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CRANDON PROJECT

PYRITE PROCESSING STUDY

APPENDIX

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1980

Davy McKee
ENGINEERS AND CONSTRUCTORS

Govt Pub
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Davy McKee

2489/0
March 1980

PYRITE PROCESSING STUDY

TABLE OF CONTENTS

PAGE	
1	Pyrites Treatment - Facts Finding Trip Report by Messrs. Beall and F. Prado
3	D.K.H. Pyrite Process
4	Process and Development Department
5	Montecatini Pyrites
8	Process for Complete Utilization of Zinc Leach Residues
15	Processing of Solutions Accruing in Connection With Chloridizing Volatilization Processes
21	Recovery of Non-Ferrous Metal Impurities from Iron Ore Pellets by Chlorination
31	Processing of Pyrite Cinders
57	Use of Pyrite Cinders in the Production of Iron and Steel
89	Processing of Pyrites
113	Sherritt Gordon Process for Production of Elemental Sulphur and Iron from Pyrites
118	Boliden Process for Roasting Arsenical Pyrite
122	BASF Double Stage Process for Turbulent Layer Roasting of Arsenical Pyrites
128	An Evaluation of the Leaching Characteristics of a Pyrite Calcine Residue Sample for Hellenic Chemical and Fertilizers Co. Ltd., Athens, Greece
158	Pircon-Peck Process
177	Estimating Information Sulfuric Acid, Phosphoric Acid and D.A.P.

continued . . .

Davy McKee

2489/0
March 1980

PYRITE PROCESSING STUDY

TABLE OF CONTENTS

PAGE	
201	Labor Rates
202	Precious Metal and Nonferrous Metal Recoveries
203	Gypsum Pond Requirements
204	Estimates of: (Summary)
205	Receiving and Reclaiming
216	Roasting
228	Iron Recovery
262	Nonferrous Metals

Davy

From	F. Prado	To	L. Engle	Copies	J. Beall J. Palombo
Company					
Location					
Reference	FP/ast				
SUBJECT	Pyrites Treatment - Facts Finding Trip Report by Messrs. Beall & F. Prado			Date	March 15, 1979

On March 5th, we visited DINFD - London, Wigmore Street - to meet with Mr. H. E. Gibbs, Process Manager (NFM). Their capabilities and past experience on the subject were reviewed. Mr. R. C. Akroyd, Director, was out of town. In 1972, Power Gas Ltd. performed an evaluation of leaching characteristics of a pyrite calcine residue for Hellenic Chemical and Fertilizers Co. (Athens), in order to assess the feasibility of recovering the copper content of the residue via a leach-solvent extraction-electrowinning process. (Copy of report in our files.) They have no experience in roasting or chloridization of pyrites, but are well aware of current technologies. Mr. G. Collins briefly joined the meeting on this subject, and copies of some published material was provided.

When we questioned them on the flash-roasting Outokumpu process, amenable for very fine feeds and for the production of elemental sulfur and granulated mattes, Mr. Gibbs stated that Outokumpu technologies are available to the Davy organization.

DINFD had made arrangements for our visit to DIPED in Stockton and also preliminary contacts with Tecnicas Reunidas in Madrid.

On March 6th, we met at DIPED with Messrs. Arthur Harvey, Manager, Process Department (Agglomeration), and Robert L. Lapin, Section Head (Agglomeration).

The state of the art was reviewed and copies of published material obtained. Head Wrightson was responsible, in the middle 60's, for the design for Montecatini, Italy, of a 330,000 TPY pelletizing plant for pyrite cinders. The plant was modified for a 440,000 TPY output and, in the early 70's, expanded with a 600,000 TPY addition by H.W.

This group has no involvement in any other process activity related to pyrites such as roasting or leaching.

As previously arranged by telephone from London and Stockton, on the 8th of March, we met in Madrid with Tecnicas Reunidas personnel: Mr. Angel Arcocha, Director of Sales and Technology, and Dr. Eduardo Diaz Nogueira, Director of Investigations.

Tecnicas Reunidas is pursuing a development program for the utilization of the Spanish pyrites as ore for the non-ferrous metals production. Today the pyrites are mined for their sulfur, with some iron and non-ferrous metals recovered as by-products.

The TR approach consists of a bulk flotation concentrate for the non-ferrous values, leaving the pyrites with the tailings. The flotation does not require fine grinding, and the pyrite residues are intended to be returned to the mining cuts. TR claims to have a technical solution for the underground stabilization of those tailings. They are also pursuing the direct leaching (pressure ?) of the concentrates to avoid smelters.

TR is willing to sell know-how and engineering. They were involved, through Holmes and Narver, in the bidding on the Exxon's Zinc Study ($1.5 million).

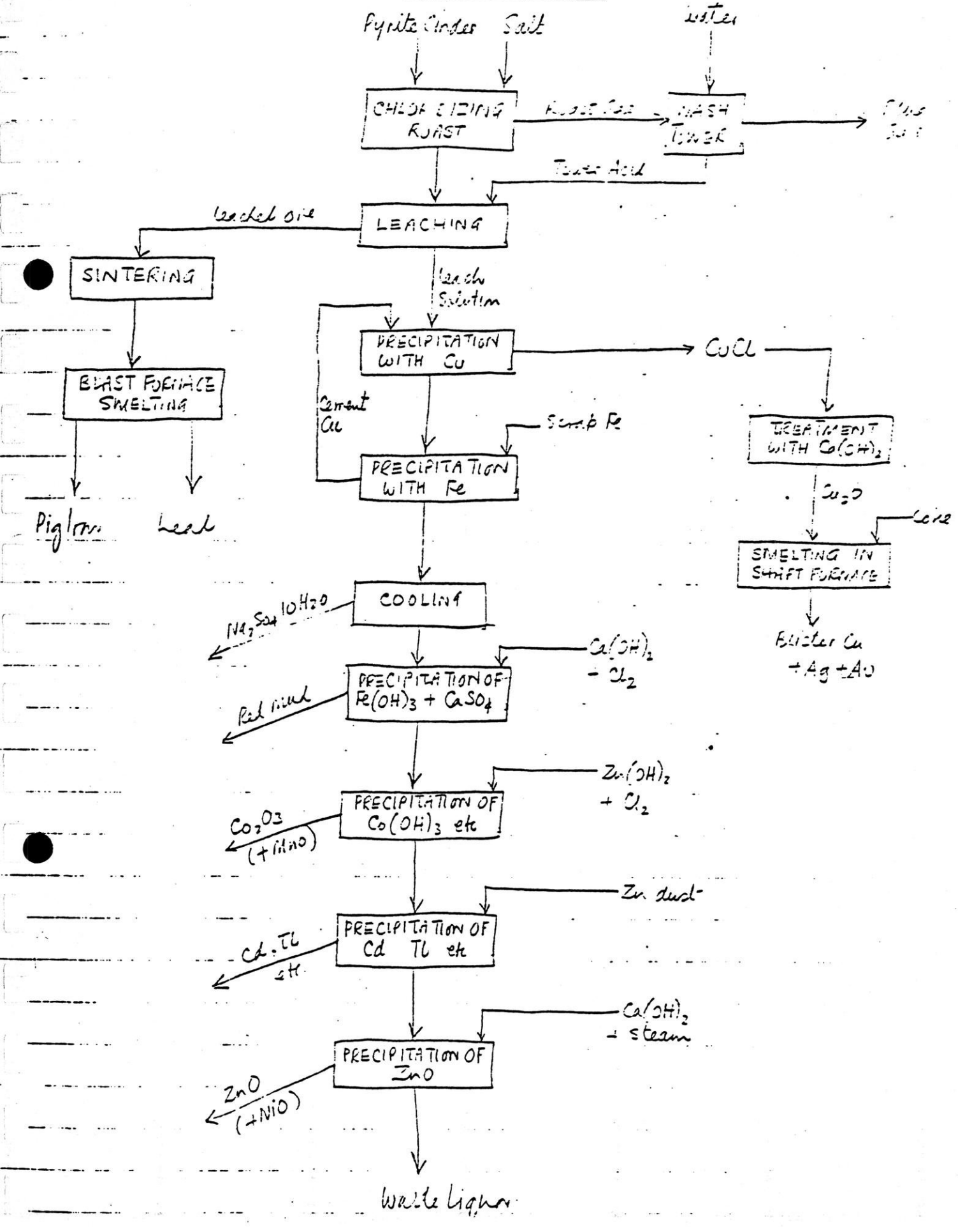
The authorization to visit the Huelva facilities - pyrites roasting for sulfuric acid manufacture - requested by TR was denied by Española Rio Tinto on the grounds of agreements with Lurgi.

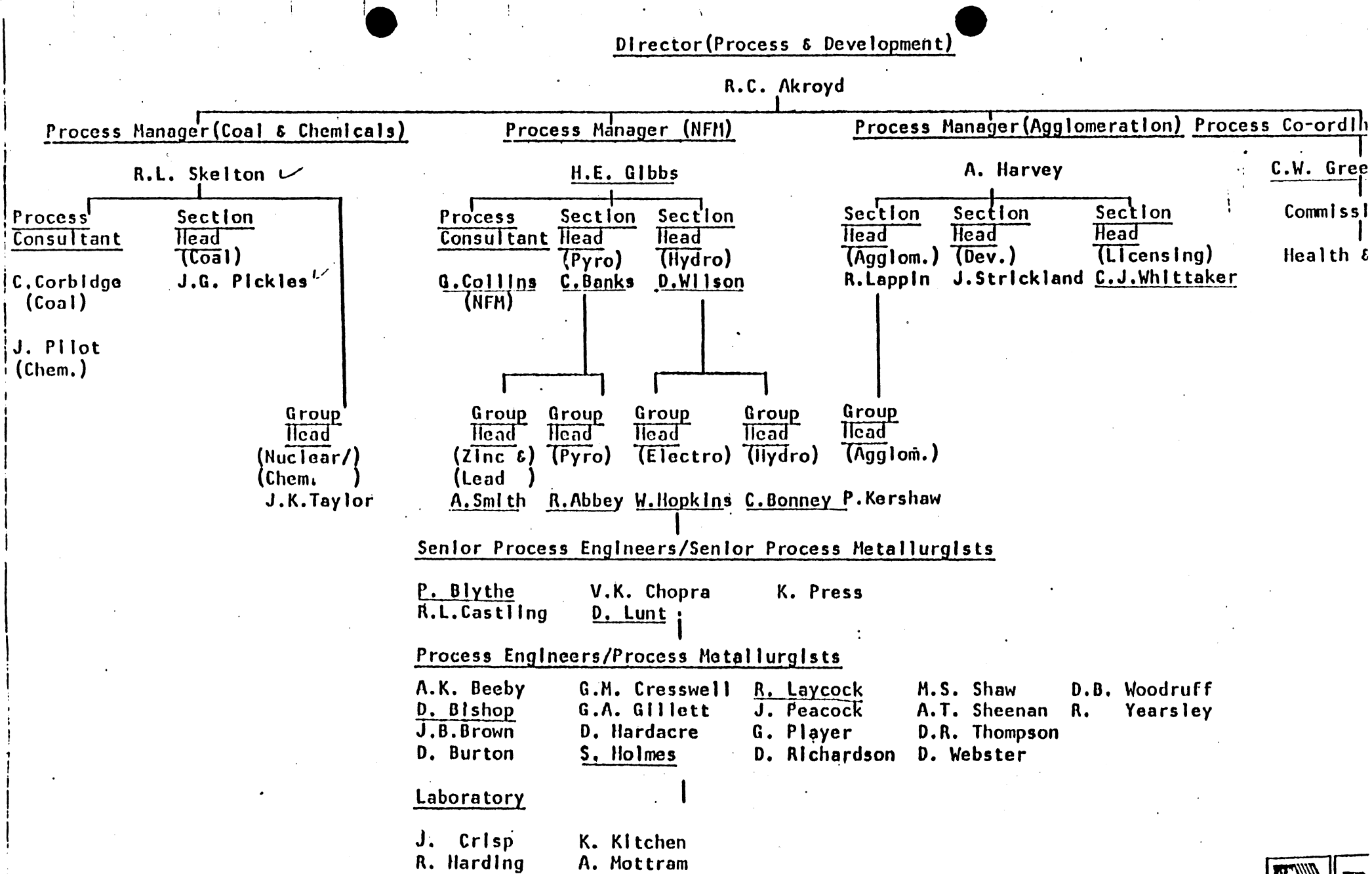
On the 9th of March, we visited the Huelva industrial zone, where pyrites from the Rio Tinto mines are processed for the manufacture of sulfuric acid used in the fertilizer complex.

The pyrites, already ground, are received in bulk by railroad. One of the facilities, ERT, processes up to 1000 TPD of pyrites. All three plants in the area use Lurgi roasters, and the cinders are trucked to the port for shipment. Some pyrites are also exported.

F. Prado

D.K.H. PYRITE PROCESS





PROCESS AND DEVELOPMENT DEPARTMENT

Davy International (Minerals & Metals) Ltd
Process Engineering Division
Non-Ferrous Metals Division

RCA
5 January 1

McKee
ENGINEERS AND CONSTRUCTORS

RECEIVED
MAR 30 1979
MINING & METALS SALES

INTER OFFICE COMMUNICATION

TO John Beall - Lakeland DATE March 27, 1979

FROM Roy J. Bierman - Hibbing

SUBJECT Montecatini Pyrites

CUSTOMER _____ CONTRACT NO. _____

(Confine Memo to one subject to facilitate follow-up)

When you were here I promised you the information on the Montecatini Pyrites plant in Follonica, Italy.

Well, I finally found it. Although it is limited in detail, here it is. There may be someone in Cleveland who was familiar with this job.

Roy J. Bierman

Roy J. Bierman

RJB/sf

cc: RJB
File

Enclosure

Montecatini

Pelletizing Plant

Follonica, Italy

McKee

A process utilized by Montecatini extracts sulfur from pyrites mined near the Italian Mediterranean coast, producing a by-product iron ore residue highly suited for iron and steel making. In the processing plant, hematite obtained from roasting is further reduced to an artificial magnetite which undergoes magnetic separation to obtain a concentrate with a 65 to 70 percent iron content.

Adjacent to the pyrite processing plant, a pelletizing facility has been constructed which employs a continuous grate system to produce approximately 1100 metric tons per day of high-purity, durable pellets. Basic features of the plant, which was completed in 1964, were developed from designs furnished by Arthur G. McKee & Company.

