No. 18. Packed in hydrated magnesia. Fairly heavy scale; packing somewhat adherent.

No. 19. Packed in fine fire clay. Specimen clean; packing hard and pinkish in color.

No. 20. Packed in ordinary iron oxide. Heavy scale; packing adherent and lumpy.

No. 21. Packed in carborundum. Thin scale; packing adherent.

No. 22. No packing. Standing in center of furnace. Heavy scale formed.

Experiment No. 1. Heat Treatment Data.

Hours.........	3	17	20	26	29	40	52	55	65	76	90	93	98	104
Temperature...	1615	1630	1610	1650	1620	1650	1650	1540	1490	1330	1310	1250	900	520

Annealing temperature of 1660° to 1650° F. maintained for 50 hours, and time of cooling also 50 hours, 20 of which to 1390°, 18 to 1250° F. and 12 hours to 500° F.

MICROSCOPIC EXAMINATION.

No. 1. Packed in lime. Edge: temper carbon and ferrite. Center: temper carbon and ferrite.

No. 2. Packed in sand. Edge: temper carbon and ferrite. Center: temper carbon and ferrite.

No. 3. Packed in alundum. Edge: thin layer of ferrite; high carbon steel. Center: temper carbon and pearlite.

No. 4. Packed in rolling mill scale. Edge: ferrite and pearlite. Center: temper carbon and ferrite.

No. 5. Packed in resister carbon. Edge: ferrite and pearlite. Center: temper carbon; ferrite and pearlite.

No. 6. Packed in manganese dioxide. Edge: heavy layer of pure ferrite. Center: temper carbon and ferrite.

No. 7. Packed in neat cement. Edge: pure ferrite. Center: temper carbon and ferrite.

No. 8. No packing. Edge: temper carbon and ferrite. Center: temper carbon and ferrite.

Experiment No. 2. Heat Treatment Data.

Hours..........	4	10	15	30	50	60	68	71	81	86	93	108
Temperature....	1200	1640	1650	1650	1650	1650	1400	1340	1290	1100	900	520

Annealing temperature of 1650° F. maintained for 50 hours, and time of cooling also 50 hours: 9 hours to 1390° F., 13 hours to 1250° F. and 28 hours to 500° F.

MICROSCOPIC EXAMINATION.

No. 9. Packed in coarse fire clay. Edge: ferrite and pearlite. Center: Low carbon steel and temper carbon.

No. 10. Packed in rolling mill scale. Edge: ferrite and high carbon steel. Center: mild steel and temper carbon.

No. 11. Packed in pure iron oxide. Edge: ferrite and high carbon steel. Center: medium carbon steel and temper carbon.

No. 12. Packed in fine graphite. Edge: ferrite and high carbon steel. Center: Medium carbon steel and temper carbon.

No. 13. Packed in alumina. Edge: ferrite. Center: medium carbon steel and temper carbon.

No. 14. Packed in chromite. Edge: ferrite and pearlite. Center: Pearlite and temper carbon.

No. 15. Packed in brass turnings. Edge: yellow metal and pearlite. Center: pearlite and temper carbon.

Experiment No. 3. Heat Treatment Data.

Hours	5	9	10	20	30	40	50	60	60	70	84	98	109
Temperature	1330	1600	1680	1660	1670	1670	1670	1670	1450	1290	1100	900	540

Annealing temperature of 1650° F. maintained for 50 hours. Time of cooling: 5 hours to 1390° F., 10 hours to 1250° F., 35 hours to 500° F.; 50 hours in all.

MICROSCOPIC EXAMINATION.

No. 16. Packed in Portland cement. Edge: ferrite and pearlite. Center: pearlite and temper carbon.

No. 17. Packed in bauxite. Edge: ferrite and pearlite. Center: pearlite and temper carbon.

No. 18. Packed in hydrated magnesia. Edge: ferrite and pearlite. Center: pearlite and temper carbon.

No. 19. Packed in fine fire clay. Edge: ferrite and pearlite. Center: pearlite and temper carbon.

No. 20. Packed in iron oxide. Edge: ferrite and pearlite. Center: pearlite and temper carbon.

No. 21. Packed in carborundum. Edge: ferrite and pearlite. Center: pearlite and temper carbon.

No. 22. No packing used. Edge: ferrite and pearlite. Center: ferrite and temper carbon.

The results obtained by the use of various packing materials warrants the conclusion that they have no important effect upon the interior structure of malleable iron. However, it is noticeable that those packings which are not stable at the annealing temperature used have seemingly been the most active in causing a removal of the carbon from and near the surface of the specimen.

The surface or skin effect is dependent upon the nature of the packing used and also upon the method of packing; that is, whether the materials are loosely packed and allow free access of the oxygen in the air. Where an oxidizing packing is used, or where a specimen is loosely packed, the carbon was entirely removed from the outside portion of the specimen.

Where a packing was used which would pack closely about the specimen, such as fine fire clay, the decarbonization took place only to a limited extent. In this case the carbon remained as a pearlitic structure of varying thickness. Experiments were run with carbon in various forms (see also Experiments No. 16, 17 and 18) as the packing materials, and a pearlitic structure generally obtained as a skin effect.

These experiments resulted in the following conclusions: The presence of oxygen is necessary for the decarbonization of the surface, and that this oxygen is supplied by the air and finds its way to the specimen owing to the looseness of the packing material.

These experiments also show that a rapid rate of cooling causes the formation of steel as the interior structure of the specimen.

THE EFFECT OF DIFFERENT TEMPERATURES OF ANNEALING.

Experiment No. 4.

No. 23. Packed in resister carbon. Fairly heavy scale; packing burned to ash.

No. 24. Packed in iron oxide. Thin scale; packing not adherent.

No. 25. Packed in sand containing 10 per cent resister carbon by volume. Sand tenaciously adherent; fairly heavy scale hard to remove.

No. 27. Packed in rolling mill scale. Fairly heavy scale; packing caked hard but not adherent.

No. 28. Packed in rolling mill scale. This specimen had previously been heated for several hours at 1600° F.

No. 29. No packing. Fairly heavy scale.

Experiment No. 5.

No. 30. Packed in resister carbon. Thin scale; packing brown in color, and not tenaciously adherent.

No. 31. Packed in iron oxide. Heavy scale; packing blue in color and tenaciously adherent.

No. 32. Packed in iron oxide containing 10 per cent of resister carbon by volume. Fairly heavy scale; packing blue in color and tenaciously adherent.

No. 33. Packed in fine fire clay. Thin scale; packing adherent and yellowish in color.

No. 34. Packed in rolling mill scale. Fairly heavy scale; packing adherent; specimen red in color.

No. 35. Packed in graphite. Previous heated specimen.

No. 36. Gray iron packed in resister carbon. Fairly heavy scale; packing adherent.

No. 37. No packing. Thin scale; specimen blue in color.

Experiment No. 6.

No. 38. Packed in resister carbon. Packing burned at ash at ends of specimen, where a fairly heavy scale was formed. Specimen so hard that saw would only touch the outside.

No. 39. Packed in iron oxide. Packing slightly adherent. Specimen too hard to saw.

No. 40. Packed in iron oxide containing 25 per cent of graphite by volume. Thin scale; packing not adherent. Specimen too hard to saw.

No. 41. Packed in rolling mill scale with 10 per cent of graphite by volume. Thin scale; packing somewhat adherent. Specimen too hard to saw.

No. 42. Packed in rolling mill scale. Thin scale. Specimen soft enough to saw in two.

No. 43. Packed in sand containing 25 per cent of resister carbon by volume. Thin scale; packing adherent. Specimen too hard to saw.

No. 44. No packing. Thin scale. Specimen too hard to saw.

No. 45. Packed in rolling mill scale. Fairly heavy scale, tenaciously adherent. Specimen too hard to saw.

Experiment No. 7.

No. 38a. Packed in resister carbon. Packing burned to ash at ends and slightly adherent. Specimen too hard to saw. This specimen was at end of furnace.

No. 39a. Packed in iron oxide. Thin scale; packing slightly adherent. Specimen too hard to saw. This specimen was at end of the furnace.

No. 41a. Packed in scale containing 10 per cent of graphite. Fairly heavy scale; packing adherent. Specimen very hard to saw in two. This specimen at center of furnace.

No. 43a. Packed in sand containing 25 per cent of resister carbon. Fairly heavy scale with packing adherent. Specimen very hard to saw. This specimen at center of furnace.

No. 44a. No packing. Thin scale. Specimen very hard to saw. This specimen at center of furnace.

No. 45a. Packed in rolling mill scale. Thin scale with adherent packing. Specimen hard to saw. This specimen at end of furnace.

Experiment No. 8.

No. 46. Packed in resister carbon. Packing burned to ash at ends where it was adherent to specimen. Too hard to saw.

No. 47. Packed in iron oxide. Very thin scale with packing not adherent. Too hard to saw.

No. 48. Packed in sand containing 25 per cent resister carbon by volume. Thin scale with packing somewhat adherent. Too hard to saw.

No. 49. Packed in rolling mill scale. Very thin scale with packing slightly adherent. Too hard to saw.

No. 50. Packed in rolling mill scale. Thin scale with packing somewhat adherent. This specimen had previous treatment for a few hours. Specimen hard to saw.

No. 51. Packed in scale containing 25 per cent of resister carbon by volume. Thin scale with packing somewhat adherent. Too hard to saw.

No. 52. Packed in chromite. Thin scale with packing not adherent. Too hard to saw.

No. 53. No packing. Thin scale. Too hard to saw in two; saw went in about $\frac{1}{8}$ in.

Experiment No. 9.

No. 54. Packed in graphite in special box. No scale with packing not adherent.

No. 55. Packed in fine fire clay in special box. No scale with packing dark in color and not adherent.

No. 56. Packed in graphite. Thin scale with packing burned at ends.

No. 57. Packed in rolling mill scale. Thin scale with packing adherent and caked.

No. 58. Packed in fine fire clay. Very thin scale slightly adherent.

Experiment No. 10.

No. 59. Packed in scale in special box. No scale with packing not adherent. Too hard to saw.

No. 60. Packed in rolling mill scale. Fairly heavy scale with packing adherent. Very hard to saw in two.

No. 61. Packed in graphite in special box. No scale with packing not adherent. Hard to saw in two.

No. 62. Packed in graphite. No scale with packing not adherent. Not easy to saw.

No. 63. Packed in fine fire clay. Thin scale with packing tenaciously adherent.

No. 64. Packed in fine fire clay containing 10 per cent of graphite by volume. Thin scale with packing tenaciously adherent. Too hard to saw. Specimen at end of furnace.

No. 65. No packing. Thin scale. Too hard to saw. Specimen at end of furnace.

Experiment No. 4. Heat Treatment Data.

Hours	2	5	15	27	38	49	54	70	87	92	99
Temperature	1300	1500	1540	1480	1510	1520	1510	1120	890	740	510

Annealing temperature of 1500° F. maintained for 50 hours. Time of cooling, also 50 hours: 4 hours to 1390° F., 5 hours to 1250° F. and 41 hours to 500° F.

MICROSCOPIC EXAMINATION.

On account of specimens being too hard to saw, no sections were made for Nos. 23, 24, 25, 26, 27 and 29, of this experiment.

No. 28. Packed in scale. Previously treated. Edge: ferrite, temper carbon and pearlite. Center: temper carbon and pearlite.

Experiment No. 5. Heat Treatment Data.

Hours	5	6	15	21	28	48	55	67	79	92	105
Temperature	1150	1390	1440	1360	1400	1400	1380	1070	880	700	540

Annealing temperature of 1400° F. maintained for 50 hours. Time of cooling, also 50 hours: 1 hour to 1390° F., 4 hours to 1250° F. and 45 hours to 500° F.

MICROSCOPIC EXAMINATION.

No. 30. Packed in resister carbon. Edge: ferrite and pearlite. Center: temper carbon and ferrite.

Nos. 31 and 32. Packed in iron oxide and oxide with carbon. Edge: ferrite. Center: ferrite and temper carbon.

No. 33. Packed in fine fire clay. Edge: ferrite. Center: ferrite, temper carbon and pearlite.

No. 34. Packed in scale. Edge: ferrite. Center: ferrite, pearlite and cementite.

No. 35. Packed in graphite. Previously treated. Edge: ferrite. Center: ferrite; cementite and temper carbon.

No. 36. Gray iron. No change in structure.

No. 37. No packing. Edge: ferrite. Center: ferrite; temper carbon and cementite.

Experiment No. 6. Heat Treatment Data.

Hours	2	4	25	40	52	61	72	86	94	103
Temperature	820	1320	1320	1320	1300	1090	920	680	610	520

Annealing temperature of 1300° F. maintained for 50 hours. Time of cooling, also 50 hours: 1 hour to 1250° F. and 49 hours to 500° F.

MICROSCOPIC EXAMINATION.

No. 42. Packed in scale. Previously treated. Edge: ferrite and pearlite. Center: only slightly changed.

All of the rest of the specimens were too hard to saw.

Experiment No. 7. Heat Treatment Data.

Hours................	2	2	14	35	51	59	71	85	86	95	100
Temperature..........	900	1350	1350	1380	1350	1200	1150	950	850	680	520

Annealing temperature of 1350° F. maintained for 50 hours. Time of cooling, also 50 hours: 7 hours to 1250° F. and 43 hours to 500° F.

MICROSCOPICAL EXAMINATION.

All of the specimens obtained in this experiment were either too hard to cut or, after being examined, showed very little change in structure from the white iron.

Experiment No. 8. Heat Treatment Data.

Hours............	3	10	31	46	57	66	80	83	100	116
Temperature......	1050	1250	1240	1180	1230	1080	920	1200	1250	1080

Annealing temperature of 1000° to 1200° F. maintained for 120 hours. Time of cooling to 500° F., 36 hours.

MICROSCOPICAL EXAMINATION.

No. 50. Packed in scale. Previously treated. Edge: ferrite and temper carbon. Center: not entirely changed.

All of the rest of the specimens were too hard to saw.

Experiment No. 9. Heat Treatment Data.

Hours..............	1	3	18	26	32	50	68	80	90	100	103
Temperature........	700	1510	1520	1550	1530	1530	1330	1120	1050	880	520

Annealing temperature of 1500° to 1550° F. maintained for 50 hours. Time of cooling, also 50 hours: 10 hours to 1390° F., 8 hours to 1250° F. and 32 hours to 500° F.

MICROSCOPICAL EXAMINATION.

No. 54. Packed in graphite. Special box. Edge: pearlite. Center: Not completely changed.

No. 55. Packed in fine fire clay. Special box. Edge: ferrite and pearlite. Center: about half changed.

No. 56. Packed in graphite. Edge: ferrite and pearlite. Center: fairly well changed.