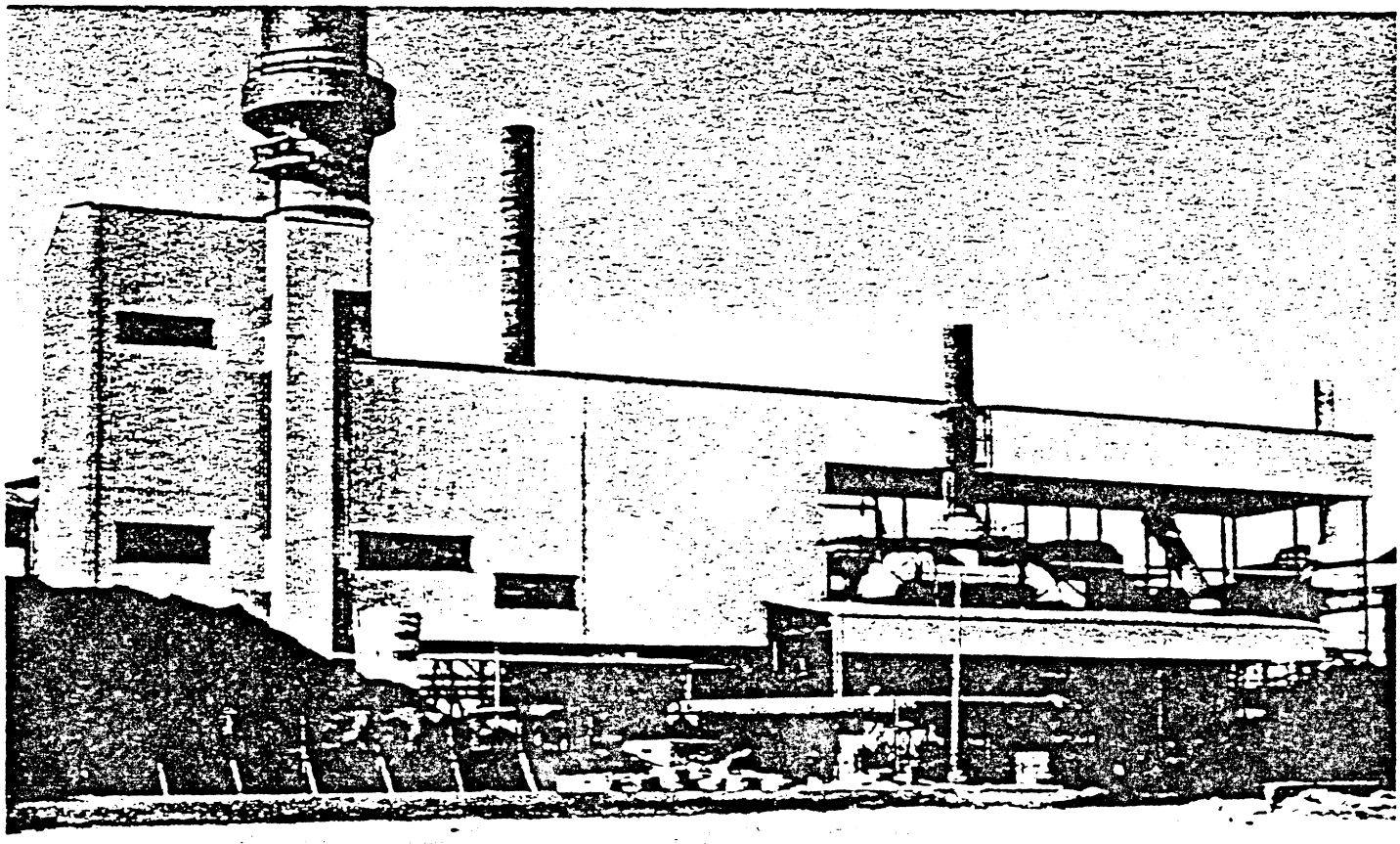
The pelletizing process involves the forming of balls in a drum. After balling is completed, green balls are fed onto a 6-1/2-foot-wide horizontal grate which is divided into four processing areas where they are subjected to updraft drying, downdraft drying, preheating, burning and updraft cooling.

Scope of Project

Complete iron ore pelletizing plant for producing 1100 metric tons per day of pellets from pyrites. Plant equipment includes a balling circuit and horizontal grate pelletizing machine whose design was developed by McKee.

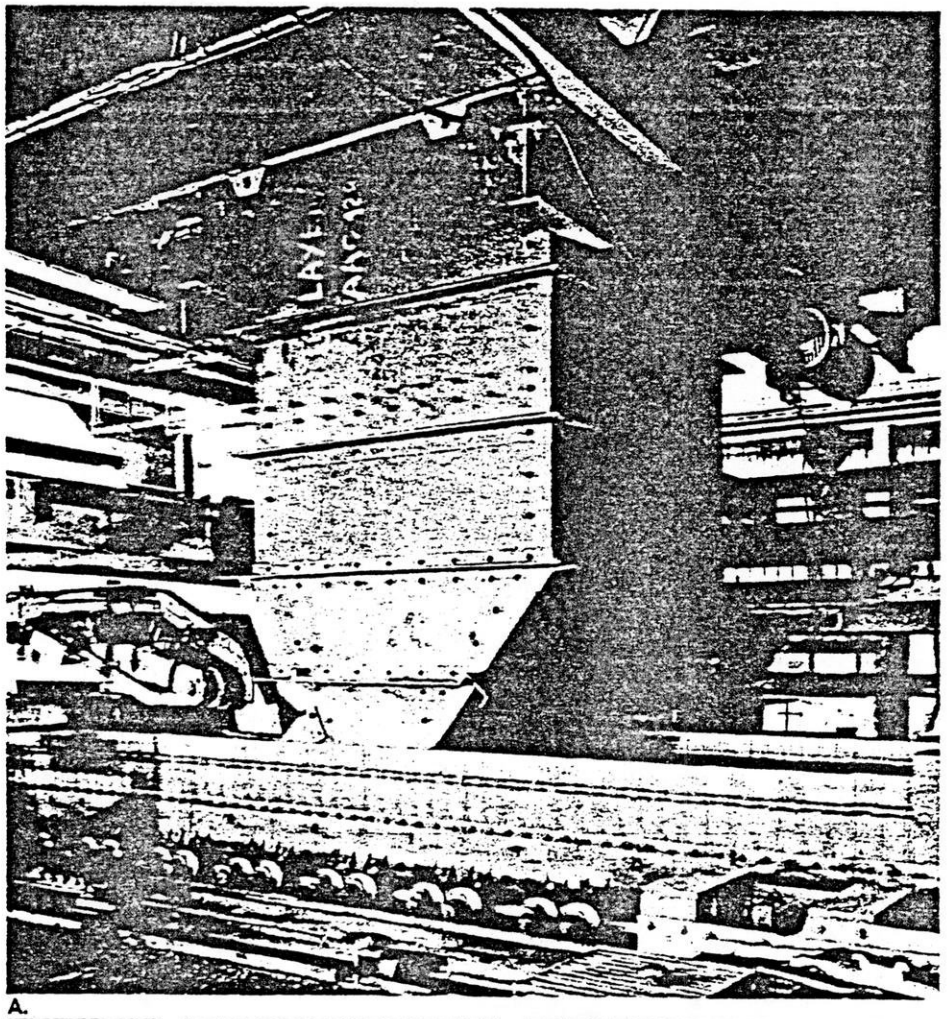
McKee Services

Process design, partial engineering and start-up services in association with Head Wrightson Iron and Steel Engineering Ltd. of England.



Montecatini

Pelletizing Plant
Follonica, Italy

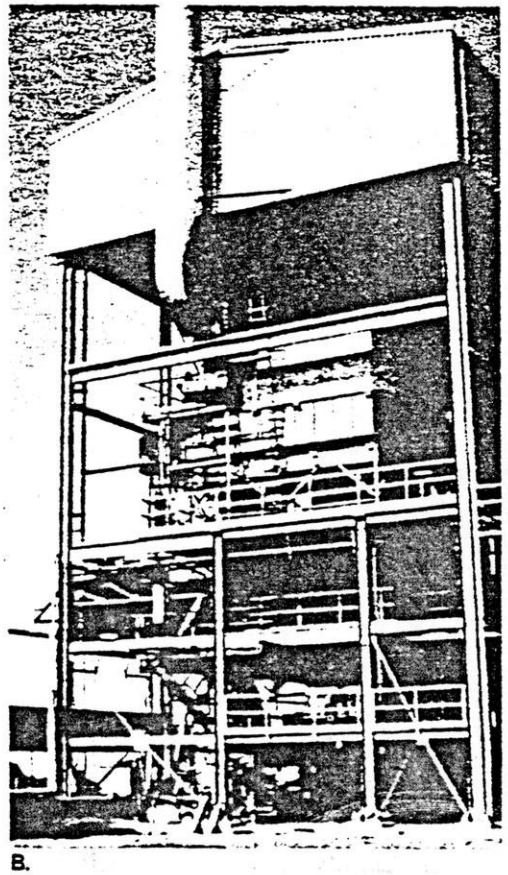


A.

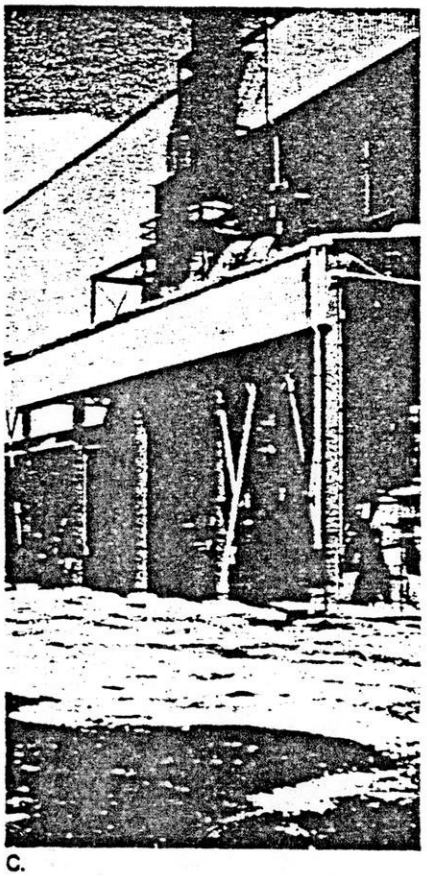
iew of the pelletizing machine showing the feed arrangement and hearth layer feed bin.

B. Exterior view showing process fan aisle.

C. Discharge end of the pelletizing machine.



B.



C.

Process for Complete Utilization of Zinc Leach Residues

by Alfred Roeder, Helmut Junghan, and Herbert Kudelka

Filter residues are mixed in high proportion with pyrite cinders and subjected to a modified chloridizing and sulfatizing roast in standard multiple-hearth furnaces. By additions of sodium chloride and of suitable sulfur-bearing materials, the metals Cu, Zn, and Cd, as well as Ag and Au, are rendered soluble to a large extent. By leaching with acid, Zn, Cu, Ag, Cd, and Au are eluted. The remaining iron oxide is conveyed into sintering or pelletizing plants.

If the residues contain in addition undesirable elements such as As, Sb, and Sn, they are first subjected to a chloridizing and sulfatizing roast; Cu, Zn, and the noble metals are extracted by leaching. The fine-grained iron oxide, containing As, Sb, and Sn, is either discarded or purified from these elements by means of chloridizing volatilization in a reducing atmosphere. Given sufficiently high contents, these accompanying elements can be recovered economically.

In recovering the nonferrous metals from the solutions, the classical precipitation and cementation processes, well tried under plant conditions, are compared with ion exchange processes with regard to cost and process efficiency. Pilot plant results of the application of ion exchangers to solutions of higher concentration are given.

INTRODUCTION

The treatment of zinc filter residues is of great economic importance in view of the fact that in the production of zinc electrolyte approximately 10% of the zinc will at first remain in the residue as zinc ferrite. In order to give a general idea of the absolute quantities involved, Table I shows the zinc production capacities of the plants at present installed in the free world. At over 3.2 million tons, electrolytic production ranks first. Apart from the electrolytic process, only the Imperial Smelting Process has achieved high rates of growth in the past few years. Given a fraction of 10% insoluble zinc in the residues, a global 300.000 tons of zinc a year will be found in the residues, an amount which is steadily increasing.

Due to the large number of accompanying elements, the metallurgical problem posed by the treatment of filter residues is an extremely interesting one. There are numerous pyrometallurgical and hydrometallurgical processes suggested for the treat-

Table I—Global zinc production capacity (1967-68).

Process		Zinc metal metr. t/a	
Vertical retort (New Jersey)	NJ	412.000	
Horizontal retort	HR	917.100	
Imperial Smelting Process	ISP	774.000	
Electrolytic	EL	3.253.600	(57%)
Electrothermal	ET	298.000	
Various		20.000	
Total		5.674.700	

Table II—Range of contents in zinc leaching residues.

Major constituents	Zn	14 — 28 %
	Fe	18 — 45 %
Group A	Cu	0,35 — 2,7 %
	Pb	0,7 — 6,0 %
	Cd	0,06 — 0,5 %
	Ag	60 — 1.200 g/t
Group B	As	0,07 — 0,4 %
	Sb	0,015 — 0,04 %
	Sn	0,02 — 0,65 %

..., physico-chemist, is head of the Research Department; DR. HELMUT JUNGHAN and DR. HERBERT KUDELKA ... Research Department, Duisburger Kupferhütte, Duisburg, ...

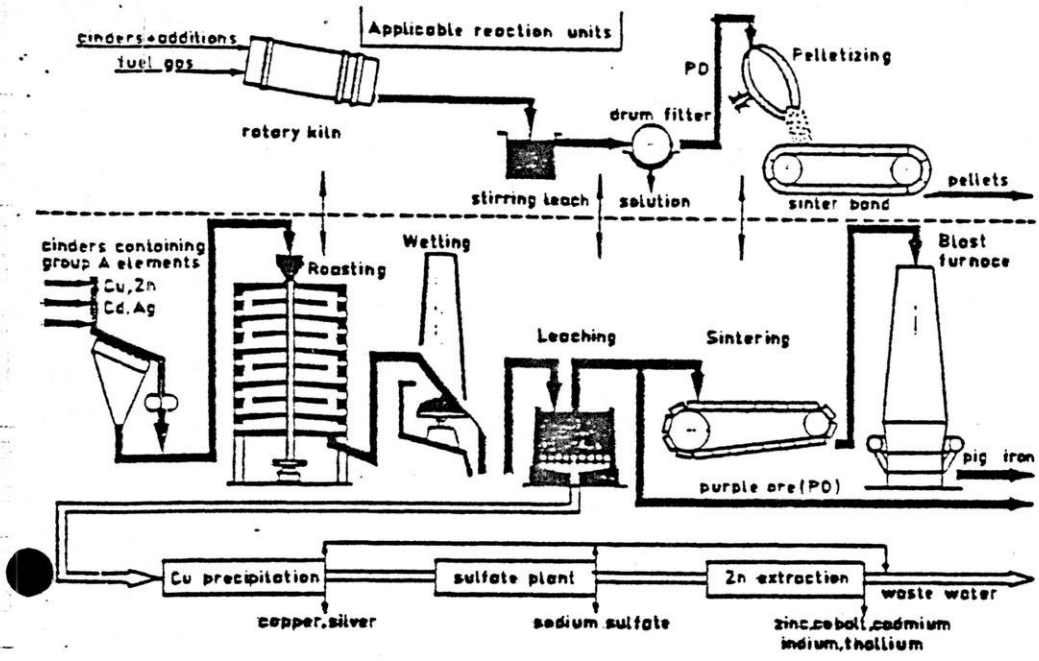


Fig. 1. Flow sheet of the chloridizing and sulfatizing roasting process.

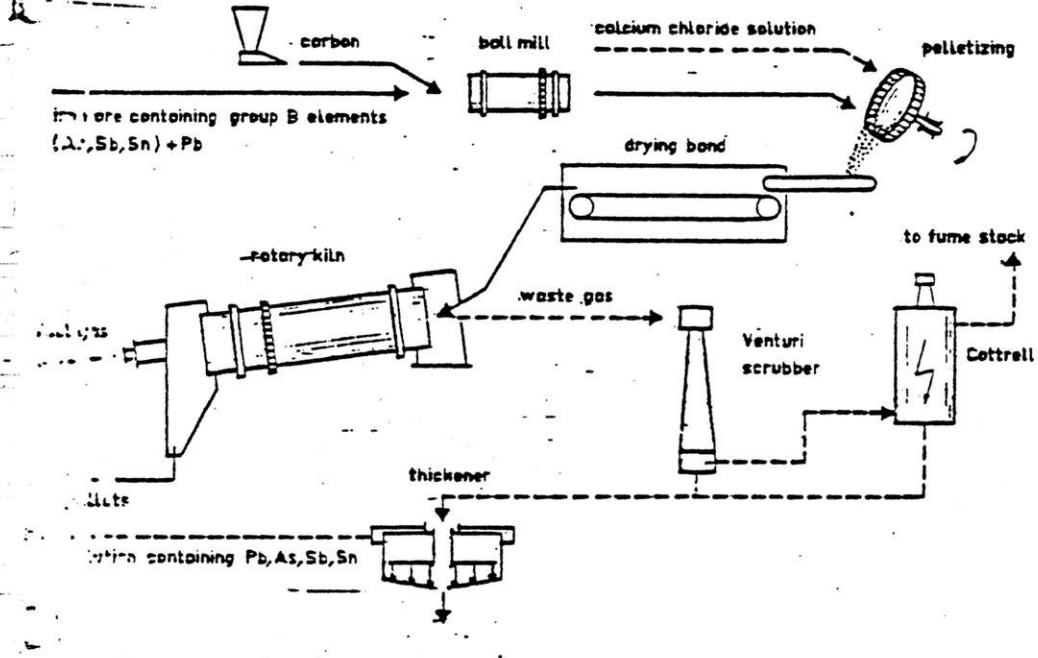


Fig. 2—Flow sheet of chloridizing volatilization in a reducing atmosphere.

...of these residues, some of which are being successfully applied.[2] What has not been considered so ... the process of chloridizing and sulfatizing roasting applied to pyrite cinders. In this paper, the ...sis will be on the successful treatment on a ...tion scale of these filter residues in accordance ... this process, and of the nonferrous metal-bearing ...ditions obtained. In conjunction with a further ..., before now tried only at the pilot plant level, ... chloridizing volatilization in a reducing at... re, practically any kind of filter residues can ...ed.

... shows the range of contents of the ele... the filter residues, determined on the basis ... taken in 1967 from an amount of about ... Apart from zinc and iron, the major ..., elements are divided into Groups A ... division, which will be adhered to in the ... examination, was made on the basis of ... behaviour of the elements.

For example, it is one of the features of the elements in Group A—i.e., copper, lead, cadmium and the noble metals—that they form stable chlorides even at higher partial pressures of oxygen, in contrast to the elements in Group B, i.e., arsenic, antimony, and tin.

For the purpose of introduction, Fig. 1 gives a flow sheet of the chloridizing and sulfatizing roasting process which is preferably suited to the purification of pyrite cinders containing elements of Group A.[3] The pyrite cinders are mixed with 10% sodium chloride. In the multiple-hearth furnace the mixture is subjected to a metallurgical extraction process at 600°C during oxidation of sulfide. The accompanying elements are converted into sulfates and chlorides which are separated from the iron oxide in the subsequent percolation leach.

In accordance with this process, over 2 million tons of pyrite cinders a year are treated by Duisburger

Kupferhuette. The purified iron oxide, the so-called purple ore, is partly sold and partly agglomerated at the plant and then processed to various special grades of pig iron. The nonferrous metals and the sodium sulfate are recovered from the solutions. The upper section of the figure suggests that the indicated steps of the process may be replaced by others; thus the multiple-hearth furnace may be replaced by a rotary kiln and percolation leaching by stirred suspension leaching, while agglomeration can also be effected by pelletizing.

If, in addition to that, the Group B elements, i.e., As, Sb, and Sn, are also to be recovered or to be separated from the iron, the process of chloridizing volatilization in a reducing atmosphere[1] is applied, a flow sheet of which is shown in Fig. 2. After grinding, the ore is mixed with carbon and pelletized with a calcium chloride solution.[4] The pellets are dried and burned in a neutral or slightly reducing atmosphere in a rotary kiln. The compounds thus volatilized are removed from the gas by means of scrubbing, and may be recovered from the solution.

PROCESSES FOR EXTRACTION OF ZINC FILTER RESIDUES

The two basic processes outlined in the introduction make it possible for zinc filter residues to be treated in a number of ways which are shown in Fig. 3. As a rule, the method in accordance with no. 1 in Fig. 3 provides for the addition of up to three percent by weight of residues containing Group A as well as Group B elements to standard pyrite cinders. After admixing NaCl and iron sulfide, which may be required as a source of sulfur, this feed mix is subjected to chloridizing roasting in multiple-hearth furnaces, and the calcine is leached by the percolation process.[5] This method has been employed on a large scale for some time. The maximum amount that can be added is determined by the fine grain size of all zinc filter residues, which exercises an unfavourable influence upon the time required by the standard percolation process. In addition to that, a limitation in the treatment of residues containing Group B elements is due to the fact that a content of these metals in the iron oxide is not reduced by roasting and leaching. The amount of B elements permissible is exclusively determined by the quality requirements for the purple ore (PO) obtained.

Even higher proportions of Group A filter residues of up to 25% by weight can be treated in combination with pyrite cinders, if the application of the economically favourable percolation process even to very fine—grained feed mixtures is made possible by means of the "gypsum supporting effect".[7] For a framework of gypsum crystals to be formed within the material bed, the calcines are sprayed with $CaCl_2$ solution in the step of the process which precedes the percolation leach and is called soaking. Gypsum crystals are formed within the material layer by reaction with the acidic sulfate solutions which are used for leaching. In the course of the leaching process, good permeability of the bed is maintained by means of stabilizing a larger intergranular volume. This method, which is in accordance with no. 2 in Fig. 3, is also applied at Duisburger Kupferhuette on a large scale. Feed material containing 40–50% material of grain size below 60 microns may be leached in this way.

Another approach, which has only been tried at pilot plant level so far, in accordance with no. 3 in Fig. 3 combines the treatment of Group B filter residues and of the flue dust obtained in roasting pyrites. This flue dust also contains higher amounts of As, Sb, and Sn. The first steps of this method correspond to those of the process according to no. 2 in Fig. 3; however, an iron oxide is obtained that can not be utilized on account of its undesirable minor constituents so that it will have to be subjected to a subsequent purification[4] (see 3a in Fig. 3). For that purpose, the leached

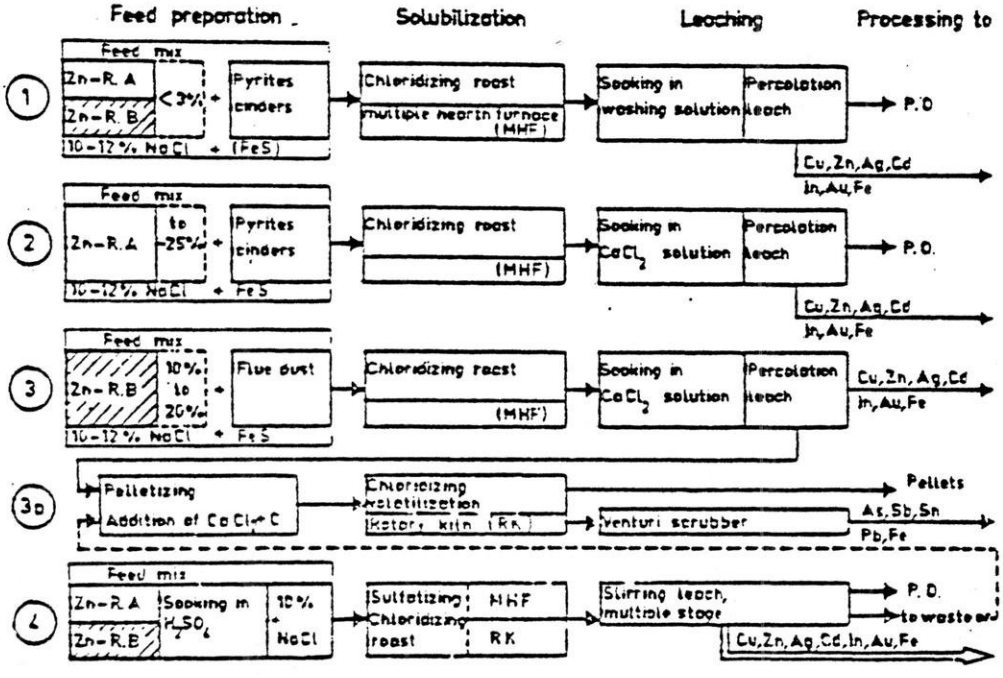


Fig. 3—Processing of zinc residues by different combined extraction methods.

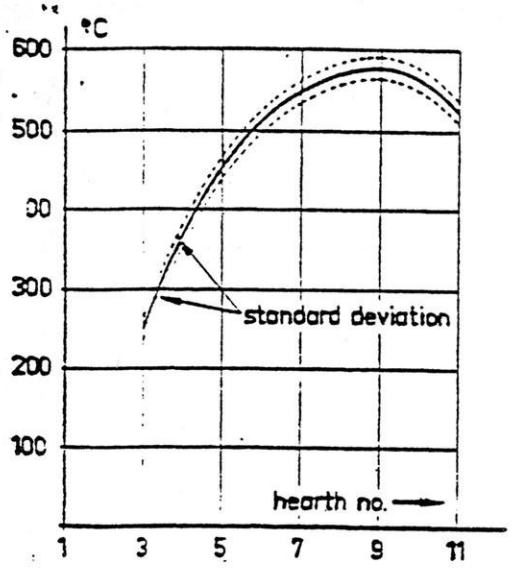


Fig. 4—Material bed temperatures in 11-hearth roaster for optimum solubilization.

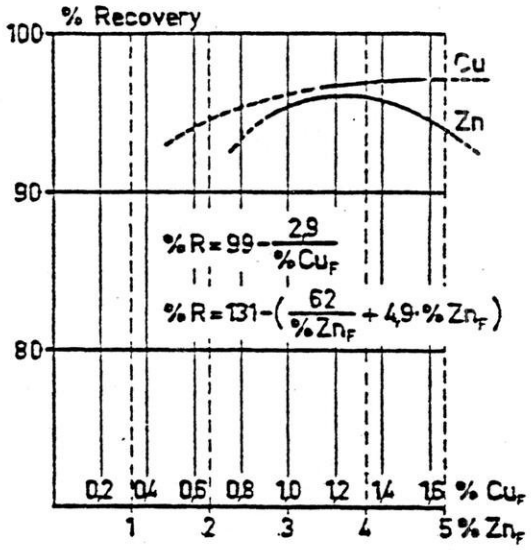


Fig. 5—% Recovery of Cu and Zn after roasting and leaching vs. content in feed.

material is mixed with carbon and $CaCl_2$, pelletized and subjected to chloridizing volatilization in a rotary kiln in a slightly reducing atmosphere, the minor constituents being removed from the gas by means a Venturi scrubber. The iron oxide is obtained in the form of pellets, i.e., in a form suitable as a feed for blast furnaces.

The method according to no. 4 in Fig. 3 has only been applied so far on a laboratory scale: however it has promises for the treatment of zinc residues of both groups in a separate process. With additions of $CaSO_4$ and NaCl, a sulfatizing and chloridizing roast can be effected in multiple-hearth furnaces or in rotary kilns. In this case, extraction by means of acid suspension leaching will be preferable. In case of treating leach residues of Group A, the resulting iron oxide can be added to standard PO for sintering, while the leached material from Group B residues will either be discarded or subjected to a pigment purification step (3a).

The treatment of metal-bearing solutions, dealt with in the second part of the present paper, will finally be illustrated by the example of solutions obtained in the last-mentioned process, and especially marked by a boldly drawn arrow.

In regard to the extraction processes mentioned the economical recovery of valuable metals is the only point of consideration. More important is the amount of minor constituents, which has to be as low as possible because the iron oxide is to be used as feed for blast furnaces. To obtain optimum extraction results, there must be maintained in the chloridizing process a definite course of reaction which can be characterized by material bed temperatures. Fig. 4 shows the desired temperature function in a 11 hearth furnace, the standard deviation being as indicated. Permissible deviations amount to ± 10-15°C, and they will have to be adhered to with particular exactitude in the case of higher metal contents in the feed mix, particularly when larger amounts of zinc leach residues are added.

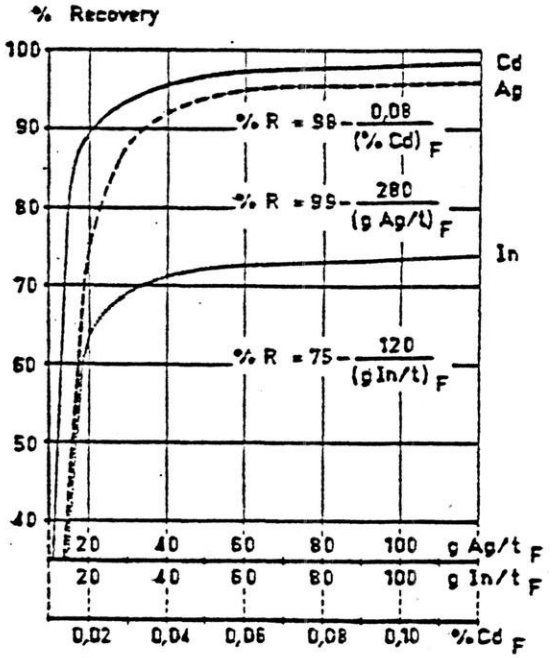


Fig. 6—Recovery of Ag, In and Cd vs. content in feed.

To give an example of the recovery of metal, Fig. 5 shows results for Cu and Zn vs. metal content in the feed mix in the case of higher additions of zinc leach residues. In the case of feed mixtures of pyrite cinders with the usual contents of 1.0–1.5% Cu and 2–3% Zn, recovery amounts to over 95% as a rule. In

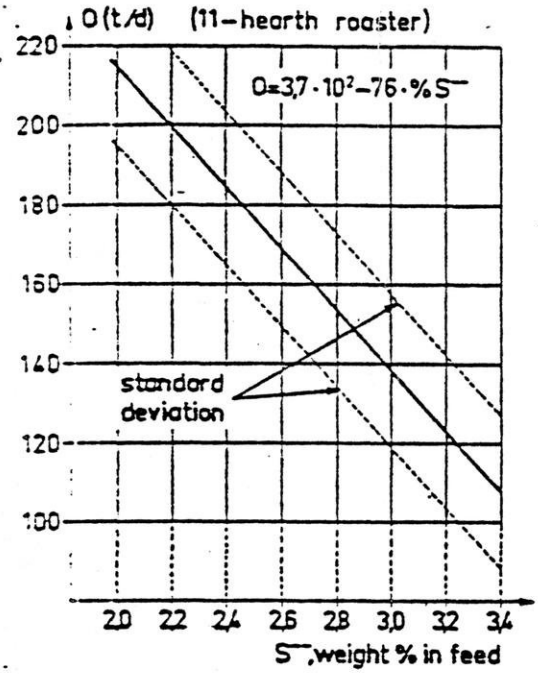


Fig. 7—Output, t/d vs. S^- in feed.

the presence of higher metal contents such as may occur, for example, in the case of Zn owing to higher additions of zinc filter residues, a decrease in recovery is suggested, so that there is no point in further increasing the zinc content in the standard chloridizing roasting process which makes use of sulfide carriers, and, particularly, of iron sulfide as a sulfurization agent.

Ag, Cd, and In contents represent a high proportion of the values to be recovered by the treatment of zinc leach residues. Fig. 6 shows the recovery of these elements which corresponds to the data expected of pyrite cinders if allowance is made for the higher metal content in the zinc residues. A decisive factor in the economical treatment of pyrite cinders as well as of zinc filter residues is the daily output of a furnace or the roasting capacity per square metre of hearth area, respectively. Output, however, is substantially determined by the sulfide content in the feed. Fig. 7 shows this dependence which may be represented to a good approximation by a straight line in the vicinity of the operating point. As additions of sulfur in the form of FeS in some excess of stoichiometry are required to extract the nonferrous metals in the feed, the figure explains the considerable decrease in output if higher amounts of zinc leach residues are added. This is caused by the fact that output in the roasting process is substantially determined by the rate of oxygen transport in the material bed.

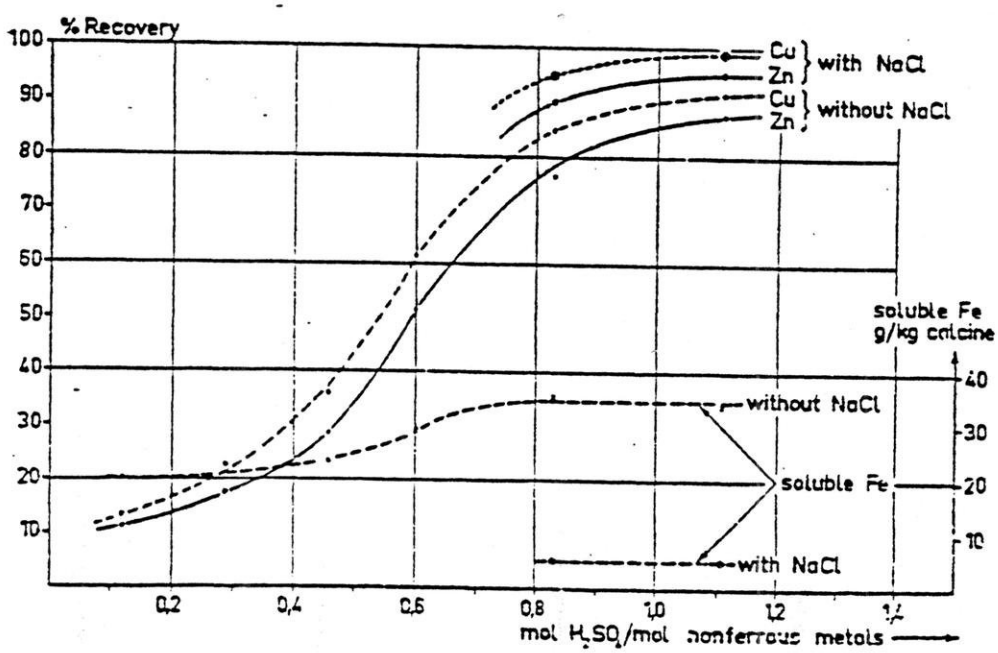
The disadvantages in evidence here can be avoided by the use of H_2SO_4 as a sulfurization agent. Fig. 8 shows the results of a combined extraction process with the addition of sulfuric acid and rock salt. For a reaction period of about three hrs corresponding to the average residence time in the roasting furnace for the standard extraction process, over 95% of the nonferrous metals will be recovered, given 17.5% Zn, 1.6% Cu, and 37% Fe in the zinc leach residue. The residue remaining after leaching still contains 0.04% Cu, about 0.8% Zn, and about 52% Fe. The addition of NaCl leads to an improvement of extraction results, and, in addition, effects an approximately six-fold reduction of the fraction of soluble Fe. In general, the dependence of the recovery of nonferrous metals on the molar ratio of the sulfurization agent, H_2SO_4 in this case, to the sum of the nonferrous metals to be extracted was as expected.