No. 57. Packed in scale. Edge: ferrite and pearlite. Center: fairly well changed.

No. 58. Packed in fine fire clay. Edge: ferrite and pearlite. Center: ferrite; temper carbon and a little cementite.

Experiment No. 10. Heat Treatment Data.

Hours............	6	6	30	50	55	61	71	80	88	102	108
Temperature.......	1320	1460	1470	1470	1470	1330	1180	1100	1090	950	520

Annealing temperature of 1450° to 1475° F. maintained for 50 hours. Cooling time, 50 hours also: 6 hours to 1390° F., 6 hours to 1250° F. and 38 hours to 500° F.

MICROSCOPICAL EXAMINATION.

All of the specimens in this experiment were either too hard to saw or showed that the original white iron structure was very slightly changed.

From the result obtained in this series of experiments the conclusion is reached that for white iron of the analysis furnished, and under the experimental conditions obtaining, a temperature of up to 1400° F. is necessary to cause a complete breaking down of the cementite into ferrite and temper carbon.

Experiment No. 8 shows that the specimens heated for 120 hours at 1000° to 1200° F. were still unchanged; with the exception of specimen No. 50, which had previously been heated for a number of hours at 1600° F., and whose interior structure was still not completely changed.

The same general results hold true for Experiment No. 6, where the annealing temperature was 1300° F., and the period of heating was 50 hours.

The results of Experiment No. 5, where the annealing temperature was 1400° F., show that only those specimens at the center of the furnace were well changed, while those near the door (or colder) still had some cementite present.

The same general results hold true for Experiments No. 4 and No. 10, so that for the following experiments an annealing temperature of 1550 to 1650° F. will be used as the constant.

THE EFFECTS OF DIFFERENT PERIODS OF COOLING FROM THE ANNEALING TEMPERATURE TO 500° F.

Experiment No. 11.

No. 66. Packed in graphite. Packing burned to ash at ends, where a fairly heavy scale was formed.

No. 67. Packed in scale. Heavy scale; packing adherent and caked.

No. 68. Packed in fine fire clay. Fairly heavy and tenacious scale; packing adherent.

No. 69. Packed in scale containing 25 per cent of graphite by volume. Heavy scale; adherent packing.

No. 70. Packed in chromite. Very heavy scale; adherent packing.

No. 71. No packing. Heavy scale.

No. 72. Packed in fine fire clay containing 25 per cent of graphite by volume. Heavy scale; adherent packing.

Experiment No. 12.

No. 73. Packed in scale. Fairly heavy and tenacious scale; adherent packing.

No. 74. Packed in scale containing 25 per cent of graphite, in special box. No scale; specimen clean.

No. 75. Packed in chromite. Fairly heavy scale; adherent packing.

No. 76. Packed in fine fire clay. Heavy scale; adherent packing.

No. 77. Packed in graphite. Packing burned and adherent; fairly heavy scale.

No. 78. Packed in iron oxide. Fairly heavy, tenacious scale; adherent packing.

No. 79. No packing. Heavy scale.

No. 80. Packed in sand containing 25 per cent of graphite by volume. Heavy, tenacious scale; packing adherent.

Experiment No. 13.

No. 81. Packed in scale in special box. Thin scale; packing not caked.

No. 82. Packed in graphite in special box. No scale.

No. 83. Packed in scale. Heavy and tenacious scale with packing adherent.

No. 84. Packed in graphite. Heavy scale; packing burned.

No. 85. Packed in a mixture of fire clay and neat cement. Packing disintegrated and not adherent.

No. 86. Packed in chromite. Heavy scale; adherent packing.

No. 87. No packing. Heavy scale.

Experiment No. 14.

No. 88. Packed in scale in special box. Thin scale; packing caked.

No. 89. Packed in scale. Heavy and tenacious scale; with packing adherent.

No. 90. Packed in fine fire clay. Heavy scale easy to remove; packing somewhat adherent.

No. 91. Packed in graphite. Heavy and tenacious scale; packing burned.

No. 92. No packing. Heavy scale.

Experiment No. 15.

No. 93. Packed in bone black in special box. No scale; packing not burned.

No. 94. Packed in scale in special box. No scale; packing caked.

No. 95. Packed in fine fire clay. Fairly heavy scale; adherent packing.

No. 96. Packed in scale. Fairly heavy and tenacious scale; adherent packing.

No. 97. No packing. Heavy and tenacious scale.

No. 98. Packed in chromite containing 25 per cent of bone black. Fairly heavy and tenacious scale; packing adherent.

Experiment No. 16.

No. 99. Packed in bone black in special box. No scale; packing somewhat burned at one end.

No. 100. Packed in fine fire clay in special box. No scale.

No. 101. Packed in fine fire clay. Heavy scale; packing adherent.

No. 102. Packed in scale. Heavy and tenacious scale; packing adherent.

No. 103. Packed in scale in special box. Specimen clean; packing gray in color.

No. 104. No packing. Heavy scale.

No. 105. Packed in iron oxide containing 25 per cent of bone black. Fairly heavy and tenacious scale.

Experiment No. 11. Heat Treatment Data.

Hours	1	2	6	19	23	31	49	52	63	71
Temperature	970	1460	1470	1660	1590	1620	1630	1610	1611	520

Annealing temperature of 1600° F. maintained for 39 hours. Cooling time, 14 hours from maximum to 500° F.

Note.—Furnace burned out, allowing a very rapid cooling to take place.

No. 66. Packed in graphite. Edge: ferrite and pearlite. Center: pure pearlite.

The rest of the specimens in this experiment showed in: ferrite and pearlite. Center: high carbon steel.

Experiment No. 12. Heat Treatment Data.

Hours	1	2	7	10	46	54	60	71	83	93	99	103
Temperature	1130	1480	1530	1490	1480	1470	1400	1400	1140	1100	980	520

Annealing temperature of 1450° to 1500° F. maintained for 50 hours. Cooling time of 50 hours also: 18 hours to 1390° F., 7 hours to 1250° F. and 25 hours to 500° F.

Nos. 76 and 77, which were in the center of the furnace, showed a fairly good structure. The rest of the specimens showed an edge of ferrite, with the interior not completely changed.

Experiment No. 13. Heat Treatment Data.

Hours	2	5	13	22	33	51	70	83	100	116	120
Temperature	1080	1530	1630	1550	1580	1540	1520	1410	1390	1250	720

Annealing temperature of 1550° to 1600° F. maintained for 50 hours. Cooling time, 70 hours: 45 hours to 1390° F., 15 hours to 1250° F. and 10 hours to 500° F.

All the specimens in this experiment showed a good structure, both edge and center.

Experiment No. 14. Heat Treatment Data.

Hours	1	5	14	19	27	39	63	78	90	92
Temperature	1110	1530	1590	1530	1560	1520	1520	1370	1230	700

Annealing temperature of 1550° F. maintained for 50 hours. Cooling time, 40 hours: 24 hours to 1390° F., 12 hours to 1250° F. and 4 hours to 500° F.

All of the specimens in this experiment showed the same general structure, as follows: Edge: ferrite and pearlite. Center: temper carbon, ferrite and pearlite.

Experiment No. 15. Heat Treatment Data.

Hours	2	12	32	40	57	80	91	102	108
Temperature	980	1520	1580	1530	1570	1480	1390	1250	520

Annealing temperature of 1550° F. maintained for 50 hours. Cooling time, 48 hours: 30 hours to 1390° F., 12 hours to 1250° F. and 6 hours to 500° F.

All of the specimens in this experiment showed: Edge: ferrite. Center: ferrite and temper carbon.

Experiment No. 16. Heat Treatment Data.

Hours	2	5	22	28	40	50	71	85	93
Temperature	1100	1550	1560	1530	1560	1550	1570	1390	520

Annealing temperature of 1550° F. maintained for 50 hours. Time of cooling, 40 hours: 30 hours to 1390° F., 1 hour to 1250° F. and 9 hours to 500° F.

No. 99. Packed in bone black in special box. Edge: almost pure carbide, and pearlite. Center: pearlite.

The rest of the specimens showed the same general structure as follows: Edge: ferrite and pearlite. Center: temper carbon; ferrite and pearlite.

It was early noticed that the rate of cooling had an important effect upon the malleableizing process. By referring to the first series of experiments, it will be seen that experiment No. 1 gave the best results. In this experiment, the time of cooling to 1400° F. and 1250° F. was much longer than for No. 2 and No. 3. In experiments No. 2 and No. 3, the interior structure was found to be composed of ferrite, temper carbon and pearlite, showing that rapid cooling tends to from a steely structure. This fact is also shown in experiment No 11 where the furnace failed and the charge cooled very rapidly; the resulting interior structure was like a high carbon steel.

Experiment No. 12 shows that a good malleable structure was obtained only for those specimens at the center of the furnace. Experiment No. 15 shows that a good structure was obtained for all specimens. In both of these experiments the total time of cooling was practically the same, but the time of cooling from the annealing temperature to 1250° F. was much longer for No. 15 than for No. 12. This fact tends to show that the rate of cooling should be slow down to about 1250° F., after which it may become rapid without endangering the malleable structure.

As the result of this series of experiments, the time of cooling will be taken as 48 hours, divided about as follows: 30 hours to 1390° F.; 10 to 12 hours from 1390° to 1250° F.; and 6 to 8 hours from 1250° to 500° F. The point 1250° F. was taken because it is about 25° below the A r_1 point on the Roozeboom diagram. This point is the critical temperature at which the solid solution of iron carbide breaks down into its constituents of ferrite and cementite, and is known as pearlite.

THE EFFECTS OF DIFFERENT PERIODS OF ANNEALING.

Experiment No. 17.

No. 106. Packed in bone black in special box.
No. 107. Packed in scale in special box.
No. 108. Packed in fine fire clay.
No. 109. Packed in scale.
No. 110. No packing.

Experiment No. 18.

No. 111. Packed in scale.
No. 112. Packed in fine fire clay.
No. 113. Packed in scale in special box.
No. 114. Packed in bone black containing $BaCO_3$ (special).
No. 115. No packing.
No. 116. Packed in bone black.

Experiment No. 19.

No. 117. Packed in scale.
No. 118. Packed in fine fire clay.
No. 119. Packed in bone black containing $BaCO_3$, in special box.
No. 120. Packed in bone black.
No. 121. Packed in cupric oxide. Oxide was all reduced to metallic copper.
No. 122. No packing.
No. 123a. Packed in a mixture of bone black, chromite and barium carbonate.

Experiment No. 20.

No. 123. Packed in bone black containing barium carbonate, in special box.

No. 124. Packed in fine fire clay, special.

No. 125. Packed in scale.

No. 126. Packed in fine fire clay.

No. 127 No packing.

Experiment No. 21.

No. 128. Packed in cupric oxide.

No. 129. Packed in fine fire clay.

No. 130. Packed in scale.

No. 131. No packing.

Experiment No. 22.

No. 132. Packed in fine fire clay.

No. 133. Packed in scale.

No. 134. No packing.

Experiment No. 23.

No. 135. Packed in scale.

No. 136. Packed in fine fire clay.

No. 137. Packed in cupric oxide in ordinary manner; the oxide was not reduced to metallic copper.

Experiment No. 17. Heat Treatment Data.

Hours	2	3	20	27	35	49	60	70	89	94
Temperature	1200	1470	1560	1520	1590	1470	1400	1390	1310	510

Annealing temperature of 1500° to 1600° F. maintained 43 hours. Time of cooling, 35 hours: 23 hours to 1390° F. and 12 hours to 1250° F.

No. 106. Packed in bone black in special box. Edge: very high carbon steel (good eutectoid). Center: temper carbon, ferrite and pearlite.

The rest of the specimens were as follows: Edge: ferrite. Center: temper carbon, ferrite and pearlite.

Experiment No. 18. Heat Treatment Data.

Hours	2	7	15	25	33	48	56	70	75
Temperature	1450	1600	1600	1540	1660	1410	1410	1350	510

Annealing temperature of 1550° to 1600° F. maintained 30 hours. Time of cooling to 1250° F., 30 hours.

No. 114. Packed in bone black and barium carbonate. Edge: cementite. Center: ferrite; temper carbon and a little carbide.

NOTE.—The rest of the specimen had an edge of ferrite and an interior of ferrite, temper carbon and a little carbide.

Experiment No. 19. Heat Treatment Data.

Hours	1	3	20	22	40	52	70	81
Temperature	1430	1600	1630	1520	1500	1420	1360	510

Annealing temperature of 1500° to 1600° F. maintained for 38 hours. Cooling time, 30 hours to 1390° F. and 3 hours to 1250° F.

All of the specimens in this experiment had a rim of either ferrite or a mixture of ferrite and pearlite; the interior structure was composed of temper carbon, ferrite and cementite.

Experiment No. 20. Heat Treatment Data.

Hours	3	5	17	29	33	53	65	70
Temperature	1330	1620	1620	1570	1410	1390	1250	500

Annealing temperature of 1600° F. maintained 18 hours. Cooling time, 30 hours to 1390° F. and 12 hours to 1250° F.

All of the specimens in this experiment showed the following structure: Edge: pearlite. Center: pearlite and cementite.

Experiment No. 21. Heat Treatment Data.

Hours	1	2	10	13	27	40	50	62	74	82
Temperature	820	1600	1650	1620	1620	1420	1420	1270	700	600

Annealing temperature of 1600° F. maintained for 24 hours. Cooling time, 30 hours to 1390° F. and 12 hours to 1250° F.

All specimens had the following structure: Edge: ferrite and pearlite. Center: ferrite, cementite and pearlite.

Experiment No. 22. Heat Treatment Data.

Hours	1	5	20	25	28	31	38	47	70	75	82
Temperature	1150	1530	1730	1210	1580	1610	1600	1420	1350	1250	510

Annealing temperature of 1600° F. maintained for 30 hours. Cooling time, 30 hours to 1390° F. and 10 hours to 1250° F.

All specimens had a good structure as follows: Edge: ferrite. Center: temper carbon and ferrite.

Experiment No. 23. Heat Treatment Data.

Hours	2	3	17	38	67	73
Temperature	1000	1600	1650	1500	1330	510

Annealing temperature of 1600° F. maintained for 30 hours. Cooling time, 26 hours to 1390° F. and 9 hours to 1250° F.

All the specimens had the following structure: Edge: thin layer of ferrite and pearlite. Center: temper carbon, ferrite and cementite.

This series of experiments shows that a malleable structure may be obtained in 36 hours, using a temperature of 1500° to 1650° F.; although 42 hours would be a safer period to use.

It is evident that a high temperature cuts down the time of heating as shown in experiment No. 22; and an experiment conducted outside of this series showed that it was possible to get a malleable structure in 18 hours when an annealing temperature of 1800° F. was used.