The problem to be discussed in the following is that of treating leaching solutions, which is of particular interest in this context.

TREATMENT OF SOLUTIONS OBTAINED

The average composition of the solution, obtained by the separate treatment of zinc residues (no. 4 in Fig. 3) is shown in Table III.

Numerous well-known processes are applicable to the recovery of the content of valuable metals (Cu, Zn, Cd, Ag, and In), such as precipitation and cementation reactions, pressure reactions, ion exchange, and liquid-liquid extraction. The number of useful



...Recovery of Cu and Zn ... kg soluble iron after separ... of filter residues us... H_2SO_4 as a source of sulfur, ... without addition of

Table III—Average composition of metal-bearing solution. (see Fig. 3).

Ion	concentration g/l
Cu^{++}	12
Zn^{++}	135
Fe^{++}	26
Cd^{++}	2
Ag^{+}	0.3
In^{+++}	0.15
Cl^{-}	90
SO_4^{--}-S	80
H^{+}(HCl)	70

Table IV—Production costs, exclusive of capital cost, for treatment of leaching solution according to Fig. 9.

Solution	Product	Cost ($/kg)
Cu^{++}	Cement Copper	0,04 + 0,09 = 0,13
SO_4^{--}	Sodium Sulfate	0,013
Fe^{++}	Iron Hydroxide	0,09
Cd^{++}, In^{+++}	Cd – In Sponge	1,30
	Cadmium Metal, Indium Hydroxide	2,75
Zn^{++}	Zinc Oxide	0,04

methods is limited by the necessity of recovering these metals in a manner as economical as possible.

The most reliable figures for production costs are available for the classical process which consists of a combination of cementation and precipitation steps (Fig. 9). In this process copper and silver are first precipitated by adding scrap iron, melted, and subjected to electrorefining. The next step consists in removing the sulfate from the solution since it would lead to the precipitation of gypsum, disturbing further operations. To this end, NaCl is added and the solution cooled to about – 2°C, with Glauber's salt ($Na_2SO_4 \cdot 10\ H_2O$), being precipitated. The salt is separated and processed to anhydrous Na_2SO_4. Subsequently, the solution is treated with chlorine, the iron oxidized to the trivalent state, precipitated by adding lime and separated from the solution together with the residual sulfate. The iron hydroxide—gypsum sludge obtained cannot be utilized in an economical manner. By adding zinc dust, cadmium and indium are recovered in the form of a mixed Zn-Cd-In cementation product and subsequently produced in pure form in a relatively complicated amalgam exchange and distillation process. In the final step, zinc is precipitated in the form of zinc hydroxide by adding lime to bring the solution to pH 6–7; subsequently the zinc hydroxide is calcined to zinc oxide.

It is obvious that, in accordance with this process, the valuable metals in the solution are recovered. In addition sodium sulfate is produced as a saleable material. Calculations of the pure costs of operation, exclusive of capital costs are compiled in Table V for the individual valuable materials. These calculations are based on a volume of solution of about 1 000 cubic metres treated per day. The right-hand column states the cost, in terms of dollars/kg, of the individual step indicated in the left-hand column.

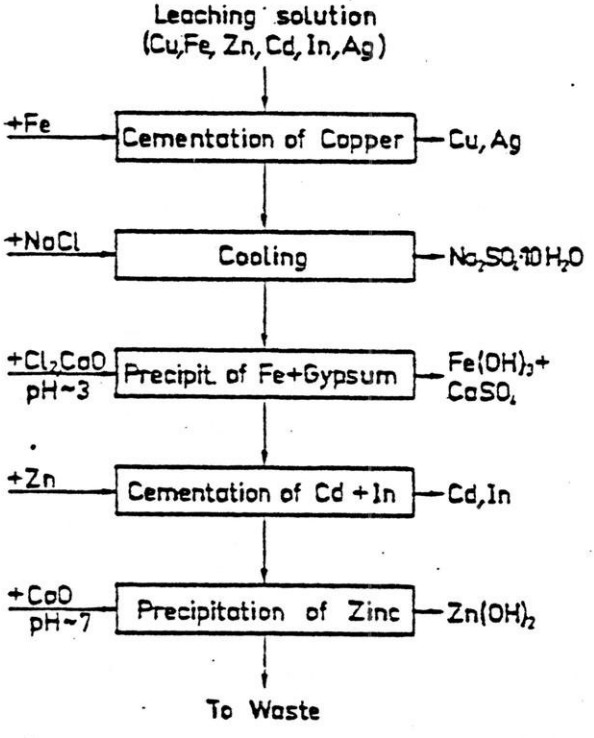


Fig. 9—Flow sheet of the treatment of leaching solution.

It is obvious that the precipitation and treatment of the cadmium and indium is the costliest step in the process.

These operating costs are precisely known because, following this process, 25,000 tons of copper, including 50 tons of silver and one ton of gold, 200,000 tons of sodium sulfate, 50 tons of cadmium, up to one ton of indium, and 55,000 tons of zinc are annually produced by Duisburger Kupferhuette.

It would be easy to compare this classical process with a process for the treatment of solutions, consisting exclusively of ion exchange and extraction methods. Processes for separating copper (using LIX 64, General Mills Co.) and copper + iron + zinc

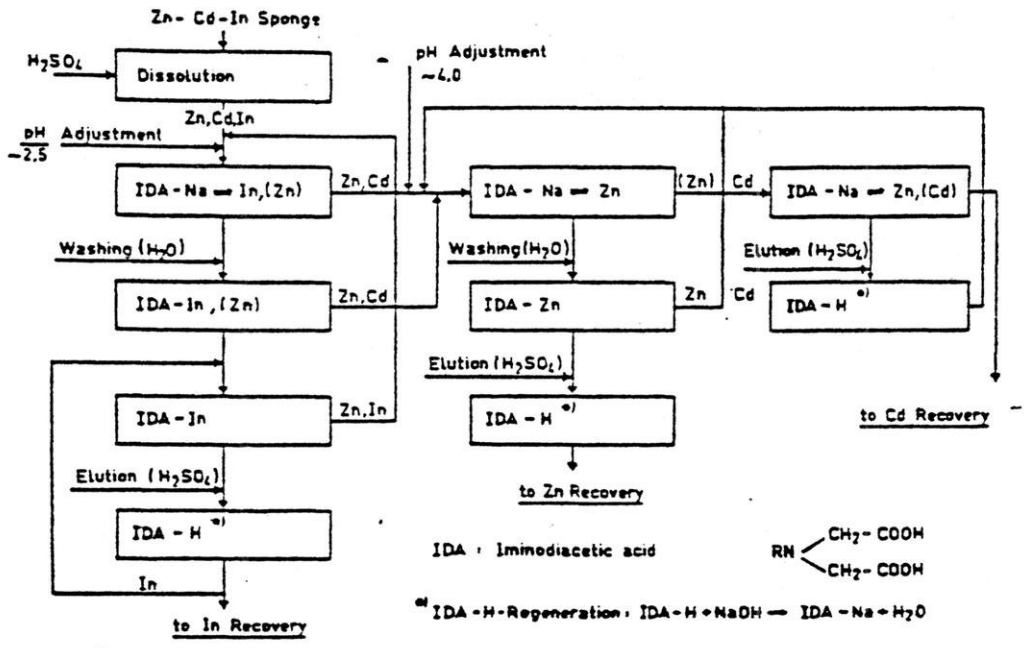


Fig. 10—Treatment of Zn-Cd-In cementation product by ion exchange.

(Dowex A 1, Lewatit CA 9207); for the extraction of copper–zinc with phosphoric acid ester (for example, ethyl hexyl phosphoric acid - E.H.P.A.); for the separation of copper from zinc (+ Cd, In, Ag, etc.) by anion exchange (Dowex, 1 or 2, Amberlite IRA 400, 401, 401S, Lewatit M 500, etc.) are well known. In comparison to the classical method of treatment, such processes cannot be economical for the treatment of solutions of relatively high concentration, for the simple reason that processes which separate ions in aqueous solution (exchange or extraction) will inevitably have to be followed by another step to produce a solid phase. As against that, the specific precipitation and cementation processes mentioned above have the advantage of simultaneously separating the metals and precipitating them from aqueous solution.

In the treatment of solutions under consideration here, ion exchange processes therefore promise profitable application only to the treatment of the mixed Cd-In sponge obtained by means of zinc dust cementation. At $1.45/kg of Cd + In, this step is also the most expensive one in the whole process. Fig. 10 shows a flow sheet for the separation of the Zn-Cd-In sponge by ion exchange. It is partly based on work carried out in our laboratory and at the moment it is being tried at pilot plant level.[9] The exchanger used is a weakly acidic cation exchanger of the iminodiacetic acid type in its Na form. Such chelating resins are known by the name of Dowex A 1 (Dow Chemical Co.) or Lewatit CA 9207 (Bayer Leverkusen). The metals Zn, Cd, and In are adsorbed on this resin with decreasing stability in the order In > Zn > Cd. The separating factors In/Zn and Zn/Cd were found to be about 2-3. If, therefore, the Zn-Cd-In sponge is dissolved in sulfuric acid and the solution fed into an ion exchange column, all the indium and part of the zinc will be adsorbed. The charging of the column is interrupted before indium breaks through; after washing, the adsorbed zinc is eluted by means of indium solution until breakthrough.

The column charged with indium is eluted with 2-4 n sulfuric acid, pure indium solution being obtained. The Zn- and Cd-bearing effluent of the first charge is fed into a second column in which sodium is exchanged for zinc until the latter breaks through. After washing, pure zinc solution is eluted with sulfuric acid. The effluent from the second column contains all the cadmium and some zinc. It is fed into a third exchange column of the same type, the effluent from which is a pure cadmium solution. The solution eluted from this column is recycled into previous stages of the process, as are the washing solutions obtained in the preceding exchanging steps. In each of the three exchange columns, the resin will finally be present in its H form from which it is regenerated to its Na form by treatment with sodium hydroxide solution.

Pure operating costs of this process, exclusive of capital cost, are estimated to be about $0.30/kg of cadmium and indium.

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Processing of Solutions Accruing in Connection with Chloridizing Volatilization Processes

by Heinz Walden

DESCRIPTION OF SELECTED CHLORINATION METHODS PROCESSING METAL CHLORIDE SOLUTION

The use of metal chloride solutions is of interest in connection with the chloridizing roasting and the chloridizing volatilization. The principle of these two processes is shown on Fig. 1.

The basic difference is the chlorination temperature. Relatively low temperatures are used in chloridizing roasting in which the chlorides formed have the lowest possible steam pressures and are not volatilized. The separation of the chlorides from the residue takes place during subsequent leaching.

In chloridizing volatilization, separation of the chloride from the residue is carried out by volatilization. Therefore, the process takes place at comparatively high temperatures when the metal chlorides are under high vapour pressure.

The chloridizing roasting process has already been used for decades in the extraction of non-ferrous metals out of pyrite cinders. The pyrites are mixed with common salt and are then roasted in multiple hearth furnaces at 500–600°C. In this process, the non-ferrous metals are converted into chlorides and partially into sulphates. The chlorides are then separated from the pyrite cinder by leaching and collected in a solution. The pyrite free of non-ferrous metal, the so-called purple ore, serves as raw material for the iron production. The valuable metal contents are separated from the leaches. Approximately two million tons of pyrite cinders are used per year by, for example, Duisburger Kupferhütte, according to this process.

The process for chloridizing volatilization can also be used for the extraction of non-ferrous metals from pyrite cinders. Chlorine gas, hydrochloric acid gas or chlorides, such as $CaCl_2$, NaCl, can be used as chloridizing agents. The chlorination can be carried out in the shaft furnace, rotary kiln, fluid bed or moving bed.

Lurgi Gesellschaft für Chemie und Hüttenwesen m.b.H. in Frankfurt and Duisburger Kupferhütte in Duisburg have jointly set up a shaft furnace large-scale pilot plant with a capacity to handle 100 tons of pyrite cinder per day by chloridizing volatilization.

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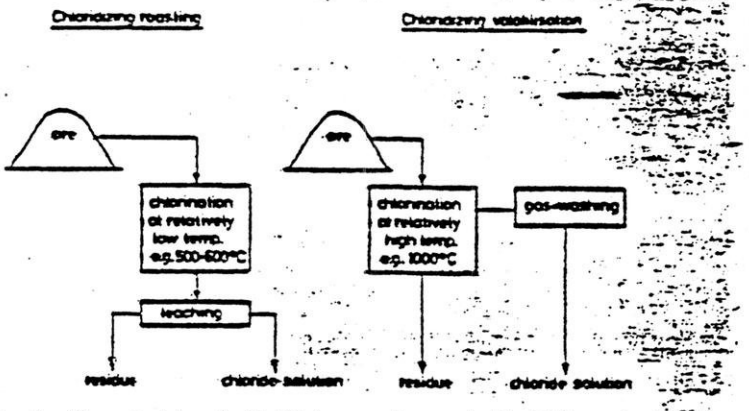


Fig. 1—The principle of chloridizing roasting and chloridizing volatilization process.

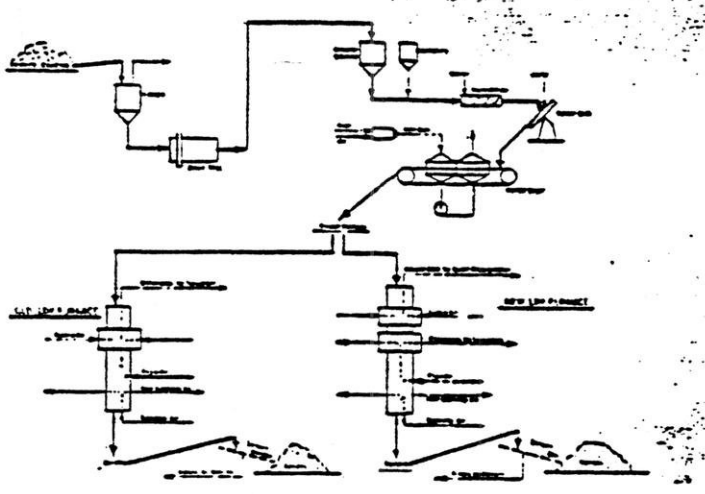


Fig. 2—Principle flow-sheet of the 100 tpd LDK pellet chlorination plant.

Fig. 2 shows the design of this so-called LDK plant. The pyrite cinder is crushed by dry grinding, pelletized, and the pellets are dried and chlorinated in a special shaft furnace. The hard burnt pyrite cinder pellets, liberated from non-ferrous metals, are a valuable raw material for the blast furnace. The valuable metals are separated from the hydrochloric solutions of the non-ferrous metal chlorides obtained during wet cleaning of the waste gases.

The plant of Kowa Seiko in Kita Kyushu, Japan, can be cited as an example of chloridizing volatilization in a rotary kiln using calcium chloride as chlorination agent. The principle of this process is shown in Fig. 3.

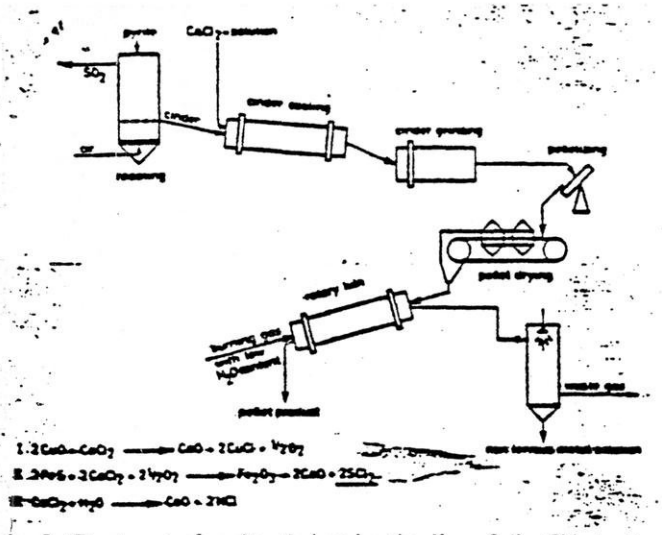


Fig. 3—Treatment of pyrite cinders by the Kowa-Seiko-Chlorination process.

The volatilized chlorides are also washed out of the rotary kiln waste gas and collected in a hydrochloric chloride solution.

Attempts are being made at Outokumpu Oy in Finland to accomplish the chlorination in a moving bed. According to this process, shown in Fig. 4, coarse-grained pyrite cinders can be utilized. An example of such pyrite cinders is the roasted iron matte obtained in the Outokumpu "B" Process. This ore is coarse-grained, has a limited grain spectre, and a nodular structure. The separation of non-ferrous metal chlorides takes place as described in the two previous processes, i.e., by wet cleaning of the waste gases during which a hydrochloric chloride solution is obtained.

The dry precipitation of volatilized chlorides is used, for instance, in titanium dioxide production by chloridizing. The advantage of dry separation in this process is the possibility of separating the titanium chloride to a high degree, by fractionized condensation, from the also volatilized iron chloride.

The dry precipitation of non-ferrous metal chlorides has also been used in the shaft furnace plant of Vuoksenniska Oy in Finland. According to the chlorination process shown in Fig. 5, 90 tons of pyrite cinders are handled per day using $CaCl_2$ as chlorination agent. It is reported that the storage and handling of the extremely fine-grained chloride dusts, separated in an electrostatic precipitator, has caused considerable problems.

The dry precipitation of the non-ferrous metal chlorides was also tested by Lurgi Chemie in a pilot plant. Corrosion in the filters posed great difficulties. Furthermore, the extremely fine-grained and highly hygroscopical dusts caused unreasonable annoyance to operating personnel, for instance, during filter cleaning. On the basis of this experience, the LDK process was provided with a wet precipitation unit for the chlorides.

THE USE OF CHLORIDE SOLUTIONS FROM THE CHLORIDIZING ROASTING OF PYRITE CINDERS

The use of non-ferrous metal chloride solutions produced by the chloridizing roasting of pyrite cinders has already been carried out for decades on an

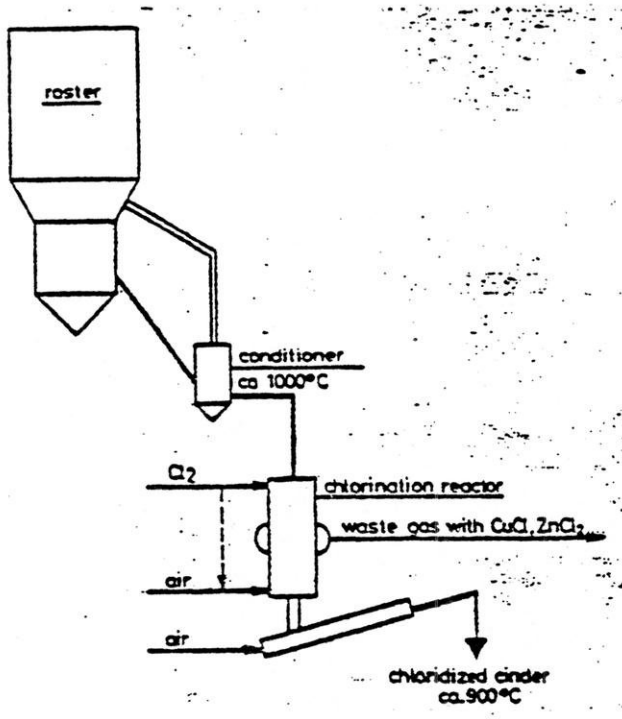


Fig. 4—Chlorination by the Outokumpu Moving Bed Process.

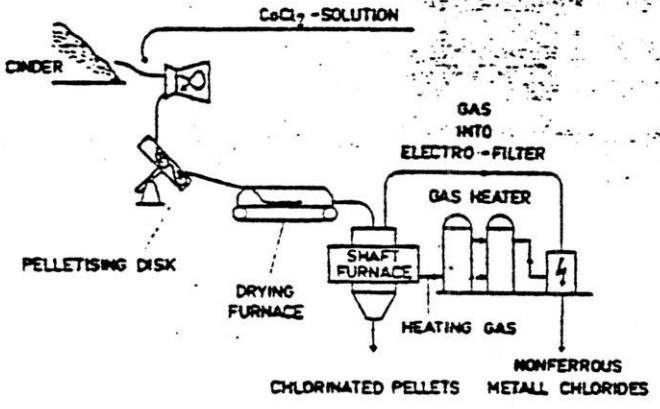


Fig. 5—Vuosenniska Chlorination Process.

industrial scale. Fig. 6 shows an example of the various possible processing steps.

The most important steps include copper precipitation as cement copper, the separation of sodium sulphate, and the precipitation of iron, cobalt and zinc by lime solution at various pH values. In addition other metals (for instance, cadmium, thallium and indium) can be obtained from the solution by cementation with zinc dust.

THE USE OF CHLORIDE SOLUTIONS FROM THE CHLORIDIZING NON-FERROUS METAL VOLATILIZATION

The solutions from the treatment of pyrite cinders by chloridizing volatilization differ in some contents from those of the chloridizing roasting, which requires modified or other processes for their treatment. The differences in the characteristics of the leaches coming from the chloridizing volatilization are:

1. High HCl content but a low SO_4 content.
2. High $PbCl_2$ content up to saturation, partially $PbCl_2$ as solids.
3. A certain content of fine-grained pyrite cinder dust.

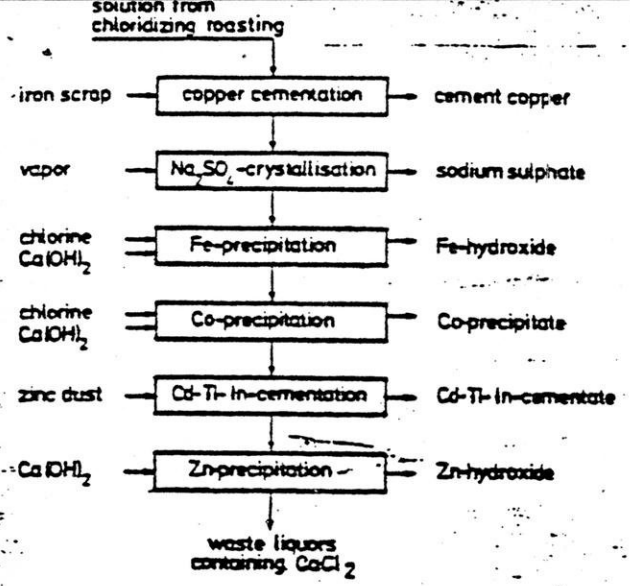


Fig. 6—Simplified scheme of possible steps for the treatment of chloride solutions out of the chloridizing roasting from pyrite cinders.

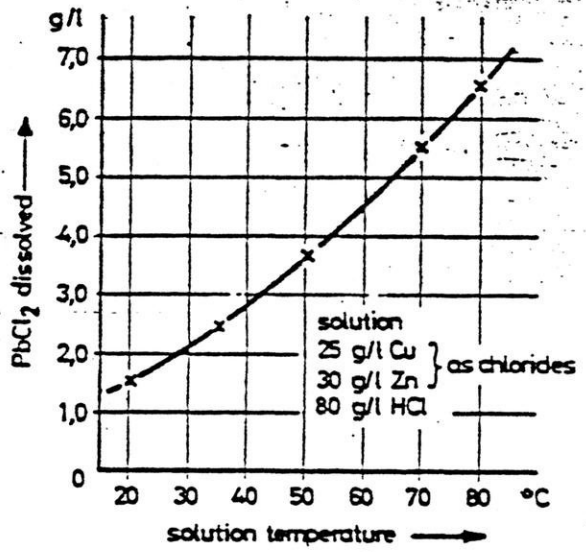


Fig. 7—$PbCl_2$ solubility in hydrochloride Cu-Zn-chloride solution. (Tests depend upon the solution temperature.)

4. Fe^{3+} content, e.g. of dissolved pyrite cinder dust.
5. Partially dissolved arsenic.
6. Copper in solution as Cu^{2+}, partially as solid CuCl.

The following is a report concerning some possible methods for the processing of solutions which are to be obtained from the chloridizing volatilization of non-ferrous metals from pyrite cinders. Special attention was given to the production of copper from the chloride leach.

Treatment of solids

The solid material consists of lead chloride as far as it is present beyond the saturation, and of very fine-grained cinder dust which was discharged from the furnace together with waste gas. The distribution of the lead chloride in solution and solids depends upon the composition of the chloride solution and its temperature. Fig. 7 shows the $PbCl_2$ solubility at various temperatures for a particular hydrochloric Cu-Zn chloride solution.

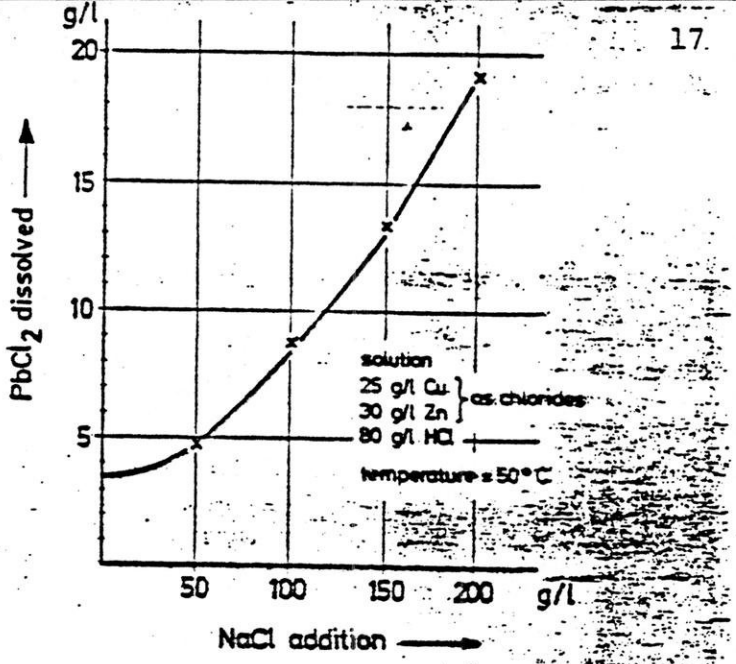


Fig. 8—Increase of solubility of $PbCl_2$ by addition of NaCl.

The separation of the solid material, consisting of pyrite cinder dust and lead chloride, can be accomplished by thickening and filtration of the thick slurry. During filtration, the solution must not be allowed to cool down. The $PbCl_2$ solubility would be decreased by cooling, precipitating very fine crystalline $PbCl_2$, which could lead to obstruction of the filter mesh.

In order to avoid these problems, the filtrate lines must be properly insulated and at some points, for instance in the interior of the drum filter, additionally heated. The precipitated solid lead chloride can be redissolved by dilution or by the addition of salts, for example common salt, which increase the solubility.

Fig. 8 shows the increase of $PbCl_2$ solubility in a Cu-Zn chloride solution at 50°C by NaCl addition. $PbCl_2$ solubility is doubled in this solution, for instance, when approximately 90 gm per litre NaCl is added.

The chlorine must be eliminated from the solid material before it can be smelted, e.g. in a lead shaft furnace. The de-chlorination can be accomplished with lime or soda during which the following conversions occur:

$$PbCl_2 + Ca(OH)_2 \rightarrow Pb(OH)_2 + CaCl_2 \quad (1)$$

$$PbCl_2 + Na_2CO_3 \rightarrow PbCO_3 + CaCl_2 \quad (2)$$

Table I—$PbCl_2$ de-chlorination.
Suspension with 200 g/l solids, 80°C.
Solids: 42% $PbCl_2$ + 58% Fe_2O_3 (= 10.4% Cl)

	Test 1	Test 2	Test 3
De-chlorination Agent	$Ca(OH)_2$	$Ca(OH)_2$	Na_2CO_3
Excess over Stoichiometry	25%	275%	15%
Cl contained in dry solids after cleaning:			
a) with hot water	2.2% Cl	1.1% Cl	1.8% Cl
b) with hot soda solution			0.2% Cl

a suspension which resulted as thickener underflow and which contains approximately 200 gm per litre solids. The solids consisted to 42% of $PbCl_2$ and 58% of cinder dust. The chlorine content is 10.4%. The best de-chlorination result was obtained with 0.2% Cl by the conversion of lead chloride with soda, and subsequent washing during the filtration with hot soda solution. During this test, the filtrate contained only 84 mg/l Pb or 0.15% of the charged $PbCl_2$ quantity.

Treatment of the solution

The solution resulting as thickener overflow contains the volatilized non-ferrous metal chlorides of the copper, zinc and of the dissolved lead chloride. Small quantities of arsenic and iron can also be present as chlorides.

Separation of arsenic from the solution

The major portion of the dissolved arsenic is precipitated together with the copper by cementation. As a consequence, the cement copper is polluted and its subsequent treatment is rendered more difficult. Extremely poisonous arsenic hydrogen can be another consequence.

It is therefore recommended to separate the arsenic from the leach prior to the copper cementation. The arsenic can be precipitated in the presence of dissolved iron, e.g. as $FeAsO_4$. Tests have shown to what extent the separation of arsenic from copper is possible for various solution.

Fig. 9, for example, shows the results of precipitation tests with a chloride solution obtained during tests on chloridizing volatilization. The investigated solution contained 13.8 g/l Cu, 2.29 g/l As, 2.8 g/l Fe and 183 g/l free acid. Assuming all copper and all arsenic are precipitated during the cementation, and that a cement copper with 80% Cu is produced, the arsenic content in cement copper is 13.3%. Approximately 80% of the arsenic was successfully extracted without simultaneously precipitating copper, on the basis of the tests as in Fig. 9, due to previous neutralization of the leach to pH = 2.0.

An 80% Cu cement copper with approximately 0.6% As can be produced from the dearsenified solution in the process of subsequent copper cementation. This arsenic content can be decreased still further by additional neutralization, although some copper will also be precipitated and lost with the Fe-As slurry.

Copper precipitation by cementation

The cementation of copper is usually carried out with iron scrap. The copper solution is, for instance, charged into converter-shaped cementation drums, and scrap with a maximum of surface added in excess. The drum is rotated temporarily. The cemented copper is precipitated and adheres to some extent to the scrap surface, from which it is removed by friction. The scrap surface is thus cleared for further copper cementation from the solution.

The disadvantages of the conventional methods of copper cementation with iron scrap in drums, launders, etc., are the batch-wise operation and the frequently low purity of the cement copper which depends to a great extent upon the quality of the iron

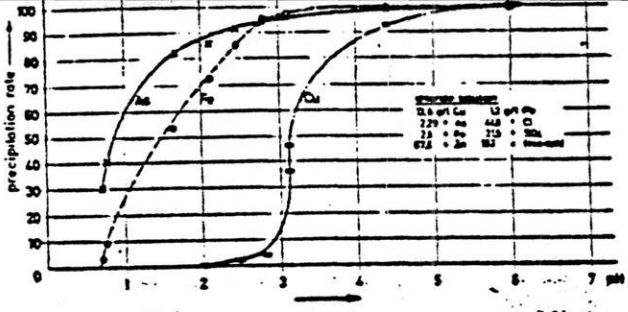


Fig. 9—Separation of arsenic from copper in a chloride solution by neutralisation with caustic soda.