The conclusion reached is that a temperature of 1600° to 1650° F. is the best temperature to use, inasmuch as it is neither too low nor too high to endanger malleableization. Be it understood, however, that this conclusion related only to the annealing of small specimens in a small annealing furnace in which the temperature changes are altogether different than in a regular annealing oven of works practice. A temperature of 1800° F. would soon end the usefulness of the saggers and so increase the cost of production that competition with the long time low temperature process—in which a maximum of 1350° F. is kept for 60 hours or even less—would be out of question. Even the 1600° to 1650° F. temperature is safe only for cupola iron, and would ruin furnace iron if continued for the regular time.

AN EXPERIMENT SHOWING WHAT BECOMES OF THE CARBON AT THE SURFACE OF WHITE CAST IRON DURING THE PROCESS OF PRODUCING MALLEABLE IRON.

The question of the disappearance of the carbon, or the decarbonization of the rim (skin effect) of malleable iron, has been a much discussed one. It is held by some that the carbon migrates to the interior and remains in the casting, while others claim that the carbon migrates out and disappears entirely from the casting. It is obvious that if the carbon migrates out and leaves the iron at the temperature used for annealing, it must do so in the form of a carbonaceous gas. Hence, an analysis of the gases evolved by the iron during the malleableizing process, using no packing material, would report their exact composition and reveal the presence or absence of carbonaceous gases. From data of this kind, the method of decarbonization could be more definitely shown.

In this connection, the following preliminary experiment was performed. A piece of white iron was annealed in cupric oxide, the idea being to detect the presence of CO by noticing the degree of reduction of the oxide. The result of this experiment showed an extended and complete reduction of the oxide to metallic copper, but inasmuch as some reduction of the cupric oxide would occur anyhow, due to the higher heat of formation of the oxide of iron over that of copper, no definite conclusions could be drawn from the result of this experiment.

The final proof of the presence of a carbonaceous gas was therefore made by collecting the gas coming off from the specimen during the annealing period, and analyzing it according to the Hempel method.

Apparatus.—1. A piece of white iron 1 in. square and 6 ins. long, weighing 700 grams, used as the specimen.

2. A closed container to hold above, consisting of a 1½ in. x 5 in. nipple, with an iron cap for one end, and reduced to a ¼ in. pipe at the other.

3. A piece of ¼ in. pipe and connections for leading gas from container to sampling tubes.

4. Glass gas sampling tubes filled with water saturated with carbon dioxide.

5. Mercury burette for gas sampling.

6. Filter pump and connections for exhausting air from container and pipes.

Method.—The container and iron piping were first thoroughly cleaned to remove any dirt or grease, and the inside of the container was given a thin coat of fire clay. Next, the specimen was placed inside of the container, and after having been tightly screwed together, the outside of the container was given a very heavy coating of fire clay. The container was then placed in the furnace with the outlet pipe leading through a hole in the door; and the heat started. After the furnace had been heated to 1600° F. for several hours, suction was applied to the outlet pipe of the container and the air exhausted for several minutes. Samples No. 1 and No. 2 were then taken.

Sample No. 1 was collected in a glass sampling bottle over water saturated with carbon dioxide. The gas came over at the rate of about twenty bubbles per minute, with the sampling bottle lying flat and the departing water creating no suction. There was sufficient gas pressure to fill the bottle when the exit of the tube was raised higher than the entrance.

Sample No. 2 was collected over mercury shortly after No. 1 was taken.

Sample No. 3 was collected after the furnace had been up to 1600° F. for 6 hours, and up to 1800° F. for half an hour. The gas came over at a rapid rate and was under considerable pressure.

Sample No. 1. Collected over Water.

	Per cent.
Carbon dioxide	13.2
Hydrocarbons	0.0
Oxygen	8.8
Carbon monoxide	21.4
By difference, N	56.6

Sample No. 2. Collected over Mercury.

	Per cent.
Carbon dioxide	13.2
Hydrocarbons	0.0
Oxygen	8.8
Carbon monoxide	26.8
By difference, N	51.2

Sample No. 3. Collected over Water, Furnace at 1800° F.

	Per cent.
Carbon dioxide	4.6
Hydrocarbons	0.0
Oxygen	3.4
Carbon monoxide	71.2
By difference, N	20.2

Attention is called to the very high percentage of carbon monoxide and the corresponding low percentages of oxygen and carbon dioxide.

From the results obtained in this experiment, the proof of the carbon leaving the casting in the form of a carbonaceous gas is indicated.

Both Samples No. 1 and No. 2 show this fact in their analyses, and are checked. The analysis of Sample No. 3 shows the presence of a very high percentage of carbon monoxide and a corresponding decrease in the amounts of oxygen and carbon dioxide. This is probably due to the fact that No. 3 was collected at a much faster rate and when the furnace was considerably hotter than for No. 1 and No. 2.

GENERAL CONCLUSIONS.

1. The nature of the packing does not affect the interior structure of the iron; while the surface or "skin" effect may vary from pure ferrite to a pearlitic structure.

2. Packings like rolling mill scale and fire clay give as good results as any and have the added advantage of being cheap. Of these two packings, fire clay would be the better because it packs closer and more effectively prevents access of the oxygen of the air to the specimen or casting.

3. Castings may be malleableized without the use of any packing, but a good muffle furnace should be used to keep down the oxidation of the surface of the castings.

4. Air-tight containers or those as nearly so as possible should be used to keep down oxidation effects.

5. A temperature of 1550° to 1650° F. has proven to be best temperature to use for iron of the analysis previously given and under the conditions tested. This range insures a complete breaking down of the carbide.

6. A temperature below 1400° F. did not cause a complete breaking down of the carbide structure; and even prolonged heating would not have produced a malleable structure when as low as 1000° F.

7. At temperatures of 1400° to 1500° F. there is danger in not getting a good malleable structure in those castings farthest from the source of heat and the oven walls.

8. The above conclusions are understood to be based upon annealing small specimens in small ovens, in which temperature variations are more marked than in the large, almost uniformly heated ovens of commercial work.

9. The time of cooling from the annealing temperature to 1200° F. is the most important variable in the process.

10. A rapid rate of cooling, even when sufficient heat and time of annealing is used, forms a pearlitic or "steely" structure.

11. The time of cooling to 1250° F. should be about 42

hours. The cooling below this temperature may be rapid and not materially affect the malleable structure.

12. A period of from 36 to 42 hours gave the best results for this range of temperature.

13. An experiment not herein recorded showed that a good malleable structure could be obtained in 20 hours, using a temperature of annealing of 1800° F.

14. The period of annealing is entirely dependent upon the temperature of annealing and the type of furnace used.

LIST OF ILLUSTRATIONS.

ALL MICROGRAPHS ENLARGED 100 DIAMETERS, AND ETCHED WITH PICRIC ACID.

Fig. 5. Shows good interior structure of ferrite and temper carbon.
Fig. 6. Shows rim of pure ferrite.
Fig. 7. Shows an edge composed of ferrite and pearlite. (Steel.)
Fig. 8. Shows an interior structure of ferrite, temper carbon and pearlite.
Fig. 9. Shows an edge carbonized; bone black used as a packing material.
Fig. 10. Shows an interior structure of ferrite, temper carbon and traces of carbide.
Fig. 11. Shows an interior white iron structure which is partially broken down.
Fig. 12. Shows an edge of steel—pearlitic structure.
Fig. 13. Shows interior of ferrite, temper carbon and pearlite.
Fig. 14. Shows an edge of very high carbon steel.
Fig. 15. Shows peculiar structure of double steel layer.
Fig. 16. Shows a heavy layer of ferrite and then pearlite.

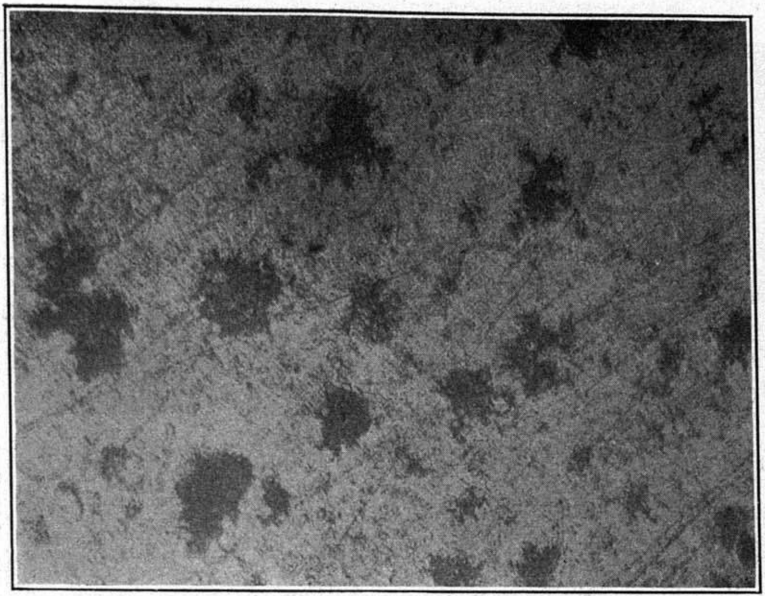

FIG. 5.

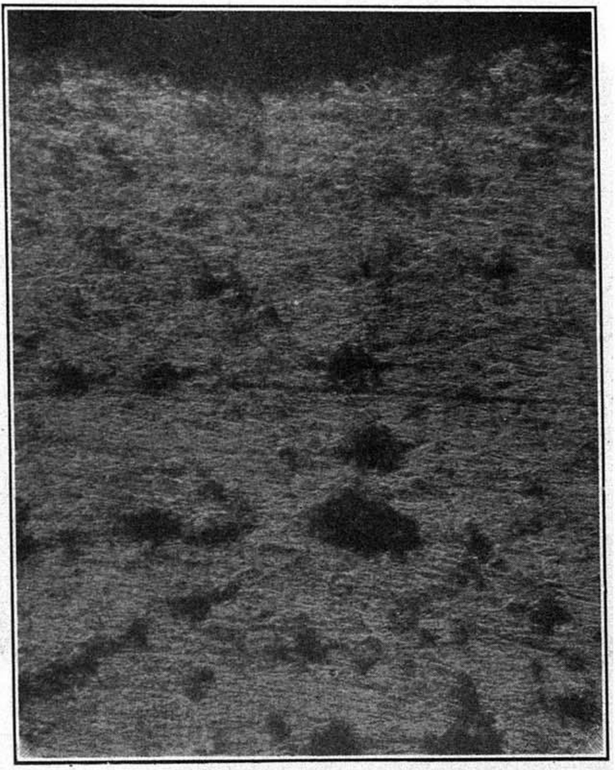

FIG. 6.

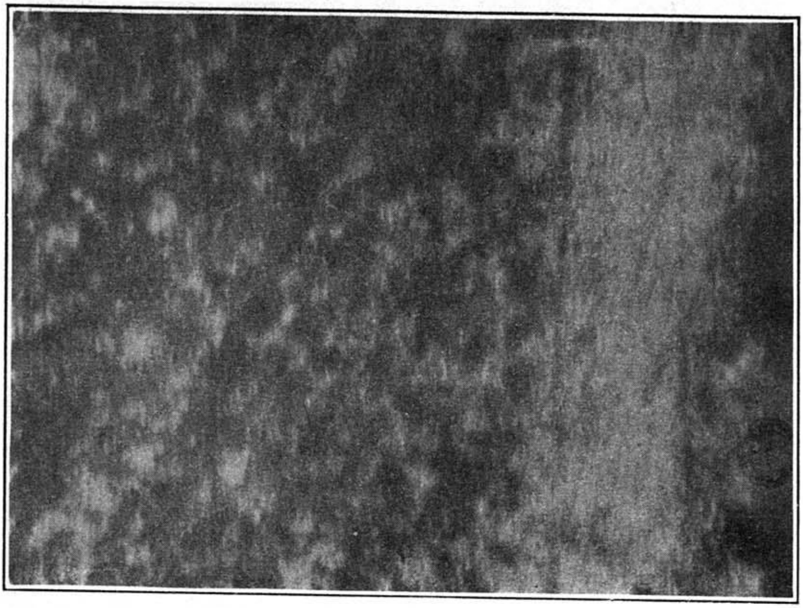

FIG. 7.

FIG. 8.

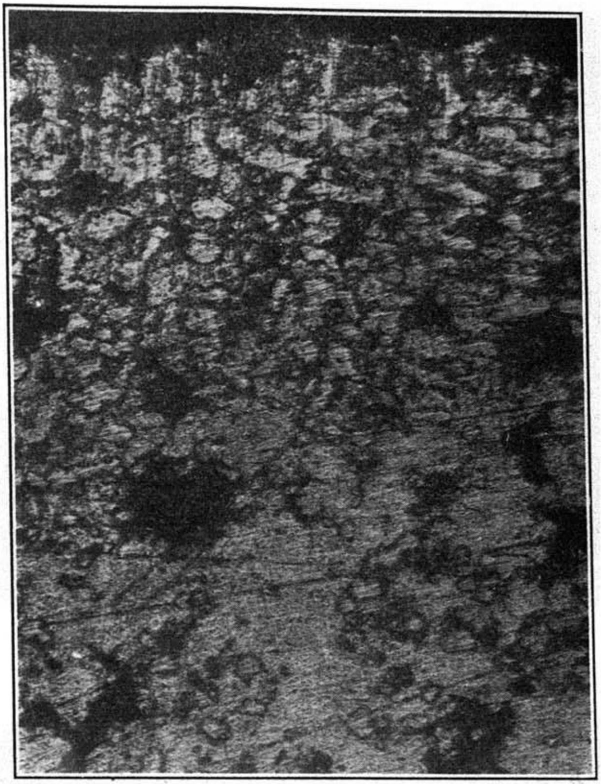

FIG. 9.

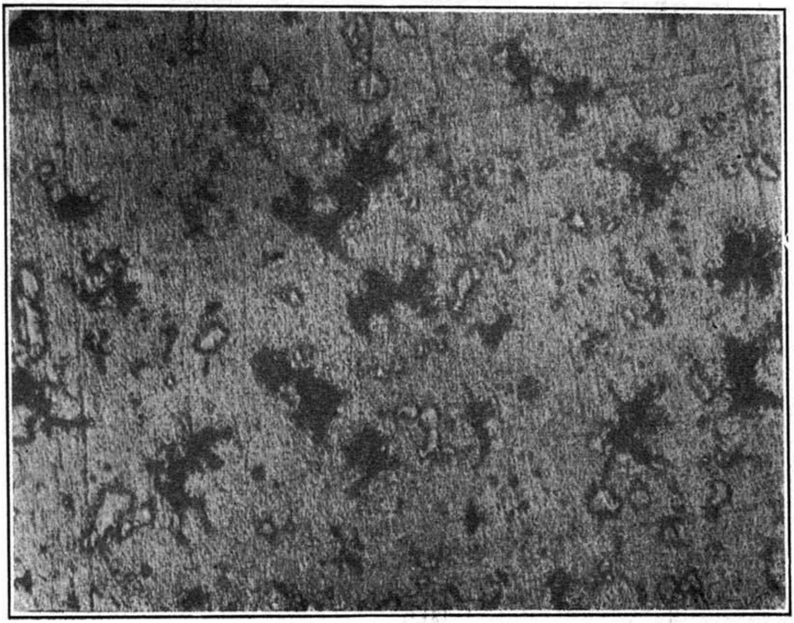

FIG. 10.

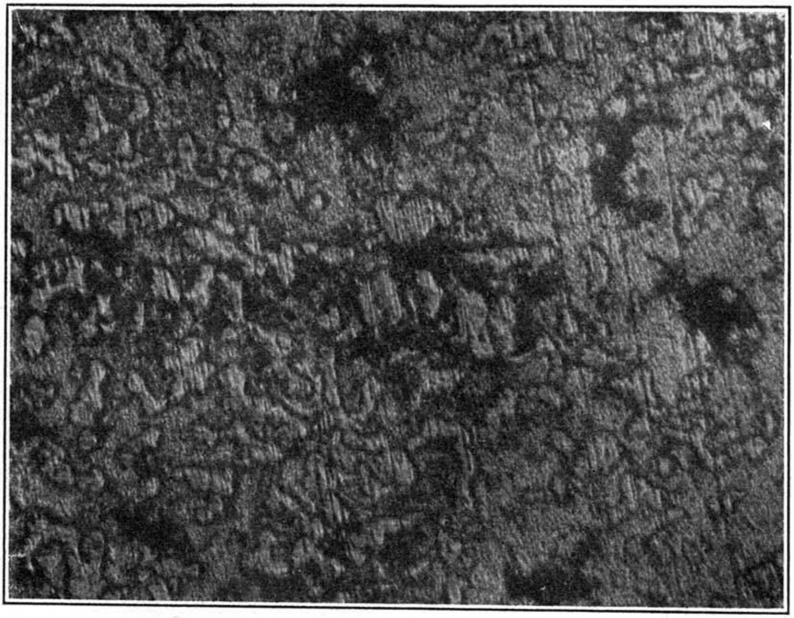

FIG. 11.

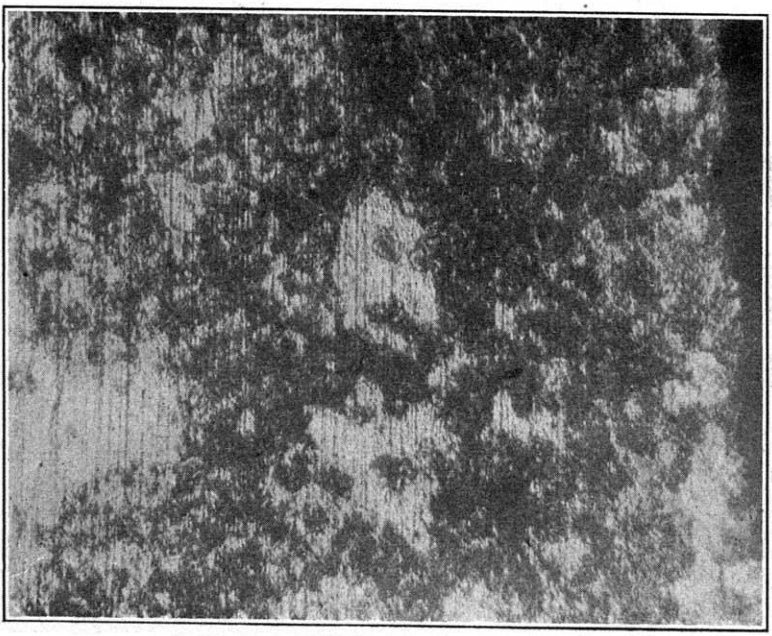

FIG. 12.

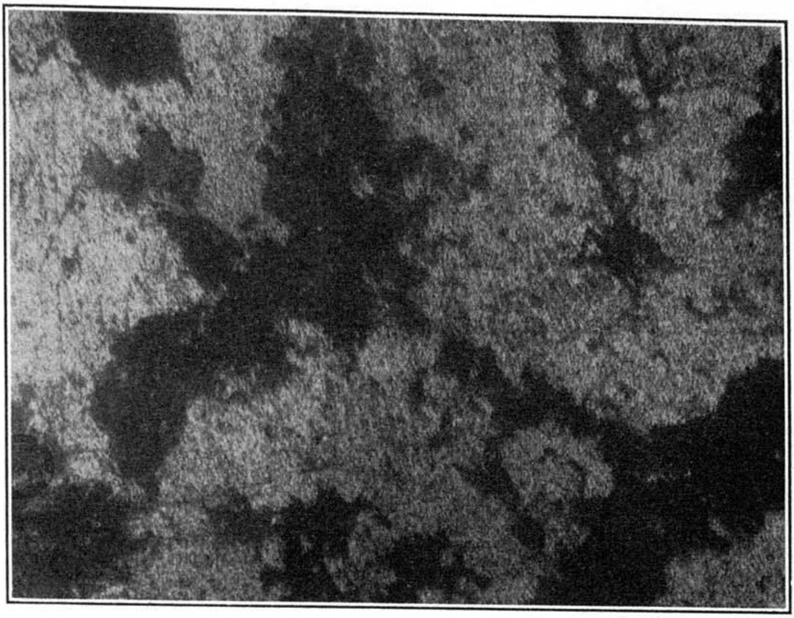

FIG. 13.

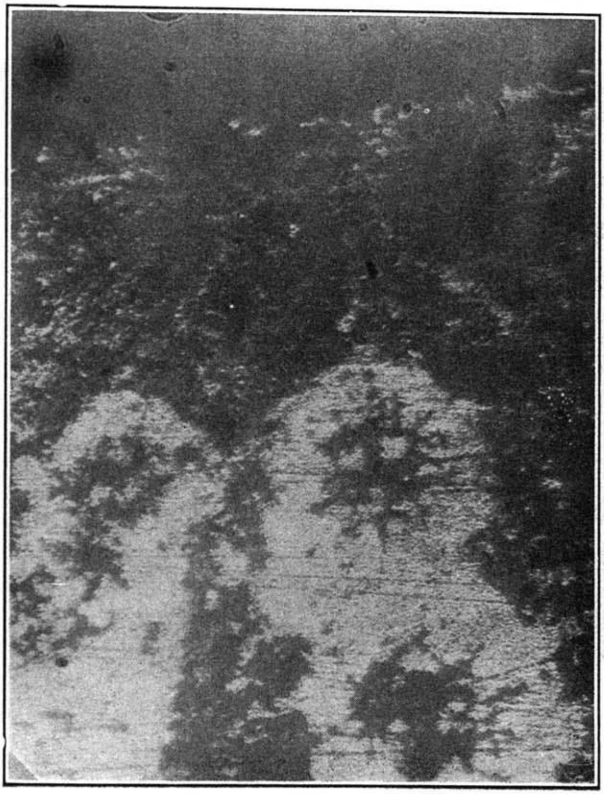

FIG. 14.

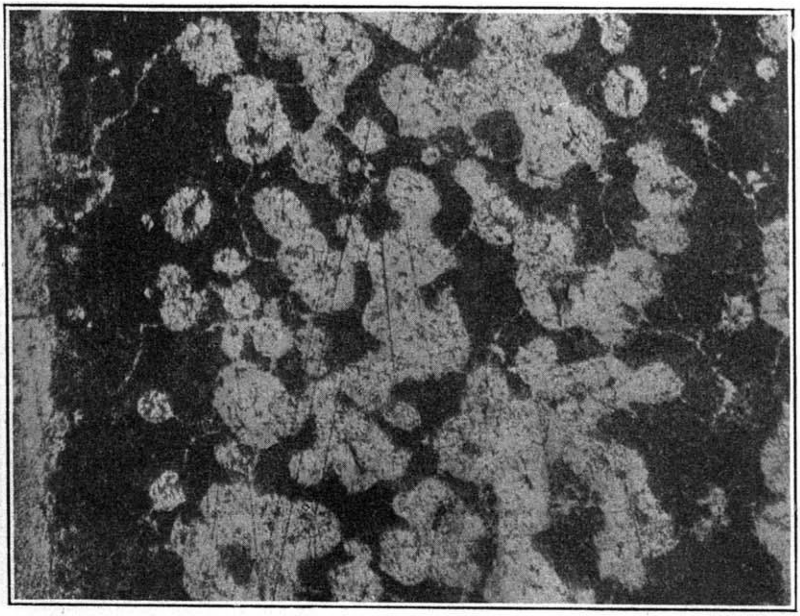

FIG. 15.

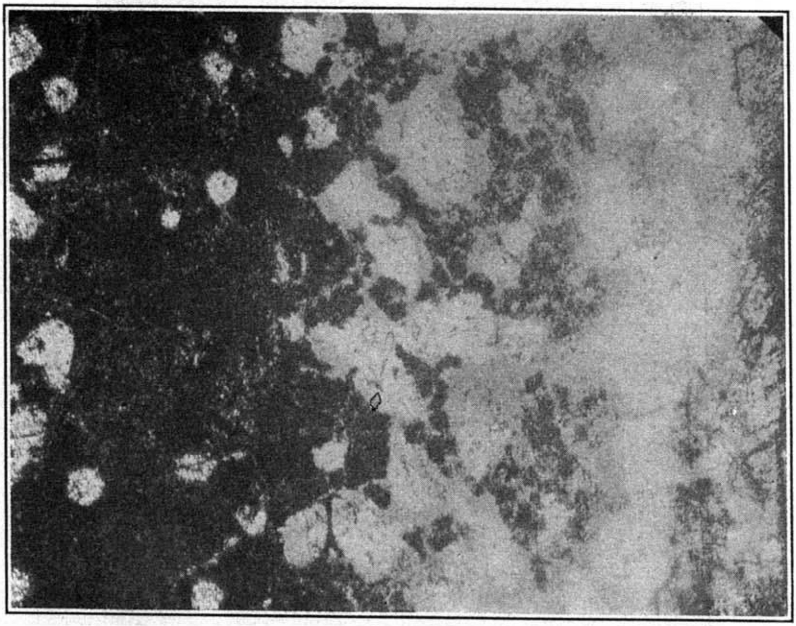

FIG. 16.

A paper presented at the Twenty-sixth General Meeting of the American Electro-1, 1914, President F. A. Lidbury in the Chair.

THE CONSTANCY OF BASE METAL THERMOCOUPLES AS RELATED TO THE MICROSTRUCTURE

By O. L. Kowalke.

In a previous paper on base metal thermocouples[1] it was shown that some couples retained a reasonably constant calibration during a series of tests, while others did not. The reasons for deviations from the original calibrations did not appear to be due entirely to mechanical strains or lack of uniformity in the metal. It seemed probable that there might have been changes in the structure of the metal due to heat treatments, or that such alloys were used in the wires which when exposed to high temperatures would produce heterogeniety. The purpose of this investigation was to establish relations between the microstructures of the wires of the couples and their calibrations under various conditions of test.

The assistance of Messrs. J. H. Wolfe and R. G. Waltenberg in obtaining these data is gratefully acknowledged.

PROCEDURE.

Five separate samples about one-quarter of an inch long were cut from each of the wires of the couples. Sections of each set of samples were prepared for microscopic examination to show the original structure and that following a two-hour heat treatment at 400°C., 600°C., 800°C., and 1,000°C. respectively.

The heat treatment of the samples was made in the following manner. A complete set of samples from each couple was mounted on an asbestos board and put into a muffle 3¾" x 3¾" x 2" high. The muffle was wound with resistance wire and heated electrically. The temperature in the muffle was measured by a

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[1] Trans. Am. Electrochem. Soc., Vol. XXIV, 1913, p. 377.

calibrated thermocouple indicating on a Keiser & Schmidt millivoltmeter, and was maintained constant at the desired point for a period of two hours. The samples were then removed from the furnace and cooled in the air.

After cooling they were polished to a mirror surface on a section perpendicular to the axis of the wire and mounted on a glass slide in the usual manner.

The samples were first examined to determine whether any structure was brought out by polishing, as would be the case with a mixture of hard and soft metals. Various etching agents were then tried. It appeared that solutions of 5 percent picric acid in alcohol, and 5 percent iodine in alcohol were the two etching agents that brought out the structures best. As soon as a good structure was obtained a photomicrograph was taken. The structures are shown on the accompanying plates.

COMPOSITION OF THE WIRES.

The wires of these couples were of sizes ranging from one-eighth inch to one-sixteenth inch (3.2 mm. to 1.6 mm.) diameter. A quantitative analysis of each wire showed the following:

	Positive Terminal		Negative Terminal	
Couple No. 6A......	Ni	86.0	Ni	94.6
	Cr	14.3	Fe	2.2
		100.3	Si	2.4
				99.2
Couple No. 7A......	Cr	10.01	Al	3.30
	Fe	30.00	Ni	96.4
	Ni	59.9		99.7
		99.91		
Couple No. 18.......	Fe	99.9	Al	1.14
			Ni	98.3
				99.44
Couple No. 20.......	Fe	99.8	Cu	52.3
			Ni	48.0
				100.3
Couple No. 21.......	Cr	16.8	Fe	1.08
	Ni	83.3	Ni	98.90
		100.1		99.98

OBSERVATIONS.

Couple No. 6A. After being heated for 24 hours at 800°C. this couple showed a departure of 125°C. at 35 millivolts from the original calibration. Inspection of the micrographs of the negative terminal shows in the dendrite structure a distinct segregation of material. These dendrites are due apparently to the presence of silicon. Binary alloys of nickel and silicon show this segregation phenomenon, while nickel iron alloys, low in iron, show a uniform structure indicating a solid solution. The micrographs of the positive terminal show the condition of a solid solution.

In some subsequent tests on a negative terminal of another couple, represented to be like the one tested, in which a break occurred, the following phenomena were observed. A longitudinal section at the point of rupture showed crystal grains and segregations about four times as large as those obtained at a point where the wire had not been exposed to the high temperatures.

It would appear, then, that the cause for the large change in calibration was due to the segregation of the material in the negative terminal and that silicon is a metal of doubtful value in thermocouple alloys.

Couple No. 7A. The departure from the original calibration to the last was gradual and increased from zero to about 25°C. at 24 millivolts. In the micrographs of both negative and positive terminals, the structure of solid solution appears throughout the tests. In the treatment at 600°C. for the negative terminal there appears to be a suggestion of crystal structure, but no change in the calibration is apparent.

Couple No. 18. The big change in calibration for this couple occurred between the initial calibration with 4 inches heated and the second calibration with 15 inches heated. This is due, no doubt, to mechanical strains. After the first heat treatment the change in calibration is no greater than other couples, being only about 30°C.