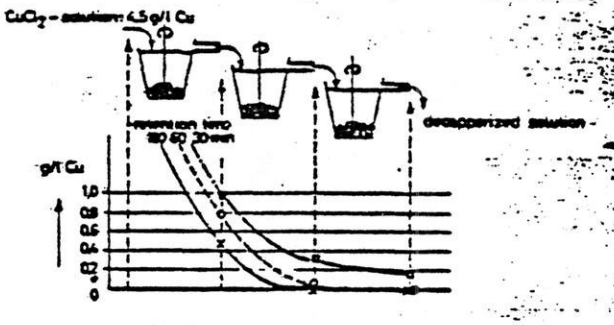


Fig. 10—Cementation of copper out of a copper chloride solution with sponge iron pellets. (Tests depending upon the retention time of the solution.)

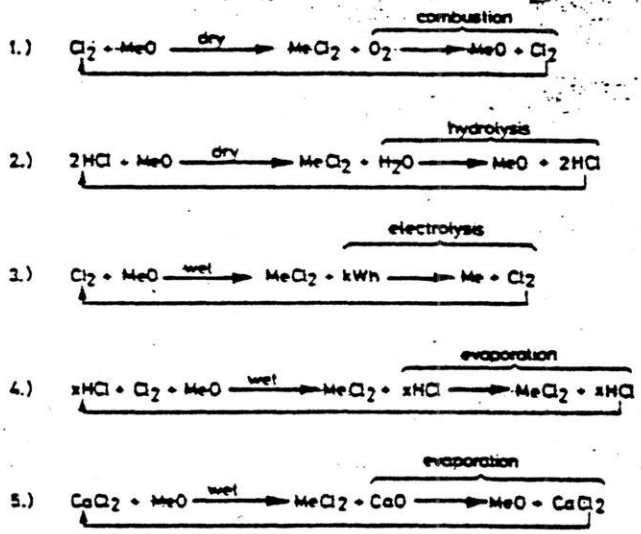


Fig. 11—Circulation of the chloridizing agent.

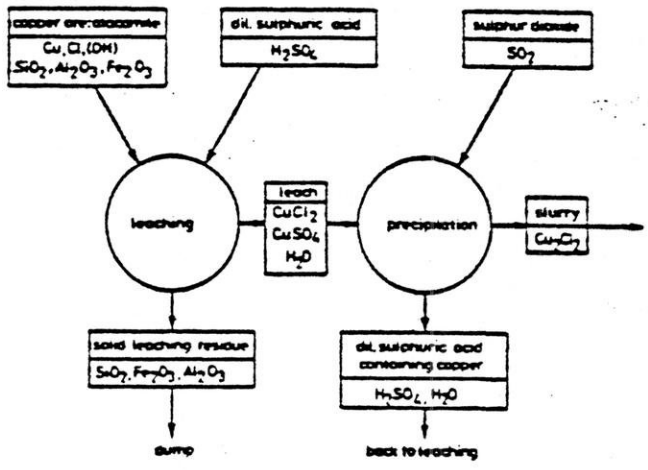


Fig. 12—Producing copper out of atacamite.

scrap used. It should be noted in this connection that the iron scrap quality can vary within a wide range as far as the contents of impurities are concerned.

A number of investigations have been made to avoid these disadvantages. One example to be mentioned is the process of the Kennecott Copper Corp., by which the copper cementation is carried out in cone-type precipitators. Various sponge iron qualities, among others, were tried as precipitants which had to be crushed to a size of less than ten mesh.

This process is used for the copper cementation of mine water on industrial scale. The following advantages are mentioned in comparison with the earlier cementation carried out in launders:

- space requirement decreased to approximately one tenth
- automatic discharge of the cement copper
- approximately 0.5—1 kg/kg copper savings in iron consumption
- complete decopperizing of the solution.
- possibility of using the resulting hydrogen for the control of the cementation procedure
- the cementation in the cone is accelerated and the reoxidation of the cement copper is prevented by the development of hydrogen.

Investigations were also made by Lurgi in order to carry out the copper cementation in a continuous process using sponge iron pellets. Tests were made, among others, in a precipitation cascade. Sponge iron pellets were used as precipitants which were not crushed and which had a diameter of 10—15 mm.

Sponge iron pellets can, for instance, be produced according to the SL/RN direct reduction process with a very high degree of metallization and when charging high-grade ores. The use of sponge iron pellets is also advantageous of the consistent quailty in which this product can be obtained.

Fig. 10 shows the precipitation cascade principle. The testing apparatus consisted of three tanks, each with 72-litre content, tapered towards the bottom. Each tank had an overflow and was provided with an agitator. The sponge iron pellets were fed in excess referring to the amount of copper to be cemented out, and the $CuCl_2$ solution was pumped into the tank standing at the highest elevation. The retention time of the solution in the cascade is determined by the pumping speed.

The cementation tests, shown in Fig. 10, were made with $CuCl_2$ solution containing 4.5 g/l Cu. The sponge iron pellets had 93% Fe_{tot} and 91.5% Fe_{met}. The retention time of the solution, between 180, 60 and 30 min. in the precipitation cascade, was changed. The tests were evaluated by analysing the overflow from each of the three tanks as to the copper content. The graphical evaluation according to Fig. 10 indicates that a retention time in the cascade of 30—60 min. was necessary for the complete decopperization of the $CuCl_2$ solution containing 4.5 g/l Cu, compared to 2—3 hr. in drums.

The tests proved in general that cement copper precipitating onto the sponge iron pellets is mechanically extracted by agitation and that the cementation continues until the pellets are completely consumed. The cement copper formed by cementation with sponge iron pellets is of very fine size. It can be removed together with the solution and separated from the remaining pellets—the pre-requisite for continuous cementation.

The iron contents in cement copper, in some cases more than 10% Fe, were relatively high. They could certainly be considerably decreased with an improved apparatus. The iron content in the cement copper was successfully reduced to less than 1% Fe by wet magnetic separation.

The behaviour of the precious metals was also investigated in the copper cementation tests. Gold and silver were volatilized by chlorination up to approximately 80–95% out of the pyrite cinders to be accumulated in the chloride solution. In the process of cementation, the precious metals were then precipitated together with the copper.

Scattering or losses can occur if the gold is precipitated out of the solution by reduction, e.g. with Fe^{++}, before the cementation. The gold precipitation can be prevented by applying a certain oxidation potential in the solution, by injecting chlorine gas, for example. The entire gold is thus collected in the precipitated copper.

There is practically no precipitation of lead in the copper cementation. From a chloride solution with 20 g/l Cu, 3.5 g/l Pb and a Ph of 2.0, the copper was precipitated out by scrap. The resulting cement copper contained less than 0.2% Pb after exhaustive copper precipitation.

Copper precipitation with simultaneous chlorine recovery

Precipitating copper from chloride solutions by cementation has the disadvantage of not reclaiming the chlorine bound to the copper. Recovery of the chloridizing agent can favourably affect the economics of chloridizing volatilization.

Generally, the chloridizing agent can be recovered from the hydrochloric non-ferrous metal chloride solutions by various processes. Fig. 11 shows five different possible ways.

The electrolysis was tested for the treatment of hydrochloric copper chloride solutions. It appeared that the copper can be precipitated free of chlorine at the cathode and an equivalent amount of chlorine at the anode under certain conditions. The primary prerequisite is that chlorides are added in a particular proportion to the copper content of the alkaline metals, or alkaline earth metals, or hydrochloric acid in the electrolytes. The separation of compact, smooth copper precipitations is problematic.

Using the copper chloride electrolysis can be of particular interest in connection with the chloridizing volatilization treatment of pyrite cinders, copper being the predominant non-ferrous metal content. Oxidic-silicate copper ores from Chile, however, were also treated with more than 95% copper volatilization by chloridizing volatilization, and the obtained copper chloride solution was then upgraded by electrolysis. These ores contained only 2–4% Cu. Concentrating the copper content by conventional upgrading methods, by flotation for instance, was not feasible.

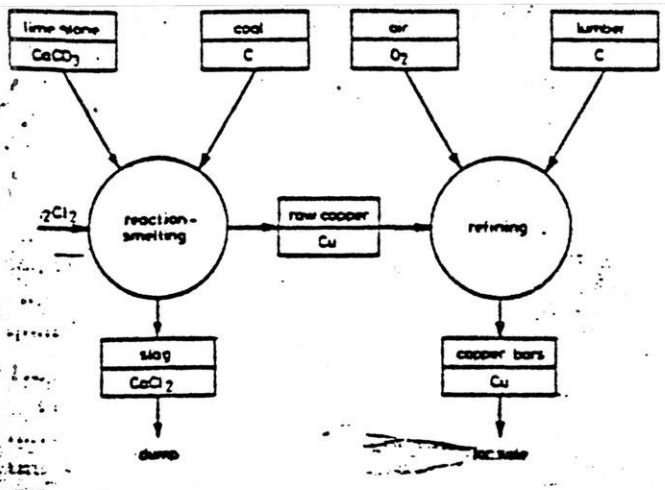


Fig. 13—Producing copper out of atacamite.

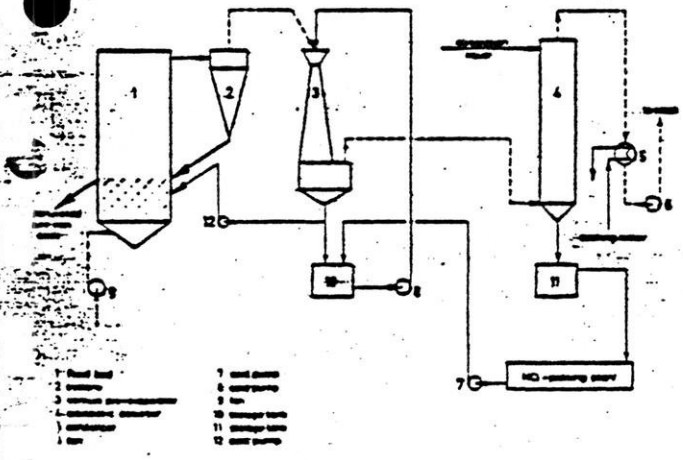


Fig. 14—Regeneration plant for hydrochloric pickling liquor.

s the direct ore smelting and reduction to copper metal was too uneconomical due to excessive slagging.

roducing copper out of solid copper protochloride

The copper is available, mostly dissolved as Cu^{+}, in the liquors from the chloridizing volatilization, although it can be obtained as solid protochloride to ome extent if the volatilization is carried out with a small excess of chlorine with reference to the stochiometrically required amount. The solubility of the in water and extremely diluted hydrochloric acid solutions resulting at a low chlorine surplus is very limited.

The solid copper protochloride can be filtered off nd, for example, by the Mantos Blancos process, upgraded to copper metal. The principle of the Mantos Blancos process is shown in Figs. 12 and 13.

The atacamite with chlorine content is leached by diluted sulphuric acid. Solid CuCl is precipitated from the resulting solution by reduction with SO_2. he solid CuCl is separated by filtration from the phuric acid solution which is recirculated into the leaching.

Fig. 13 is a simplified diagram of the CuCl treatent. The copper protochloride is pelletized and smelted for copper metal together with lime and coal in short drum furnaces. The slag consists mainly of calcium chloride. The raw copper can be processed in the Mantos Blancos plant by refining (air oxidation and lancing with tree trunks) for high-grade copper metal of a purity equalling that of electrolyte copper.

Another method of treatment is the conversion of CuCl with slaked lime, as applied by Duisburger Küpferhütte. The reaction occurs according to the equation.

$$2CuCl + Ca(OH)_2 \rightarrow Cu_2O + CaCl_2 + H_2O$$

The chlorine-free copper oxide can be smelted either directly or after agglomeration, then to be reduced to copper metal.

Also investigated was the splitting of CuCl into Cu_2O or CuO and HCl, which can be recirculated into the chloridizing process. The tests were run in adherence to the process developed by Lurgi Gesellschaft für Wärme—and Chemotechnik, for the regeneration of hydrochloric leaches containing Fe Cl, which takes place in the pickling plant.

The principle of this process is shown in Fig. 15. The iron chloride is split in a fluid bed built up from the forming iron oxide. The fluidizing is affected with air which also participates in the $FeCl_2$ splitting according to the following equation

$$2FeCl_2 + 2H_2O + \tfrac{1}{2}\,O_2 \rightarrow Fe_2O_3 + 4HCl$$

The iron-oxide contains less than 0.1% Cl and can be used in the iron production. The hydrochloric acid is washed out of the waste gas and returned to the pickling plant.

The tests with copper protochloride were run in a fluid bed roaster with 100 mm grate diameter. Iron oxide with 0.5–1 mm grain diameter from pickling regeneration served as bed material. The bed temperature was set for 850, 800 and approximately 600°C for the various tests. The product contained between 0.5% and a maximum of 1.5% chlorine. Such contents were also achieved in the treatment of lumpy CuCl with > 5 mm, for example.

Zinc-lead precipitation from the solution

After the precipitation of copper, the proportions of zinc and dissolved lead remain in the solution. The separation can be achieved by neutralization with slaked lime of pH 7–8. It may be appropriate after copper precipitation by cementation that the iron dissolved in this process is first separated in one precipitation step at pH ~ 4.5 in order to obtain a Zn/Pb product of improved purity.

The zinc-lead hydroxide contains approximately 6–8% Cl which cannot be removed by scrubbing. The extraction of chlorine can be achieved during calcination by volatilizing the chlorine as $ZnCl_2/PbCl_2$ which are washed out of the waste gases and returned into the solution, thus preventing losses and waste gas problems.

In conclusion, it should be noted that it is, of course, impossible to give a detailed description of all mentioned processes within the scope of this paper, the aim of which is to point out various possibilities of treatment for non-ferrous metal chloride solutions out of the chloridizing volatilization.

impurities from iron ore pellets by chlorination (CV or LDK process*)

669.094.4 : 622.7–366.121 : 669.054.822

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Synopsis

Pyrite cinders containing non-ferrous metals can be processed into iron ore pellets by the chloridizing volatilization (CV) process. The cinders are pelletized after grinding, the pellets being burned in a special shaft furnace in which the non-ferrous metals are volatilized by chlorine gas.

In a large pilot plant (capacity, approximately 100 tons per day) various types of cinders were treated—non-ferrous metal contents of up to 0·83 per cent Cu, 1·86 per cent Zn and 1·87 per cent Pb. The pellets produced contained 0·02–0·05 per cent Cu, 0·04–0·25 per cent Zn and < 0·05 per cent Pb, and showed good resistance properties during the blast-furnace reduction.

Chlorine consumption was 1·3 to twice the theoretical requirement; more than 90 per cent volatilization of gold and silver was achieved.

In the production of sulphuric acid from iron sulphide ores, mainly pyrites and pyrrhotites, residue cinders are obtained, the iron content of which may vary considerably.[1] 5 300 000 tons of cinders was available in Europe in 1964, distributed as shown in Table 1.†

Table 1 Pyrite-cinder production in Europe, 1964*

	Tons
West Germany	1 382 000
Italy	1 205 000
Spain	806 000
France	378 000
Sweden	350 000
Portugal	231 000
Holland	190 000
Belgium	162 000
Great Britain	143 000
Finland	103 000
Denmark	95 000
Others (including East Germany, but excluding Communist countries)	291 000
	5 336 000

*From reference 2.

Non-ferrous metals, primarily copper, are extracted from these cinders in several plants after chloridizing roasting. The cinders are mixed with approximately 10 per cent sodium chloride and treated in multiple-hearth roasters at about 550°C. The largely insoluble non-ferrous metal compounds are converted so that they become water- and acid-soluble. After extraction of the non-ferrous metals, the iron oxide remaining as the so-called purple ore is agglomerated by sintering so that it can be used in the blast-furnace.

Table 2 lists the chloridizing roasting plants for cinders in various countries and their production in 1963 and 1965.