The micrographs of the negative and positive terminals show a constancy of structure throughout the treatments except for that at 1,000°C. where a large crystal structure appears in the iron. The nickel-aluminium alloy of the negative wire does not change from the characteristics of a solid solution.

Couple No. 20. A change in calibration of only about 20°C. was observed over the entire range. The micrograph of the negative terminal shows that here again the solid solution of nickel in copper has maintained constant calibration. The micrograph of the positive terminal of iron shows characteristic structures for the various temperatures.

It would seem fair to predict that "constantan," an alloy of 60 percent copper and 40 percent nickel, would give equally good results as the above alloys of copper and nickel.

Couple No. 21. This couple was not reported in the first paper, but gave results in calibration that were similar to those of Couple No. 7A. Couple No. 21 had for its positive wire an alloy known to the trade as "Excello," and the negative wire was known as "Pure Nickel." Both of these wires were purchased originally as resistance wire and were made into couples in this laboratory.

The micrographs of both wires show conditions of solid solutions in all cases.

CONCLUSIONS.

From these data it would appear reasonable to conclude that those metals which form solid solutions with one another, give the best results, providing that the thermoelectric force is satisfactory and the melting point high.

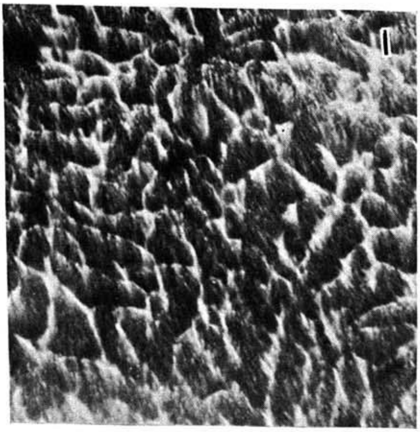
Silicon does not appear to be a desirable constituent in a nickel alloy for thermocouple material.

Any segregation of the metal has an undesirable effect on the constancy of the couple.

Wires containing but one metal showed a satisfactory structure.

Chemical Engineering Laboratory,
University of Wisconsin.

Couple No. 6A. Positive Terminal.
Etched with Iodine. $Ni = 86.0\%$; $Cr = 14.3\%$.



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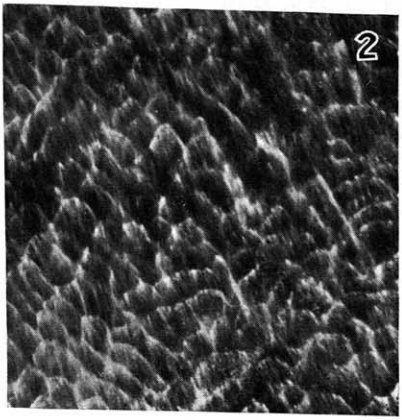

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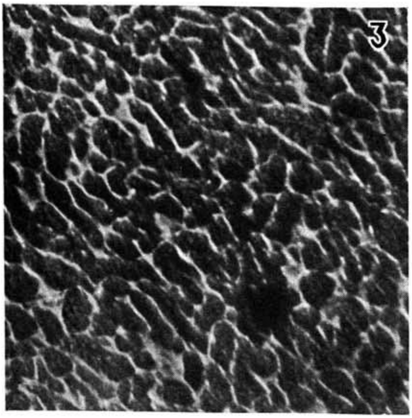

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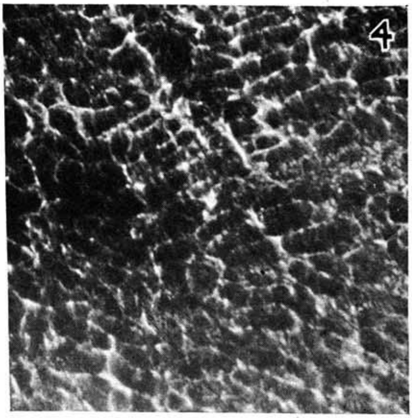

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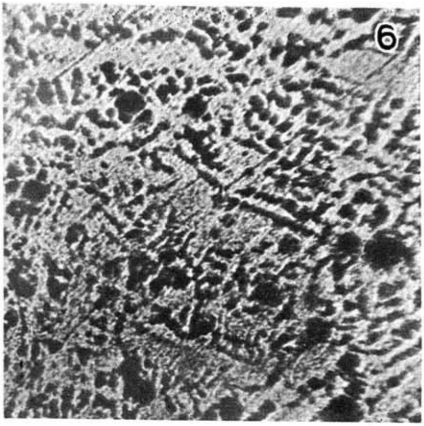
× 225

Fig. 1. Original Structure.
Fig. 2. Heated at 400° C.
Fig. 3. Heated at 600° C.
Fig. 4. Heated at 800° C.
Fig. 5. Heated at 1000° C.

Couple No. 6A. Negative Terminal.
Etched with Iodine. Ni = 94.6%; Fe = 2.2%; Si = 2.4%.



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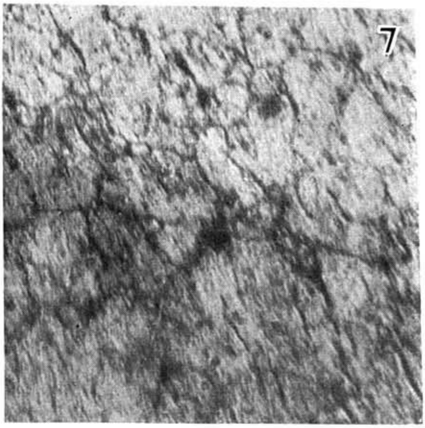

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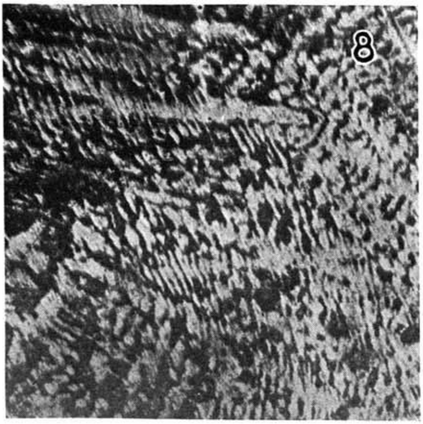

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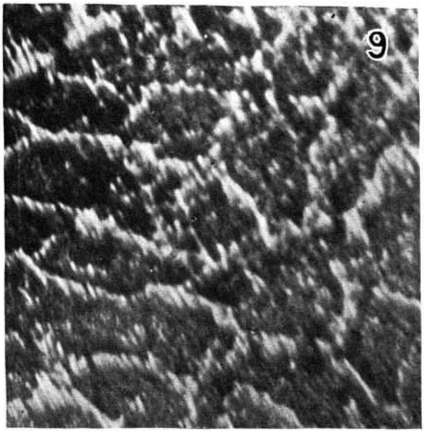

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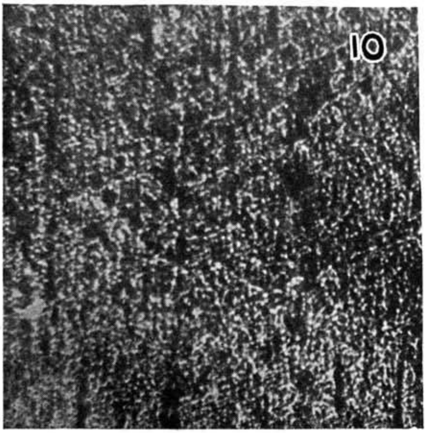

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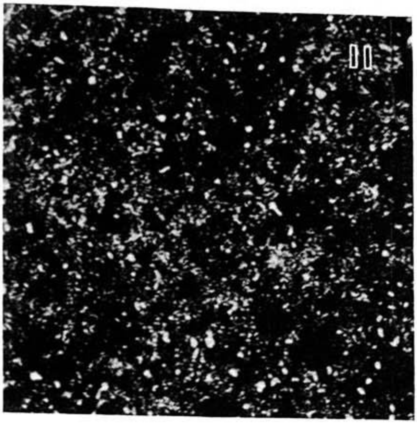
Fig. 6. Original Structure.
Fig. 7. Heated at 400° C.
Fig. 8. Heated at 600° C.
Fig. 9. Heated at 800° C.
Fig. 10. Heated at 1000° C.

Couple No. 7A. Positive Terminal.
Etched with Iodine. Cr = 10.01%; Fe = 30.00%; Ni = 59.90%.



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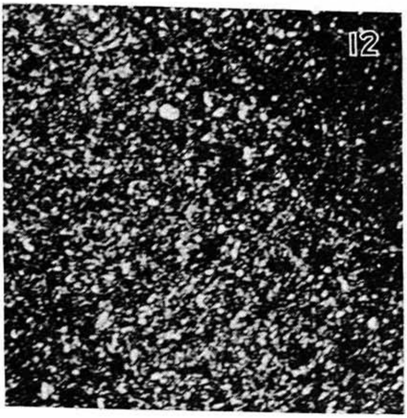

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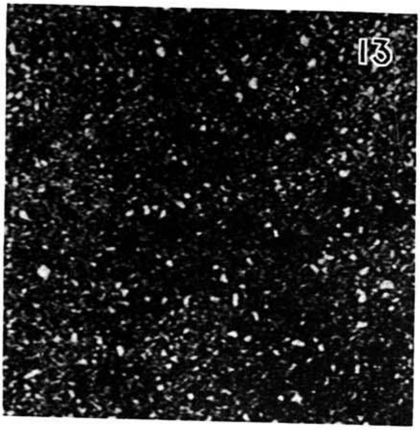

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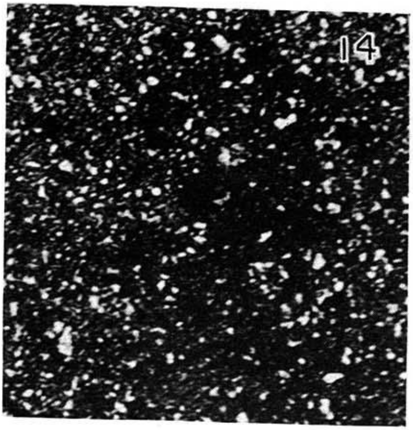

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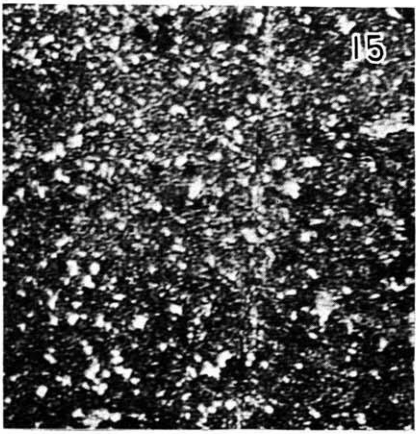

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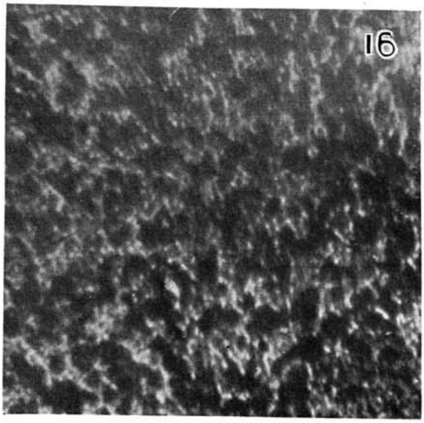
Fig. 11. Original Structure.
Fig. 12. Heated at 400° C.
Fig. 13. Heated at 600° C.
Fig. 14. Heated at 800° C.
Fig. 15. Heated at 1000° C.

Couple No. 7A. Negative Terminal.
Etched with Iodine. Al = 3.3%; Ni = 96.4%.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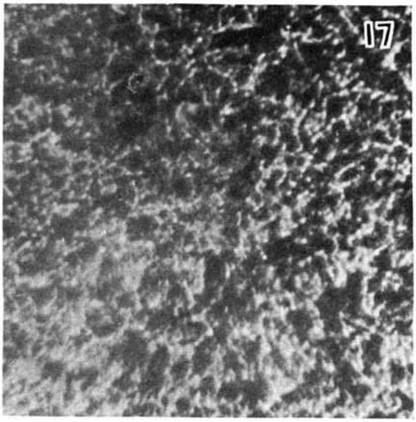
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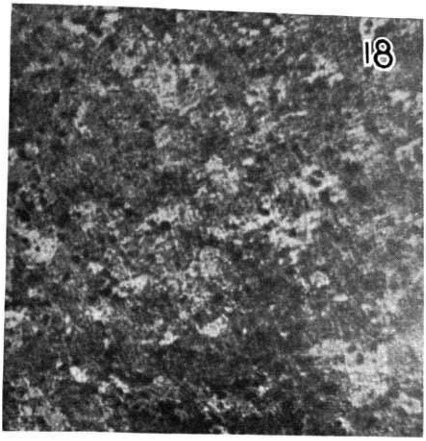
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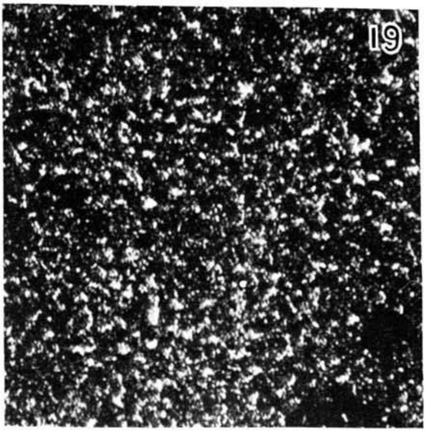
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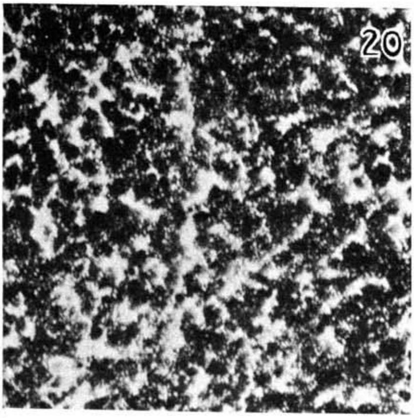
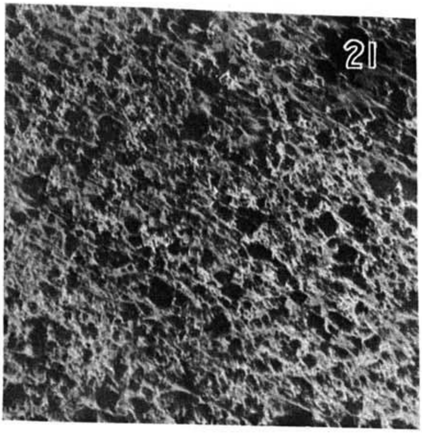

20

× 225

FIG. 16. Original Structure.
FIG. 17. Heated at 400° C.
FIG. 18. Heated at 600° C.
FIG. 19. Heated at 800° C.
FIG. 20. Heated at 1000° C.

Couple No. 18. Positive Terminal.
Etched with Iodine. Fe = 99.9%.



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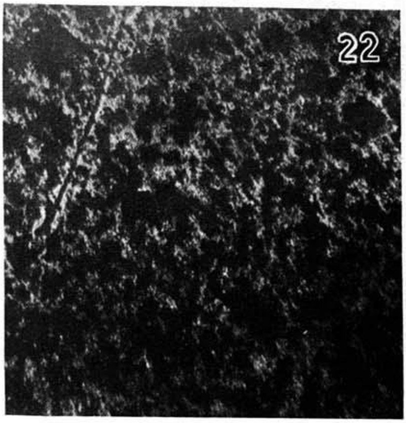

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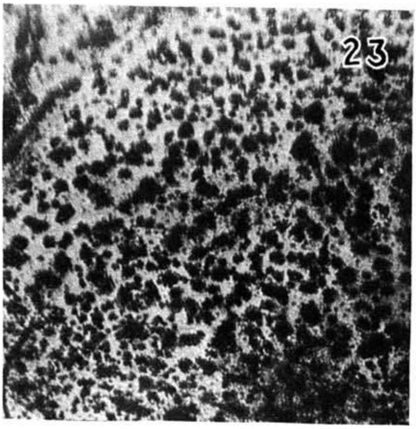

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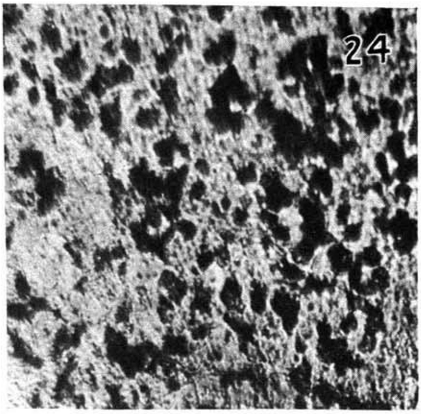

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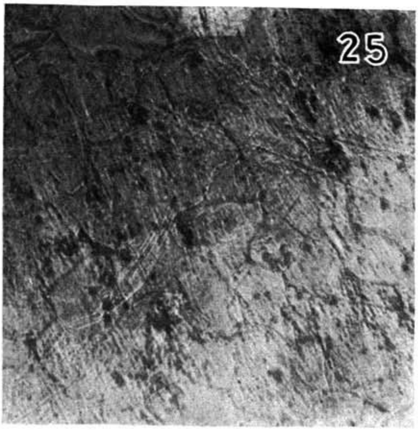

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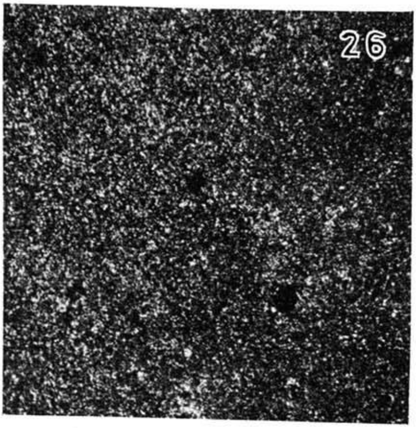
FIG. 21. Original Structure.
FIG. 22. Heated at 400° C.
FIG. 23. Heated at 600° C.
FIG. 24. Heated at 800° C.
FIG. 25. Heated at 1000° C.

Couple No. 18. Negative Terminal.
Etched with Iodine. Al = 1.14%; Ni = 98.3%.



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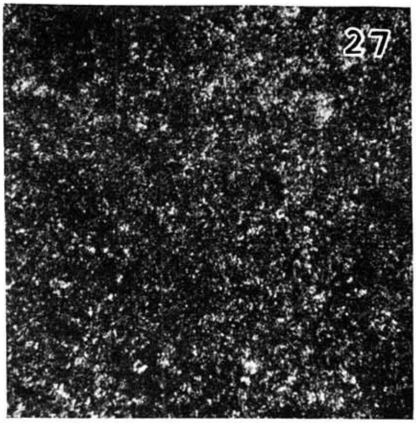

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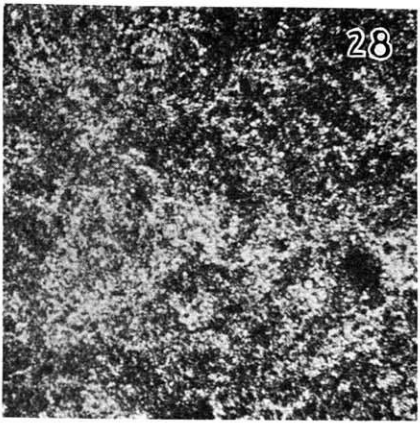

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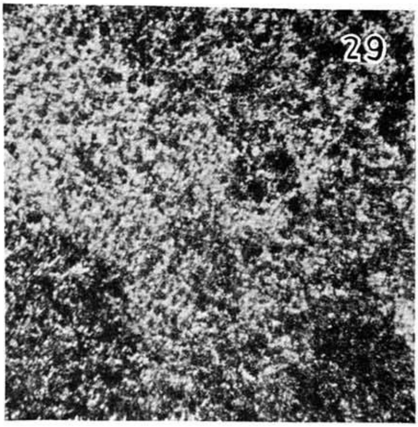

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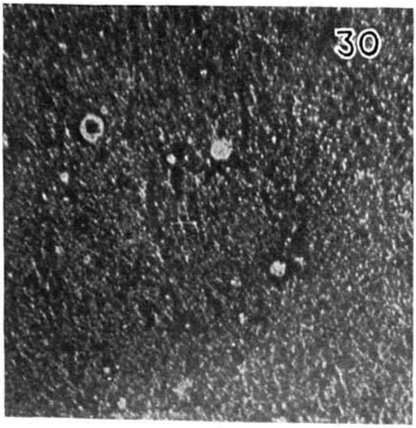
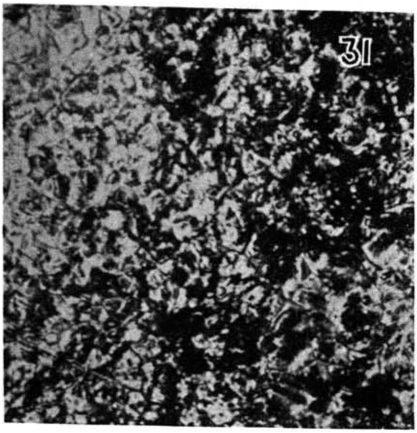


× 80

Fig. 26. Original Structure.
Fig. 27. Heated at 400° C.
Fig. 28. Heated at 600° C.
Fig. 29. Heated at 800° C.
Fig. 30. Heated at 1000° C.

Couple No. 20. Positive Terminal.
Etched with Picric Acid. Fe = 99.80%.



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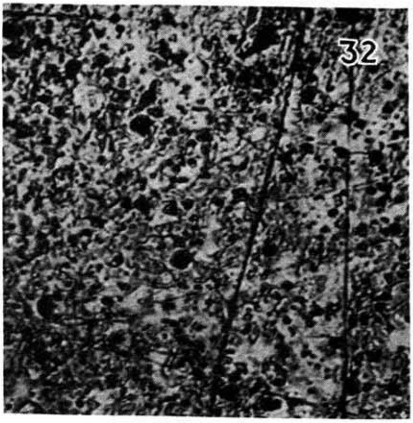
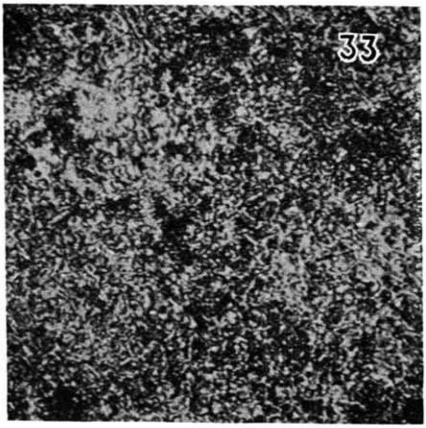
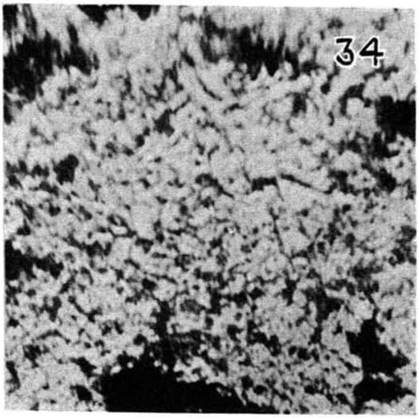


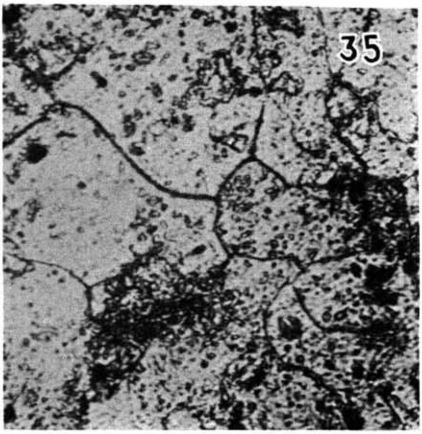
X 225



X 225



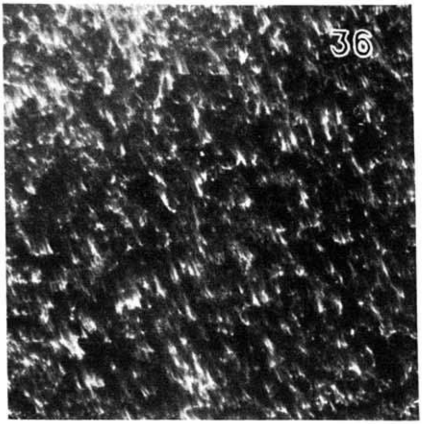
X 225



X 225

FIG. 31. Original Structure.
FIG. 32. Heated at 400° C.
FIG. 33. Heated at 600° C.
FIG. 34. Heated at 800° C.
FIG. 35. Heated at 1000° C.

Couple No. 20. Negative Terminal.
Etched with Iodine. Cu = 52.3%; Ni. = 48.0%.



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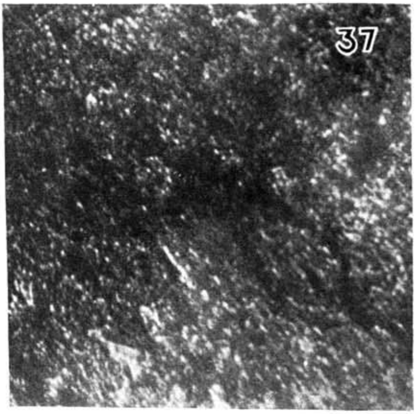

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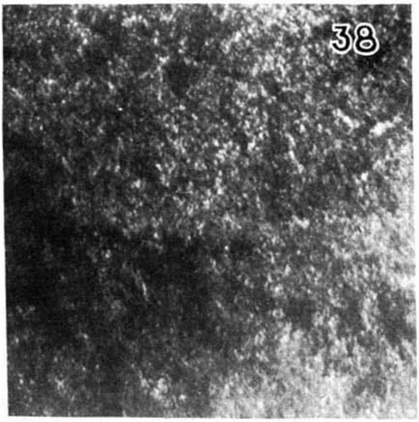

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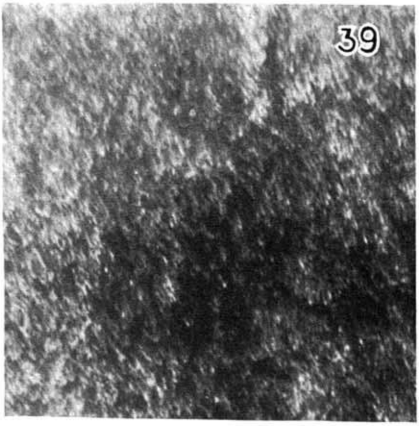

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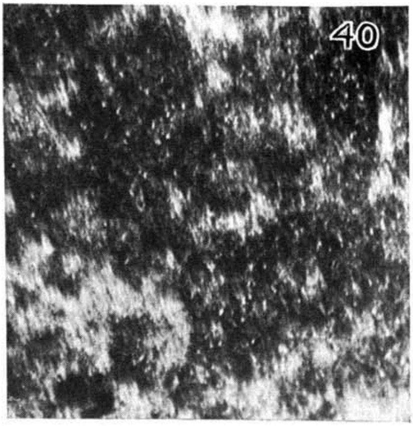

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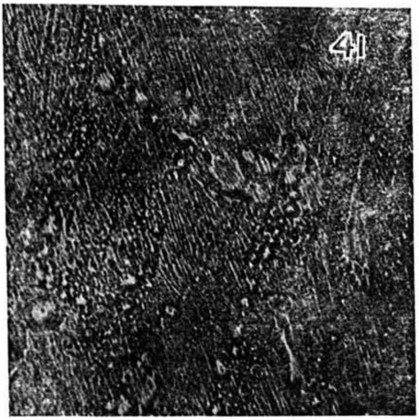
FIG. 36. Original Structure.
FIG. 37. Heated at 400° C.
FIG. 38. Heated at 600° C.
FIG. 39. Heated at 800° C.
FIG. 40. Heated at 1000° C.

Couple No. 21. Negative Terminal.
Etched with Iodine. $Fe = 1.08\%$; $Ni = 98.90\%$.