Table 2 Pyrite cinder purification by chloridizing roasting and leaching*

	Tons 1963	1965
(1) Duisburger Kupferhütte	2 000 000	2 000 000
(2) Ertel, Bieber and Co., Hamburg	300 000	300 000
(3) Metallhüttenwerke Lübeck AG	200 000	200 000
(4) Sachtleben AG, Homberg	200 000	200 000
(5) Reymersholm Gamla AB, Hälsingborg		
Reymersholm Gamla AB, Oskarshamn	150 000	150 000
(6) Montecatini, Werke Porto Marghera	150 000	150 000
(7) Companhia União Fabril Barreiro	200 000	300 000
(8) Metal Química del Nervion SA, Bilbao	150 000	150 000
(9) Rumania	150 000	150 000
(10) Japan	100 000	100 000
	3 600 000	3 700 000

*From reference 3.

For the economic application of the chloridizing roasting process a certain minimum content of non-ferrous metals, primarily copper, zinc, cobalt and precious metals, is required. When no non-ferrous metals other than copper are present, a copper content of approximately 0·7 per cent is needed to cover the processing costs, this figure depending, of course, on the current metal price.[4]

Apart from a sufficient content of non-ferrous metal, a suitable particle size distribution is required for percolation leaching to be carried out economically. Owing to the use of beneficiation processes, in particular flotation, and the ever-increasing use of turbulent-layer roasters instead of multiple-hearth roasters and rotary kilns for the primary roasting, cinders tend to become more and more fine-grained. It has recently become possible to extract such cinders by percolation leaching after chloridizing roasting, but this extraction involves higher operating costs.[5]

Frequent attempts have been made to find a process for converting cinders into a first-class raw material for

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*CV, Chloridizing Volatilization; LDK, Lurgi Duisburger Kupferhütte.

†The short ton of 2000 lb is used throughout this paper.

the iron and steel industry, especially for cinders of extreme fineness which cause difficulties during percolation leaching and for cinders of a non-ferrous metal content too high for direct smelting in the blast-furnace but too low for covering the costs of chloridizing roasting and leaching. It was found that chloridizing volatilization of non-ferrous metals from pyrite cinder pellets is a very appropriate process for this purpose. Lead, which is not eliminated by chloridizing roasting, and which may require a separate leaching, is removed.

Following investigations into chloridizing volatilization in the laboratory and in semi-commercial plants with a capacity of up to 3 ton/day, carried out by Lurgi Gesellschaft für Chemie und Hüttenwesen m.b.H. and Duisburger Kupferhütte, a 100 ton/day pilot plant was built jointly and operated at Duisburg to test the LDK process.

Principle and historical development of the process

In general, chloridizing volatilization of metals is facilitated by relatively easy formation of chlorides from oxides and sulphides, high vapour pressures at relatively low temperatures and selective volatilization and condensation of individual metals. In particular, the extraction of non-ferrous metals from pyrite cinders by chloridizing volatilization is based on the different behaviour of iron oxides and non-ferrous metal oxides during chlorination under oxidizing conditions. Suitable chlorinating agents are calcium chloride, hydrogen chloride gas and chlorine. Equilibrium with the particular elements, especially lead, copper, zinc and precious metals, is most favourable for volatilization with chlorine, so the investigations were concentrated upon this chlorination method.[6] Reaction pressures for the oxide chlorination are shown in Fig. 1; the following reactions are involved:

$$2Fe_2O_3 + 6Cl_2 = 2Fe_2Cl_6 + 3O_2$$
$$2H_2O + 2Cl_2 = 4HCl + O_2$$
$$2ZnO + 2Cl_2 = 2ZnCl_2 + O_2$$
$$2Cu_2O + 2Cl_2 = 4CuCl + O_2$$
$$2PbO + 2Cl_2 = 2PbCl_2 + O_2$$

The vapour pressures of chlorides of the principal metals contained in the pyrite cinders are shown in Fig. 2. The boiling points of, for example, $ZnCl_2$ (732°C) and $PbCl_2$ (954°C) are very low, but those of the copper chlorides Cu_3Cl_3 and CuCl are well above 1000°C, whereas the vapour pressure at 1000°C, the usual chlorination temperature in this process, is already so high that considerable quantities can be removed by the carrier gas on a commercial scale.

Although the physical chemistry of the chloridizing volatilization process has been described in many publications and patents, this process has, to date, been utilized only rarely on a commercial scale.[7–19] In the 1920s silver was volatilized in Mexico by heating ore, calcium chloride and sulphur in a rotary kiln, using the Pohlé–Croasdale process. In the early 1950s the non-

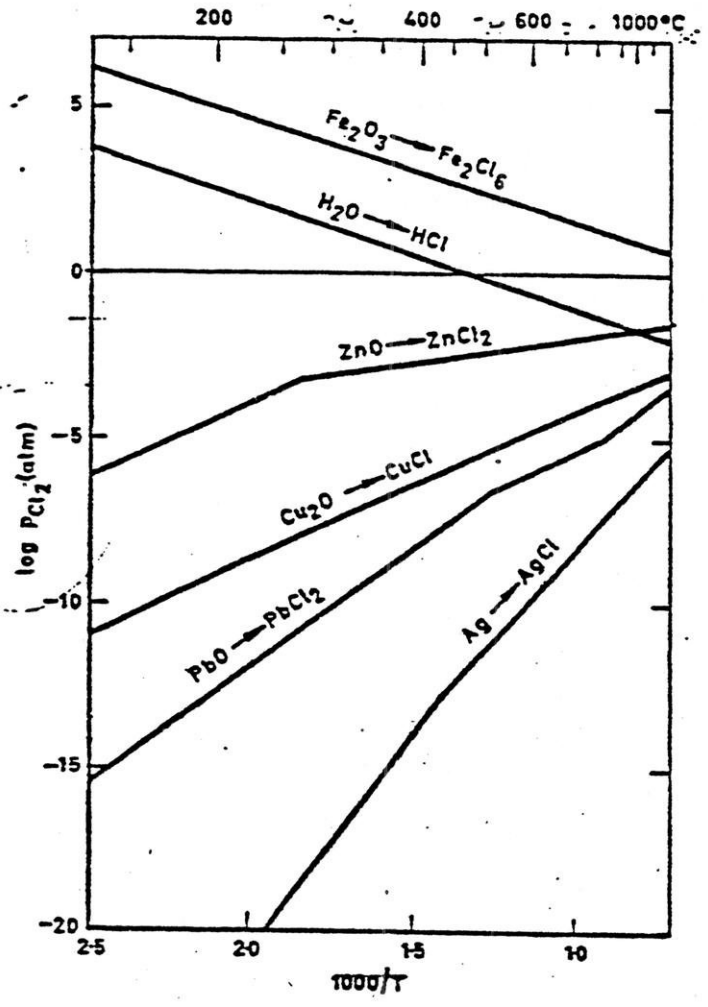


Fig. 1 Chlorination of oxides (activities and partial pressures of reactants assumed equal to unity)

ferrous metals copper, zinc, lead and cobalt, as well as gold and silver, were volatilized by burning pyrite cinder pellets mixed with calcium chloride in a shaft furnace (Vuoksenniska process) in a 90 ton/day plant in Finland.[20] Fig. 3 shows the simplified flowsheet of the

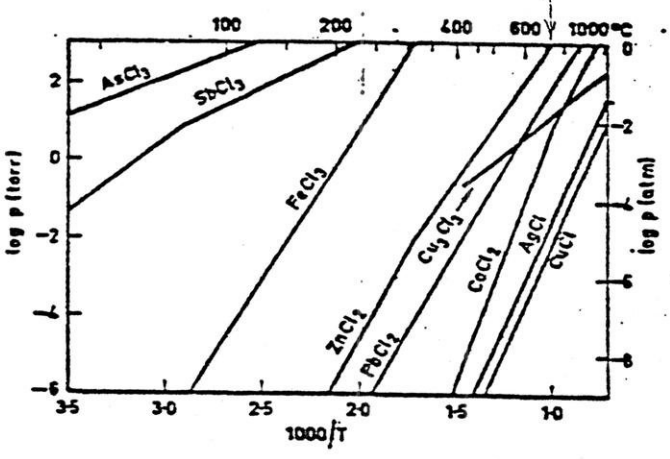


Fig. 2 Vapour pressures of metal chlorides

Vuoksenniska process. In the early 1960s this process was further developed by Dowa Mining Co. and is presently applied as the Kowa-Seiko process in a rotary kiln, with a daily throughput of approximately

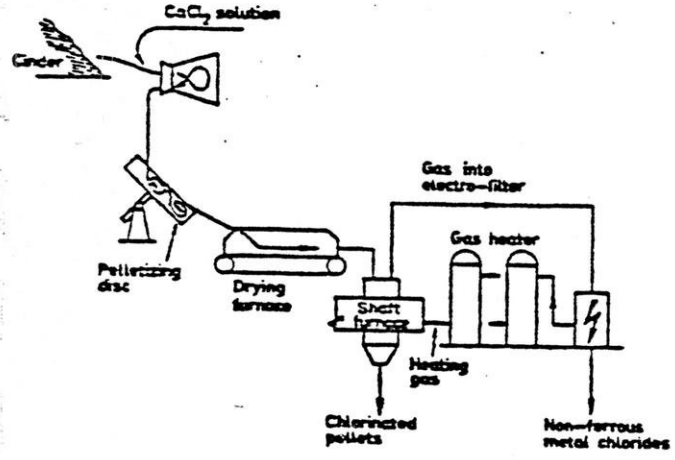


Fig. 3 Flowsheet of Vuoksenniska process

350 tons.[21] Fig. 4 is a simplified flow diagram of this process.

With regard to chlorination with calcium chloride, it should be noted that this process requires fuel gas with

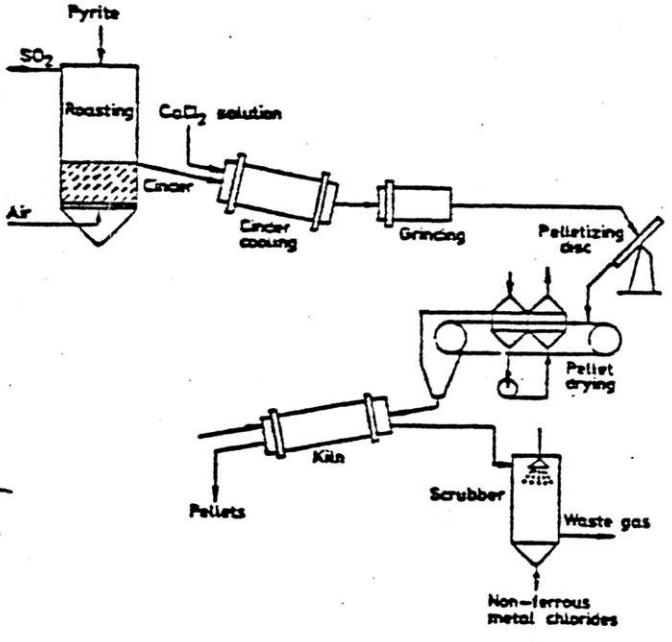


Fig. 4 Flowsheet of the Kowa Seiko process

low hydrogen content. Calcium chloride undergoes partial hydrolysis at temperatures which do not allow substantial volatilization of non-ferrous metals. Furthermore, only the treatment of cinders relatively low in non-ferrous metals and sulphur is possible. In the Kowa Seiko process, cinders containing less than 0·5 per cent Cu, 0·5 per cent Zn, 0·2 per cent Pb and 0·7 per cent S are treated.[21]

When chlorine is used it is also possible, however, to treat cinders containing more than 3 per cent residual sulphur. Oil, town gas and natural gas can be employed as fuel. In the Federal Republic of Germany one ton of elemental chlorine costs approximately DM 250, whereas one ton of chlorine contained in calcium chloride costs DM 350–DM 400.

For these reasons the research work was concentrated on the use of chlorine gas. The 100 ton/day plant at Duisburg, jointly built by Lurgi Chemie and Duisburger Kupferhütte, was designed primarily for this chlorination method in order to test the LDK or CV process by the use of several cinders of different composition.[22]

Pellet chlorination plant

Fig. 5 shows a partial view of the chlorination plant at Duisburg, which was built in 1965 and started up in 1966. The flowsheet of the plant is given in Fig. 6.

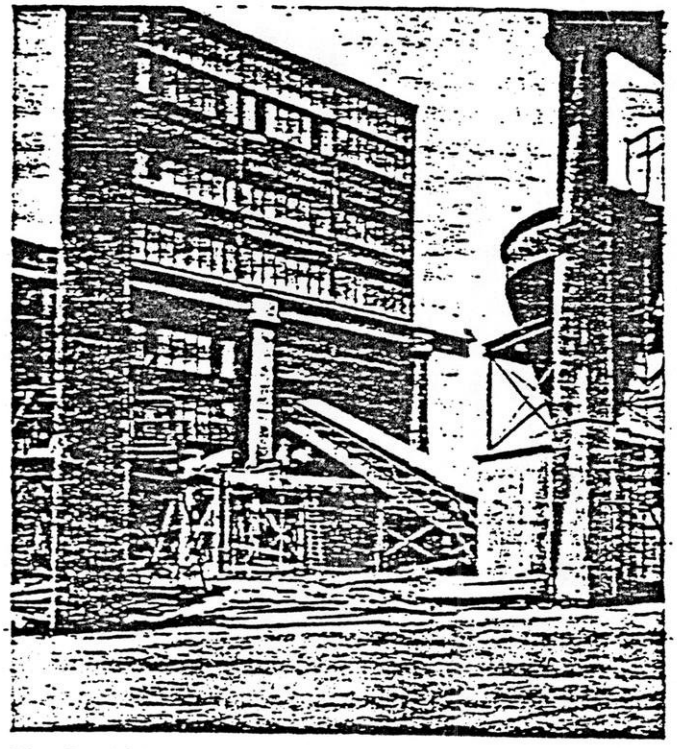


Fig. 5 100 ton/day LDK chlorination plant

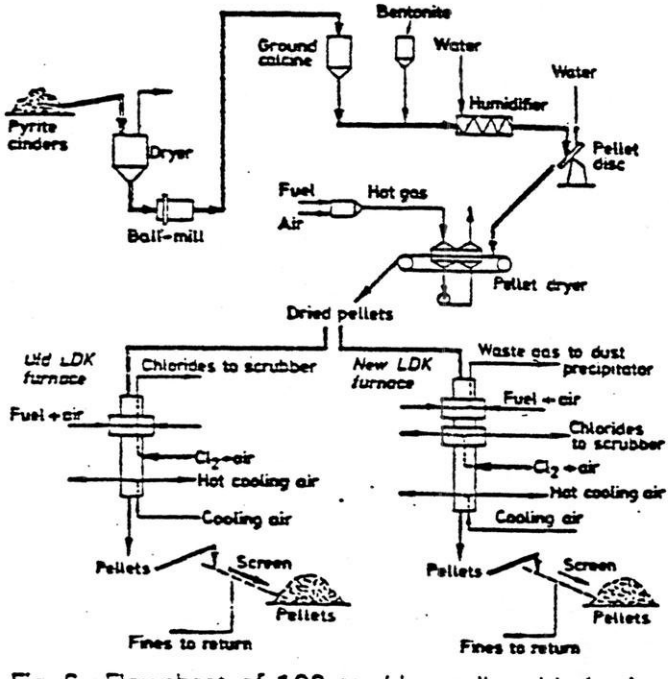


Fig. 6 Flowsheet of 100 ton/day pellet chlorination plant

Production of dried pellets

The cinders pass through the feed hopper shown in Fig. 5 below the crane track and via the weighing feeder below into the grinding section. As parts of the non-ferrous metals are present in the pyrite cinders in soluble form, the cinders are ground dry. After the cinders have been subjected to countercurrent cyclone drying, they are carried with a residual moisture content of approximately 2 per cent H_2O to the ball-mill, where they are ground to the fineness required for pelletization. The ground material, stored in a bin, is extracted by means of a weighing feeder, mixed with additives (e.g. bentonite) and raised by bucket elevator to the pelletizing plant on the top floor of the building. The dry ground material is pre-wetted in a screw conveyor to about 8 per cent moisture and conveyed to the pelletizing disc (Fig. 7), where further water required for the formation of pellets is added.