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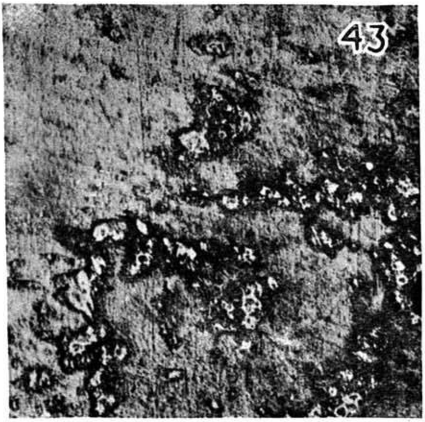

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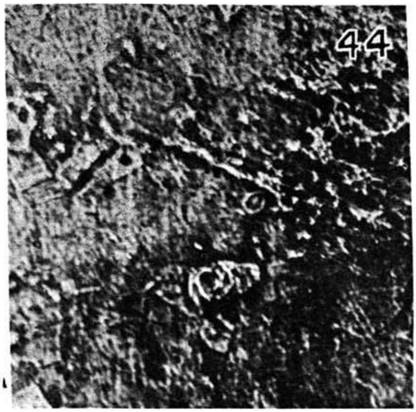

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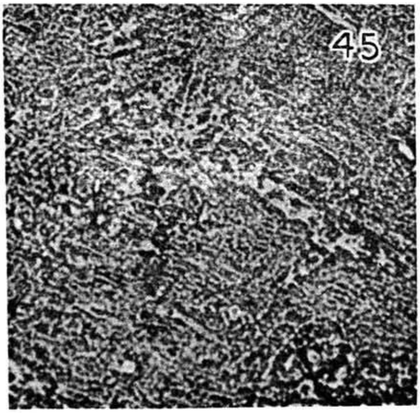
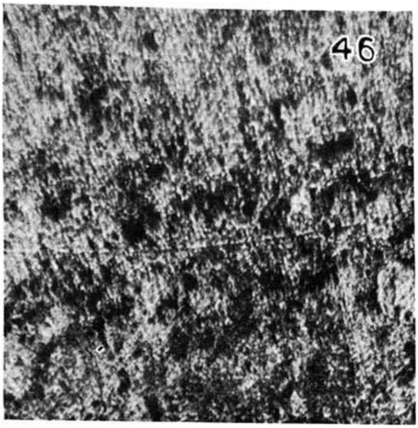


× 80

FIG. 41. Original Structure.
FIG. 42. Heated at 400° C.
FIG. 43. Heated at 600° C.
FIG. 44. Heated at 800° C.
FIG. 45. Heated at 1000° C.

Couple No. 21. Positive Terminal.
Etched with Iodine. $Cr = 16.8\%$; $Ni = 83.3\%$.



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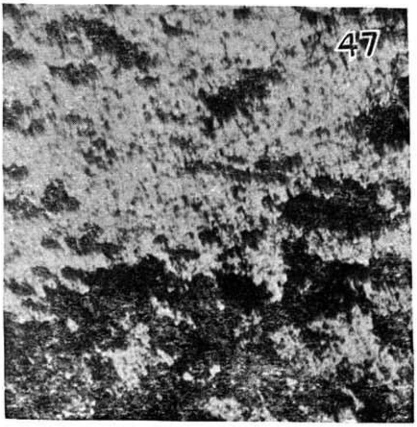

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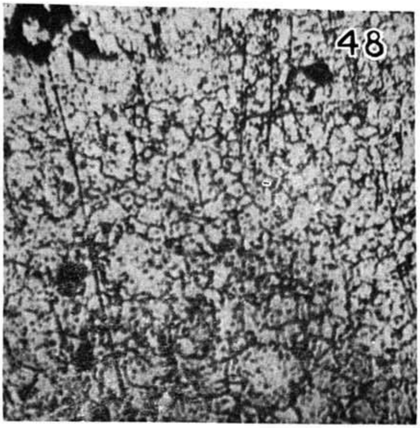

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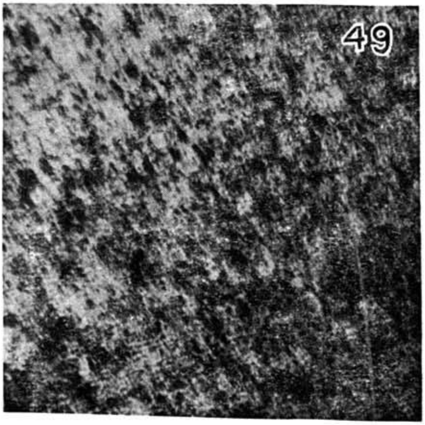

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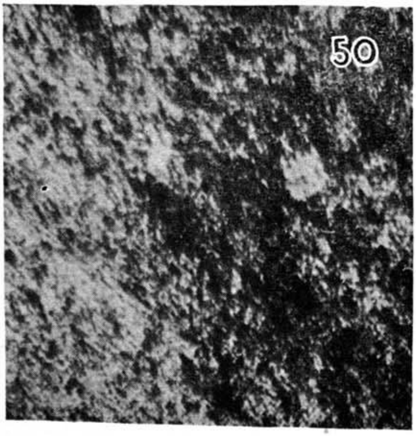

× 225

FIG. 46. Original Structure.
FIG. 47. Heated at 400° C.
FIG. 48. Heated at 600° C.
FIG. 49. Heated at 800° C.
FIG. 50. Heated at 1000° C.

DISCUSSION.

W. R. Mott: I believe Mr. Tone will bear me out in the statement that freshly made alloys of silicon with iron or manganese, frequently recrystallize shortly ofter being taken out of the furnace.

Silicon is interesting in another way, as regards its thermoelectric characteristics. Messrs. F. Fischer, R. Lepius and E. Boerwind have reported on the thermoelectric power of silicon.[2] If it is deoxidized, the e. m. f. is exactly in the reverse direction from silicon which contains dissolved silica, and the difference amounts to almost 1000 microvolts per degree.

Charles B. Thwing (*Communicated*): I for one am grateful to Professor Kowalke for carrying his researches on thermocouples to so interesting a conclusion. While seeking a relation between thermo-electromotive force and co-efficient of expansion, some ten years ago, I met some striking exhibitions of the effect of aggregation of crystals as changed by heat upon both of these properties of certain metals and alloys.

Antimony, for example, when cast in an iron chill crystallized radially. With repeated heating to 100 degrees, the length continued to increase and the electromotive force to diminish for several successive heatings. Since the electromotive force differs for different axes, I attributed the change to a re-arrangement of the crystals in which some crystals were oriented more nearly parallel to the axes, or as they would have arranged themselves if the metal had cooled more slowly when cast. The change of electromotive force on the first heating was more than ten percent.

I hope that Professor Kowalke will apply the same tests to platinum thermocouples that have been damaged by long use. Such couples may often be restored by glowing them with a current not sufficient to melt the wire but to reach, say 1500 degrees. Microphotographs taken before and after such a restoration would be of exceeding interest.

Jos. W. Richards: Some of the so-called standard couples which have been standardized, and probably accurately standardized, in the laboratory of the maker, when they have been brought into the works and used again, will show a variation of from

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[2] Physik. Zeit., **14**, 439-46: Zeit. anorg. Chem., **81**, 243-65.

10° to over 100° C. from the standardization. The changing micro-structure is probably the cause of this great deviation, which makes them almost unusable for accurate work.

B. L. Glascock: The couples that come from the maker direct to the user generally are not calibrated by the user, who assumes that the calibration of the maker is correct. Four couples supposed to have been standardized by the manufacturer, when they were checked against a platinum—platinum-rhodium couple, were found to vary from 8° to 52° at a temperature of 1000°. We have had couples which had been used and repaired that varied as much as 100° at 1000° C.

M. G. Lloyd: I think it would add a great deal to the value of this information if the last two speakers would say what the materials of the couples were.

W. A. McKnight: The makers of the couples on which these tests were made will not state the composition of the alloy used and no analyses have been made which would tend to show the composition of the couple. However, it is one that is manufactured for use at 1250° C., and at 1000° C. the conditions stated by Mr. Glascock were found to exist.

SOME NOTES ON THE MANUFACTURE OF TIN PLATE AND THE RECOVERY OF TIN WASTES

O. L. KOWALKE.

Associate Professor of Chemical Engineering.

As early as 1620[1] the trade of making tin plate had existed for many years in Bohemia and about this time it was introduced into Saxony, Germany. In 1670 the secret of manufacture was carried to England, but it was not until 1720 that the industry was firmly established. Soon after the art was introduced into England it began to flourish because of the excellent deposits of tin in Cornwall. It was not until about 1890 that the tin plate industry in the United States assumed any importance. Under the stimulus of the protective tariff a number of large plants were built, which, by the application of machinery and shop management, were able to produce more than enough for home consumption. The supply of tin must, however, be obtained largely from abroad and this has led to numerous processes for the recovery of tin from tin scrap.

Tin plate consists of a thin sheet of iron or steel coated with tin. The thickness of this coating depends on the uses of the product; tin plate for toys, fruit and meat cans has only a very thin coating, while the material used for milk cans has a thick coating. Roofing tin plate is frequently made by coating the iron sheet with an alloy of tin and lead in the proportions of one of tin to three of lead. Such an alloy of tin and lead will not rust so easily as pure tin.

Unlike iron, tin is not oxidized easily nor is it affected by moisture; hence if iron can be protected by such a coating it will resist rusting for a long time. If, however, the iron is imperfectly coated or if a scratch develops, the contact of moisture with the tin and iron produces a galvanic couple in which the tin is the cathode and the iron the anode and by which rapid rusting results. It is frequently noticed that tin pails or cans rust in round spots. Since this means that there is a minute point of iron which has not been covered with tin it is

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[1] History of Trade in Tin, by C. W. Flower, p. 37.

imperative to have a smooth and perfect covering of tin over the iron. An alloy of tin and lead makes a better covering and does not exert such a strong galvanic action.

The iron or steel from which the plate is rolled is a bar about 8 in. wide and 0.25 to 0.75 in. thick. The heated bar is rolled into sheets perpendicular to the direction in which the original bar was rolled. Assume that sheets 20 by 28 in. are desired. The original bar is given singly five passes in the rolls until it is a sheet 28 in. long. Two such sheets are heated again and rolled, superimposed one on the other, until their length is 56 in. During each rolling the sheets are pulled apart so that the formation of a scale is promoted and sticking prevented. The two sheets are folded to make four thicknesses and after being heated are rolled out again to a length of about 54 in. These four thicknesses folded again to make eight are heated and rolled until the length is about 56 in. After the eight rolled sheets are cut and squared into small sheets 20 by 28 in. they are ready for the pickling.

The packs of eight sheets 20 by 28 in. are opened so that they do not adhere to one another and are piled on carriers, which move up and down in a pickling bath of hot eight per cent. sulphuric acid for about ten minutes. This pickling removes all the scale and leaves the iron bright and clear. After removal from the acid the plates are washed in clear water to free them from acid. For further particulars regarding pickling methods the reader is referred to an article by Mr. O. W. Story in Met. & Chem. Eng. Vol. X, p. 45 (1913).

To remove the stains set up by the rolling the washed sheets or plates are packed in annealing stands, carefully covered to exclude air, placed in a furnace and annealed at 1,500 degrees fahr. for twelve to eighteen hours. They are allowed to cool slowly away from contact with air. When cold the annealed sheets are cold rolled singly between polished rolls to give them a smooth surface and close any pores. Two or three passes are usually sufficient. After being rolled they are packed in cases away from air and again annealed for five or six hours at 1,200 degrees fahr. After the second annealing the plates are again pickled in a weak sulphuric acid solution to remove the last scale and are washed in clean water. To guard against rusting they are put into tanks of water and carried to the tinning house.

The tinning bath consists of an iron box, the lower half of which contains the molten tin, and the upper half of which is divided into two compartments by a partition which dips into the molten tin. Floating over the molten tin in one of these compartments is a fluxing solution, usually zinc chloride; in the other is palm oil. At the surface of the molten tin in the palm oil compartment is a pair of rolls. The iron sheets are taken from the water, passed into the fluxing bath in the first compartment, thence down through the tin, caught by the rolls and brought out through the palm oil in the second compartment. The rolls are so set that they not only draw the plates out of the bath, but they also press off any surplus tin and leave the plates somoth. The palm oil is intended to keep the plates bright and protect them from the moisture in the air during storage. The plates are now put into a machine which takes off the surplus oil by bran and lime. From this point the plates go to the sorting room where they are closely inspected and packed. At all points of the process close watch must be kept. Since each sheet must be handled, it can readily be seen that the cost of tin plate is high.

Excellent articles on tin plate manufacture will be found in Scientific American of Oct. 4 and Nov. 1, 1902, and in Metal Worker of Feb. 14, 1903, and July 21, 1905.

Owing to the limited supply of tin ores and metal much attention has been given to the recovery of tin from waste. In the process of coating iron sheets with tin a waste material called dross is obtained from the bath. Various methods are used for recovering the tin from dross. Among them is that devised by R. S. Wile,[2] by which the tin dross is reduced in the electric furnace by being fed with a carbon charge into a molten bath of inert slag having a lower specific gravity than tin. The reduced tin falls through the slag to the bottom of the bath, where it can be tapped off. Any metal which is vol-

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[2] Met. & Chem. Eng. Vol. XIII, 1910, p. 151. Trans. Am. Electrochem. Soc. Vol. XVIII, 1910, p. 205.

atilized is caught by the charge of dross and carbon. Thus the loss of tin is kept down to less than one per cent. In his furnace with an energy consumption of 88 kw Wile has reduced about 2,500 lb. of dross per day.

Tin cans and tin scrap also are worked over to recover the tin. For this purpose the electrolytic and the chlorine detinning processes are in use. The former is more expensive than the latter, which seems to be gaining considerable ground in this country.

The chlorine or Goldschmidt process [3] is based on the fact that dry chlorine does not attack iron, but only the tin, forming tin tetrachloride. The tin scrap compressed into bundles is put into a chamber and dry chlorine gas admitted under several atmospheres pressure so that the gas gets into every crevice. On account of the heat developed due to the action of chlorine on tin during the stripping, great care must be exercised. When the gaseous chlorine forms liquid tin tetrachloride the pressure drops, and as long as the pressure continues to drop detinning takes place. When the pressure becomes constant it is evident that the chlorine has found all the tin. The tin tetrachloride thus recovered is greatly prized by silk dyers for use as a mordant.[4] The value of tin tetrachloride is about $0.14 per lb. of 50 degrees Beaume strength. The iron remaining after washing can be used in open hearth processes for making steel.

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[3] Met. & Chem. Eng. Vol. VII, 1909, p. 80.

[4] Met. Chem. Eng. Vol. VI, 1908, p. 150.

REINFORCED CONCRETE BUILDING IN MEXICO

J. F. ABBEY.

From the contractor's point of view, reinforced concrete building in the Republic of Mexico is in its infancy, for it is only within the past five years that concrete building has made any great strides as compared with other classes of building in the country. The few concrete buildings that have already been erected have been less expensive than any other class of structure. From every point of view the results to the owners have been not merely satisfactory, but gratifying. Due to the uniformly hot weather which prevails in the greater portion of the country, the first important requisite of a building is imperviousness to heat. In this respect concrete structures have proved equal to the very adaptable and therefore universally popular adobe building. There are only four or five contractors in the entire republic engaged in this particular line of work, hence the field is practically untouched, a condition that must appeal to the young engineer.

It seems especially worth while to consider the conditions the contractor will encounter in entering the field.

As heretofore intimated, the adobe building predominates in the greater portion of the country. This type of construction consists of blocks of ordinary clay, which after being mixed with a little straw is baked in the sun until it becomes sufficiently hard to be handled. Since these blocks are made in moulds 3 by 10 by 14 in. they give a minimum wall thickness of 10 in.; but in many cases two and three blocks are used, so that two and three foot walls are common. The mortar used to set these blocks is made from the same clay, and the building is finished off with ordinary lime plaster, some of which is smooth, some rough cast and decorated with gay designs and colors.

Besides adobe, brick, stone and structural steel are used extensively. The brick is of rather poor quality, and does not come up to the poorest common brick made in the United States. Sand lime brick is used to some extent in the northern part of the republic. Faced brick is neither made nor used in the coun-

SOME OBSERVATIONS ON NICKEL PLATING SOLUTIONS.*

BY DR. OLIVER P. WATTS.†

Electro-plating is a branch of electro-chemistry which has engrossed my interest more and more, and its problems furnish a most fascinating line of research. During a recent period I have been conducting a series of experiments upon certain phases of the deposition of nickel and I have considered the results of sufficient interest to display here.

The first topic to which I would call your attention is the composition of the anode. For many years it has been the practice of the makers of anodes in the United States to add to the nickel varying amounts of iron, carbon and tin, so that the resulting anode contained only about 92 per cent of nickel. The following formula for making nickel anodes is taken from one of the plating trade journals:—"Nickel 92 per cent, tin 4 per cent, old files 4 per cent." (Metal Ind., 1907, p. 116). Why old files are preferred to any other form of iron is not stated. A more recent article says, "The anodes are cast in varying degrees of purity, the average commercial anode consisting of about 92 per cent nickel and 8 per cent tin, while other grades, consisting of 85 to 89 per cent nickel and 11 to 15 per cent iron and tin, are especially adapted to certain work. A few are made of pure nickel free from alloy, but are too hard for ordinary purposes." (Foundry, 1913, p. 17).

The purposes of these impurities has been explained as follows:—"Commercial nickel anodes contain in addition to nickel, iron, tin, and carbon. These are introduced intentionally to render the anode "soft", *i. e.* so that it will dissolve easily in the solution during plating." (Brass World, 1911, p. 154). Analysis of samples of commercial nickel plate (J. Amer. Chem. Soc. 1917, 29, p. 1268) has shown the presence of 0.08 to 0.09 per cent of iron, and one writer (Trans. Amer. Electrochem. Soc. 9, 217) has ascribed the rusting of nickel plated articles to the presence of this iron. Whether this is true or not, these impurities in the anode are of no benefit either to the solution or to the nickel plate, and their presence in nickel solutions should no longer be tolerated. For a number of years European platers have been using anodes containing 98 per cent of nickel, and it is time that American platers followed their good example. In a solution containing only sulphates these pure anodes do not corrode well, but the addition of one or two ounces per gallon of a soluble chloride remedies this trouble. Nickel, sodium, or ammonium chloride should be added to a solution in which pure anodes are used.

The little 25-gallon plating tank at the University was formerly equipped with the standard American anode, containing iron, carbon, and a trace of copper. A heavy brownish sediment of ferric hydrate continually collected in the bottom of the tank, and when standing unused coper was precipitated on the anodes and a scum of iron rust formed on the surface of the solution. Becoming dissatisfied with this state of affairs, I precipitated the iron, added some sal ammoniac to cause good anode corrosion, and replaced the impure anodes by sheets of electrolytic nickel, (obtained from the Orford Copper Co.) Electrolytic nickel anodes have now been used for seven years, and have proved satisfactory. At that time it was, I think, impossible to secure cast anodes of high purity in this country, but today the plater who wishes to avoid introducing impurities into his solution from his anodes is not confined to the use of electrolytic anodes, as cast anodes of high purity are now obtainable.

Another improvement in nickel plating which has come to us from Europe is the high-power nickel solution. It may be profitable to consider for a moment what constitutes a high-power nickel solution. It is not some mysterious chemical of wonderful potency, but is merely a solution containing much more nickel than the old style bath, and which therefore permits of using a greater number of amperes per square foot of plated surface without causing a burnt deposit. Since the rate of deposition increases directly as the number of amperes, the time of deposition is lessened proportionally.

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* A paper read at the Annual Banquet of the Chicago branch, American Electroplaters' Society.

†Laboratory of Applied Electrochemistry, University of Wisconsin.

There seems to be a prejudice on the part of many platers against strong nickel solutions, as indicated by such statements as the following, taken from periodicals which regularly devote considerable space to plating. "A new bath composed of double sulphates and water not infrequently gives trouble from peeling in addition to the dark color, especially if the solution stands in excess of 6 degrees Beaumé. To remedy, reduce the density to 4½ or 5 degrees and add the conducting salts." (Foundry, 1913, p. 106).

"*Question.* Our nickel deposits come out dark gray and rough after 1½ hours deposit. The solution stands at 10 degrees, and we have added single salts.

Answer. Your solution is too concentrated. In America solutions that register 5½ to 6 Beaumé give the best results, provided the metal content of the solution is correct. Concentrated solutions produce dark deposits that readily stain, and often cause peeling." (Metal Ind., 1911, p. 353).

Yet today many platers are paying 35 cents a pound for an imported mixture of unknown salts, making solutions having a density of 16 degrees, and obtaining extremely satisfactory results from these dense solutions.

I have here a good nickel deposit made at 18 amperes per square foot from a solution of nickel and magnesium chlorides having a density of 31.3 degrees. In thickness it is equivalent to a deposit for 20 hours at 3 amperes per square foot. If high density of solution were capable of ruining a deposit, this would be the worst sample of nickel plating which you have ever seen. It is time that platers recognized that poor nickel deposits are due to some other cause than too dense a solution.

I have tested but one of the high-power salts now on the market, but for a period of two months this has done all that the dealer claimed for it. I cannot conceive that a plater who has once tried this salt would ever use the old double sulphate solution, if he could obtain the price of this high power salt. It must be admitted that the expense is great, 100 gallons of solution costing $70, instead of about $7 for the double sulphate soltuion. Even if we grant that one tank of highpower solution will do the work of four tanks of the double sulphate, the ratio of costs is still over two to one against the high-power solution. Only when the composition of these salts becomes known, or platers discover equally good combinations of salts themselves, will the high-power solution compare favorably with the old style solution as regards cost per unit output. When, however, freedom from peeling, and burning, and when in many cases a more satisfactory anode-corrosion is secured, even at present prices, the greater capital outlay required for the high power solution may be fully justified. There is, too, the possibility of using the new salts in half the concentration specified, thus cutting the investment in half, and running the solutions at 5 amperes the square foot instead of ten.

There are several methods of making a dilute solution do the work of a concentrated one. One method is to circulate or stir the solution, or to move the object,—any process that will break up the film of dilute solution formed around the object, and supply metal as fast as it is needed for deposition. Circulation and stirring of the solution have long been used successfully in the electrolytic refining of metals, but because of stirring up the sediment always present in plating tanks, or possibly for some other reason, these methods have not come into regular use in commercial plating. Where heavy deposits are necessary, as in silver plating, some means of shortening the time is desirable, and motion of the cathode rod has frequently been resorted to, thus allowing an increase of current density and a corresponding lessening of the time. This method is applicable in any case where a heavy deposit of metal is necessary, and its use has already been extended to the deposition of nickel.

But there is another, and more effective way of transforming an ordinary dilute nickel plating bath into a high-power solution—that is to heat it. For the past three weeks I have been experimenting with hot nickel solutions. From a solution containing 10 ounces per gallon of the double sulphate at a temperature of 194 deg. F. and a current density of 29 amperes per square foot a good deposit was obtained in twenty minutes, which would have required 3½ hours in the cold solution at the usual current density of 3 amperes per square foot. Similarly the current density in a high-power bath of full strength at 165 deg. F. was increased at intervals to a maximum of 206 amperes per square foot, without spoiling the deposit; this is the equivalent of 19 hours at 3 amperes per square foot. To establish a record for the rapid plating of nickel a brass ube ¾ inch in diameter was used as cathode, and rotated at 1000 R. P. M. Many trials were made at increasing current densities and although a current density of 1257 amperes per square foot was reached in one trial, the deposit was still excellent. Two minutes at this current density gives a deposit equivalent to 14 hours plating at 3 amperes per square foot, and in spite of this heavy deposit, 2 to 3 minutes with tripoli and rouge was sufficient to give it the polish of the sample shown. How much higher the current density can be carried under the conditions of these three experiments I am at present unable to say, and it really does not matter to the electroplater, as it has been shown that in a hot nickel solution the current density can be carried to such a point that the ordinary plating bath becomes a high-power solution. The efficiency of deposition on a rotating cathode at 625 amperes per square foot was found to be 99.8 per cent. But there is another result obtained in the hot solution which I regard as of more value to the nickel plating industry than rapidity of deposition—that is the softness, toughness and freedom from peeling of the deposit.

In the case of thick nickel deposits from cold solutions their hardness makes buffing difficult and expensive, they are more liable to peel than thin deposits, and the time required for their production is excessive unless a high-power solution is used. In view of these facts it is not surprising that in the past many platers have used altogether too light deposits. Much of this thin plating affords no protection to the underlying metal and is not even ornamental, for after a few months' use it wears off in spots and the articles look worse than if they had never been plated. Too much nickel plate is made to sell instead of to wear.

What could so much increase the popularity and extend the use of nickel plate as to have every bit of it which ever gets into the hands of the public put on to stay, and thick enough to protect iron from rusting and to last for years?

I believe that this can be accomplished by the hot nickel solution. Its use will enable the plater to produce a thick deposit in less time than is now required for a thin deposit. By heating the regular plating solution to 180 deg. F., or above, deposition can be carried on at twice or three times the rate of the present high-power solutions. By using a hot high-power solution, current densities of 100 to 200 amperes per square foot may be used on stationary cathodes, or, since such great current densities as these are not needed in plating, the high power solution may be diluted to three times its original volume and yet be used at 20 amperes per square foot. The deposit from a hot solution is soft, never peels from a clean surface, and is quickly and easily polished even though it appears dull as it comes from the bath. This ease of polishing should result in a considerable saving in the time and labor required for buffing, and would partly defray the cost of heating the solutions. The heating coils should be made of lead.

It has long been known that hot nickel solutions give soft deposits and the following extracts would seem to indicate that hot nickel solutions have been tried and found wanting:

"*Question* No. 1283. What is the advantage of running a nickel solution hot and what are the disadvantages?

Answer. The advantage gained in using a hot nickel plating solution is that the nickel deposits faster and is brighter. In addition the nickel is apt to be slightly softer and more free from pits. Beyond these advantages a hot nickel solution has no other benefits. The disadvantages are the fact that the solution must be heated, and requires far more care and must be maintained at a constant temperature in order to obtain uniform results. Cold plating solutions are always used wherever possible, and in the case of nickel solutions it is generally considered that the slight advantage gained by using them hot does not warrant the extra labor involved. It is possible to obtain sufficiently good results in cold solutions of nickel." (Brass World, 1913, p. 145.)

"*Question* No. 1324. What will happen if a nickel solution is run hot?

Answer. Nickel solutions can be run hot and give good results and soft deposits. They should, however, be used much weaker than when employed cold. It is generally found unnecessary to use them hot as the trouble of heating and maintaining them is more than the gain in quality. Hot solutions deposit nickel very rapidly." (Brass World, 1913, p. 258.)

In general these statements agree with my experiments, that a hot solution yields a soft nickel deposit, and permits of more rapid deposition, but on the question of whether heating will pay or not we have come to opposite conclusions. This is a matter which cannot be settled by argument, but only by trial on a small commercial scale. Cannot some local branch of the A. E. S. take up this question and carry it to a definite conclusion? Its potential importance merits an early and decisive trial by practical men.

It will probably be found that careful temperature regulation is not essential to success when the plating tank is equipped with an ammeter so that the plater knows what current he is using, although it may prove otherwise if he has to depend entirely upon the voltmeter in controlling the current. This leads me in closing to speak of the necessity of an ammeter, or ammeters, of suitable range so connected that the current passing in each tank may be read. It is the number of amperes per square foot of surface receiving the metal which determines whether the deposits will be good or bad; and not the volts across the tank. The voltage itself has no influence on the character of the deposit, and may have any value that is necessary to send the proper number of amperes to the objects which are being plated. The voltmeter is better than nothing since, with its aid, the plater can make a better guess at the proper adjustment of the rheostat than he could without it, but it is a poor substitute for the ammeter. The plater needs both voltmeter and ammeter for proper regulation of current and solutions. If a record is kept of the volts and amperes it will not only tell what current to use on a particular tank when partly, and when completely, filled with work, but it will indicate changes in resistance of the solution. To calculate the resistance of a plating tank read the volts and amperes, open the switch, or otherwise break the circuit for a second,—just long enough to get a reading of the voltmeter. Subtract the second voltmeter reading from the first, and divide by the current; the quotient is the resistance in ohms. Since the resistance diminishes greatly with increase of temperature, a change in the resistance of a solution does not surely mean a change in composition unless the temperature is the same as when the resistance was measured before. It is not necessary that there should be as many ammeters as there are plating tanks, for a single instrument may be arranged to read the current in any one of the several tanks. At the outset it might be well to purchase only one ammeter, and use it until convinced that it is a great help in plating before putting in a full equipment.

A NEW DIXON CRUCIBLE BOOKLET.

This reproduction of the cover design from a new edition of the booklet "Dixon's Graphite Crucibles" is merely suggestive of the valuable information contained in the sixteen pages that follow. In addition to a preface and the table of crucible sizes, information is furnished of steel melting crucibles, file crucibles, crucible covers, tilting furnace crucibles, retorts, bottom-pour crucibles, stirrers, skimmers, dippers, and self-skimming crucibles. Some good advice is given in the two pages of "For Oil Furnaces" and "General Hints." Foundry facings and a highly refractory cement for the repair of worn or cracked firebrick are also described. Altogether this little booklet is most worth while to the men interested in the subject of better foundry practice. A copy is gratis to those who take the trouble of writing to the Joseph Dixon Crucible Company, Jersey City, N. J.

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HARDENING AND WELDING COPPER.

Once again the problem of hardening copper, to such an extent that it will take an edge and may be used for cutting purposes, claims to have been solved. The latest inventor of a process for hardening and welding copper is Charles Bittner, of Stafford, Kansas (U. S. Patent 1,122,062).

The hardening compound used in this instance is composed of 16 oz. hyposulphite of soda, ½ oz. sulphite of soda, 3 oz. No. 8 acetic acid (25 per cent pure acid) and 1 oz. powdered alum. The treatment consists in heating the copper to a good cherry heat, dusting a little of the powder over the surface, heating for about thirty seconds to burn this off, turning the metal over and repeating the operation until the entire surface has been so treated. In the second stage of the process, the same operations are performed but at a lower degree of heat. At this stage the metal is soft enough to be hammered into shape or welded. When this has been done, it is allowed to cool, and the process is completed.