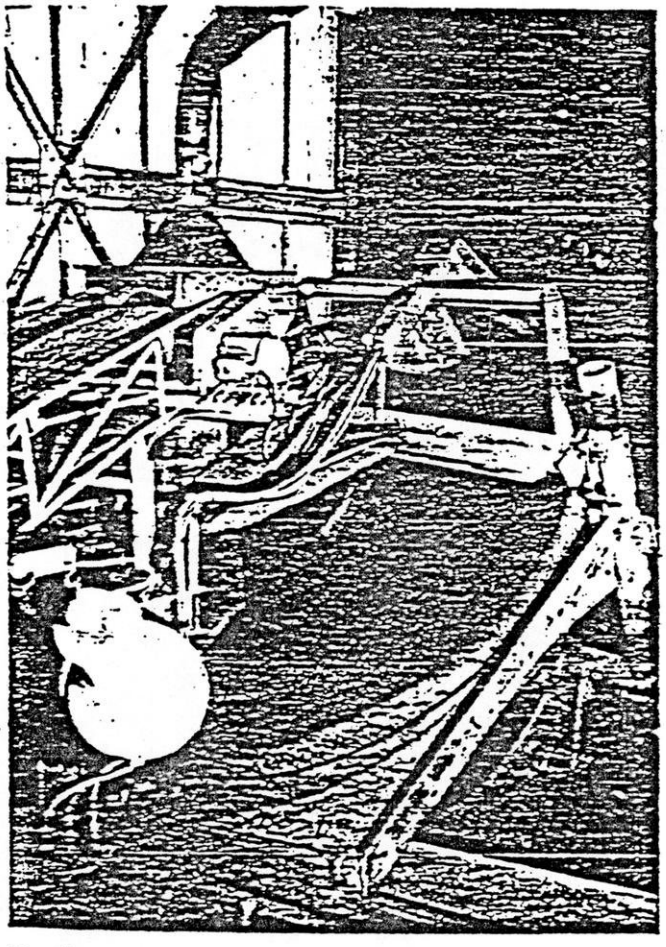


Fig. 7 Pelletizing disc

The green pellets are transferred from the pelletizing disc on to a roller conveyor, which also serves to separate the undersize. Subsequently, the green pellets are dried with hot gas on a belt dryer until they are practically free of water.

The belt dryer is divided into preheating, heating and cooling zones. In the cooling zone the dried and hot pellets are subjected to downdraught air cooling. Hot gas produced by the combustion of blast-furnace gas and the addition of heated cooling air to attain the desired temperature is drawn by fan through the pellet bed in the heating zone and forced upward through the wet pellets in the preheating zone. The waste gases from the preheating zone are maintained above dew-point and are discharged through a stack to atmosphere.

The dry pellets delivered from the belt dryer have sufficient strength to withstand charging into the chlorination shaft furnace. To separate fines abraded from the pellets during drying, the dry pellets pass through a parallel wire type screen to the shaft furnace.

Burning and chlorination of pellets in shaft furnace "Old operating method"

Although the process stages and equipment described above were well known, there were no data available in respect of the 100 ton/day shaft furnace for the treatment of hardened pellets with gaseous chlorinating agents, e.g. chlorine, apart from those from the small (3 ton/day) shaft furnace tested earlier. The lower part of the 100 ton/day shaft furnace is shown in Fig. 8.

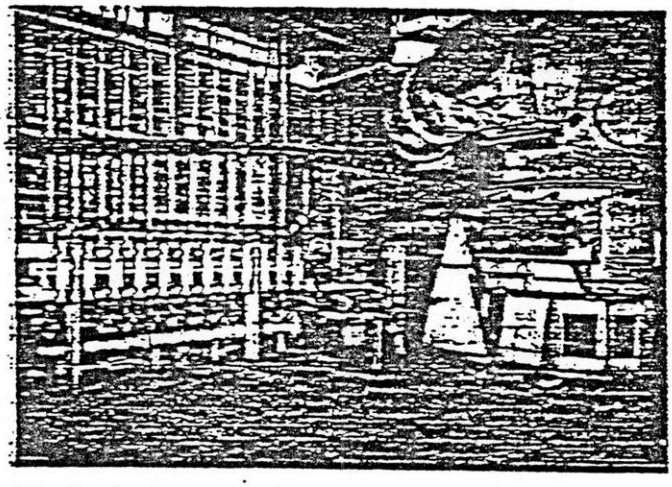


Fig. 8 Lower part of 100 ton/day LDK chlorination furnace

Experience with ordinary pellet burning in shaft furnaces could only be applied to a very limited extent to the chlorination shaft furnace. Fig. 9 represents the gas flow in a normal pellet induration shaft furnace. The gases, i.e. hot gases and cooling air, rise countercurrently to the pellets through the whole pellet column. Part of the heated cooling air is sometimes drawn off below the combustion chambers and utilized for the production of hot gases in the combustion chambers. If it were intended to adopt this method for chlorination, the chlorination gas would be considerably diluted by the cooling air or by the combustion gases. This would result in incomplete recovery of non-ferrous metals, and it would require a high excess of chlorinating agents.

A further important difference is that in presently operated pellet shaft furnaces magnetite pellets are indurated almost exclusively, whereas practically all the iron contained in pyrite cinders is in the form of hematite. It was, therefore, necessary to develop a furnace in which hematite pellets could be indurated

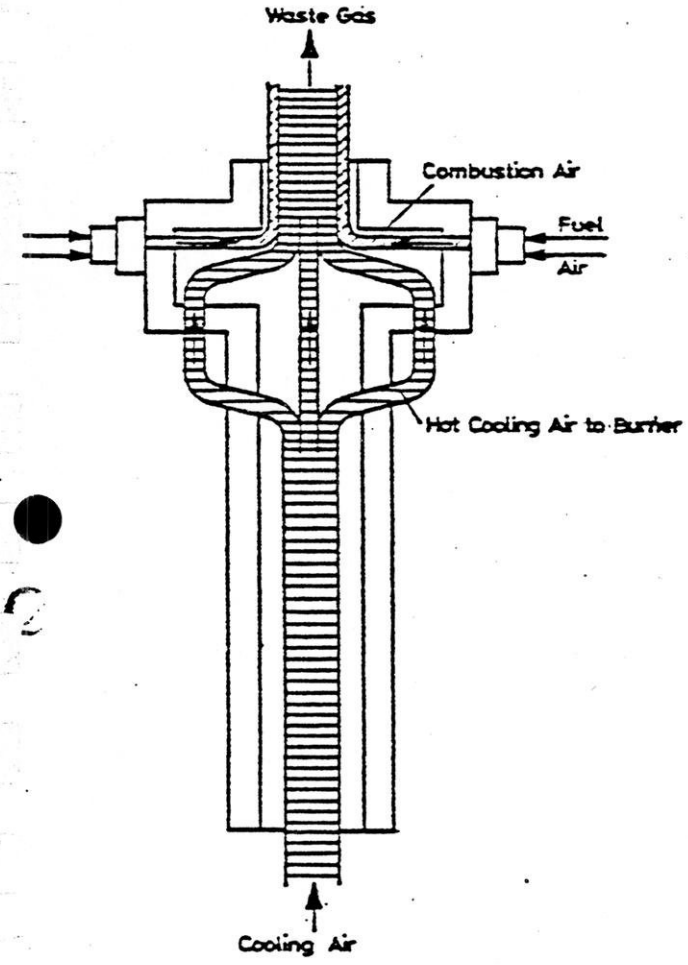


Fig. 9 Gas flow in shaft furnace for pellets

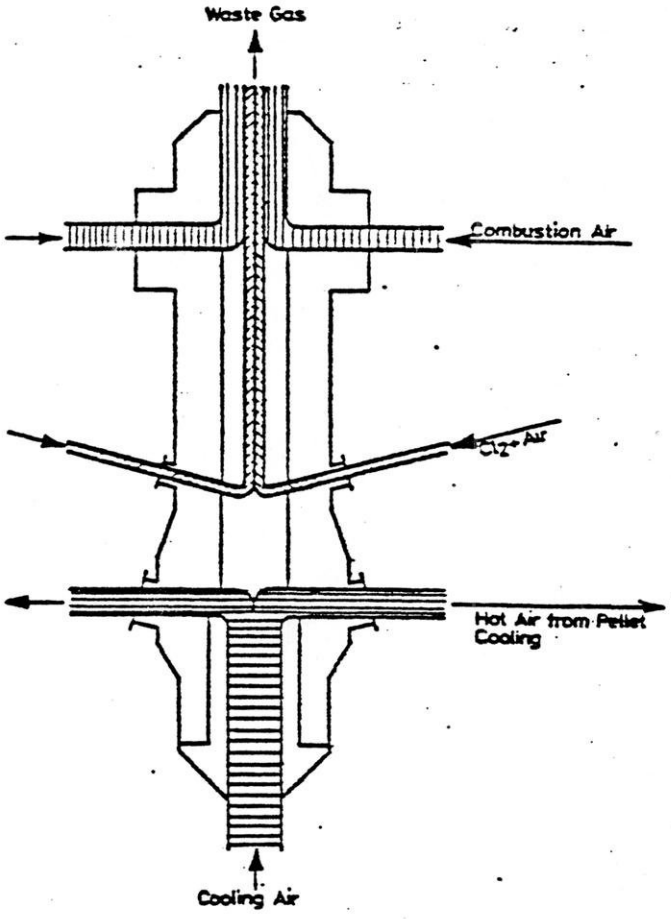


Fig. 10 Gas flow in old LDK furnace

satisfactorily and then treated with chlorination gas of a high chlorine concentration. Consequently, the 100 ton/day shaft furnace was initially designed to operate as shown in Fig. 10. This is referred to as the 'old operating method'.

In the top part of the shaft furnace, the induration zone, dried pellets are heated countercurrently by hot gases to the induration temperature and thus desulphurized. Subsequently, they pass down into the chlorination zone, at the lower end of which cold chlorine gas, together with carrier air, is blown through tuyères into the hot pellet bed. Chlorine and air are rapidly heated while they rise countercurrently through the pellets and volatilize the non-ferrous metals copper, zinc, lead and precious metals as chlorides. The carrier air charged with the chlorides passes through the induration zone and is drawn off together with the waste gases from the top of the furnace into the gas cleaning plant. The pellets descend into the cooling zone, where they are countercurrently cooled with cold air. The cooled pellets are discharged through a lock and, after separation of undersize, are ready for despatch.

The heated air derived from pellet cooling is drawn off from the furnace below the chlorination zone and can be used to dry the wet green pellets. Adequate control of the pressure difference between the cooling air outlet and the chlorine gas inlet, in conjunction with analysis of the heated cooling air for traces of chlorine, would enable the furnace to be operated so that almost complete separation of cooling air and chlorine gas was maintained and the laterally injected chlorine gas penetrated through the whole pellet column.

The furnace waste gases including the volatilized chlorides are drawn off at the furnace top and conveyed to the gas cleaning plant. A venturi scrubber is provided for rapid gas cooling and for washing out a high percentage of chlorides; subsequently, a wet electroprecipitator eliminates fumes still contained in the gas.

The dissolved chlorides leaving the scrubber and electroprecipitator contain a low percentage of abraded dust and free hydrochloric acid from excess chlorine. This solution is treated by conventional techniques.

'New operating method'

The furnace was operated for some 18 months with the 'old operating method'. Several cinders of different composition were treated and the gas flow and gas separation were studied.[22] Since the exhausted cooling air could successfully be kept separate from the injected chlorination gas, the furnace was reconstructed so that the gases carrying the volatilized chlorides could be drawn off separately from the combustion gases.

The 'new operating method' of the furnace is as follows (Fig. 11). The dried pellets are countercurrently heated in the induration zone with heating gases to induration temperatures. The waste gases from the

induration zone are drawn off at the furnace top, dedusted and conveyed to the stack. In the chlorination zone below, the indurated hot pellets are countercurrently treated with a cold chlorine–air mixture whereby the non-ferrous and precious metals are volatilized as chlorides. These chlorides are discharged hot below the induration zone and pass through a

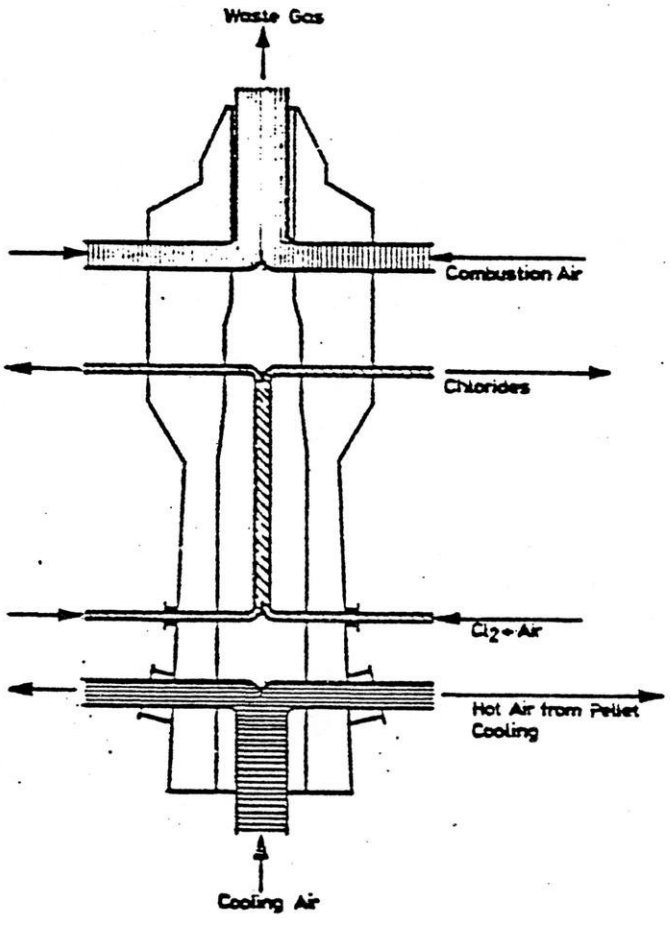


Fig. 11 Gas flow in new LDK furnace

venturi scrubber and electroprecipitator, as described above, to separate the volatilized chlorides. With the 'new operating method' the volume of gas containing the volatilized chlorides is much smaller than that formerly present. Separation of the incoming heating gases from the outgoing gases with the chlorides is done by automatic regulation of the differential pressures between the respective zones.

Subsequently, the pellets pass through the cooling zone, where they are countercurrently cooled with air. The heated cooling air is discharged below the chlorination zone separately from the chlorination gases, as described above. Thus, with the new method all three gas streams are kept separate.

Fig. 12 shows the control panel of the chlorination shaft-furnace plant. The following advantages resulted from the separate drawing-off of the chlorination gases. (1) The chlorine consumption was reduced considerably. Formerly, the chlorides partially reacted with the flue gases in the induration zone, owing to a shift in the chlorination equilibrium. Reoxidation or, for instance, with zinc, hydrolysis of the chlorides with water vapour from the combustion gases could be avoided only by increasing the partial pressure of chlorine and, hence, the chlorine consumption.

(2) In the new operating method the amount of

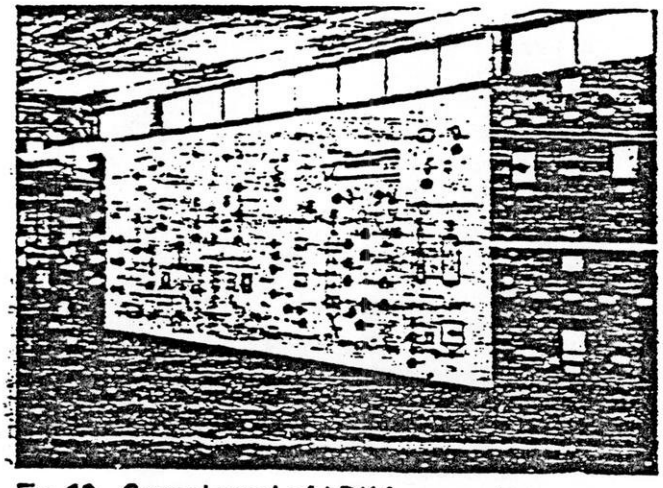


Fig. 12 Control panel of LDK furnace plant

chloride-containing exit gas to be scrubbed is only one-fifth to one-tenth of that previously produced. The solution obtained by precipitating the chlorides according to the new method is practically free from cinder dust and, hence, from dissolved iron. In the old

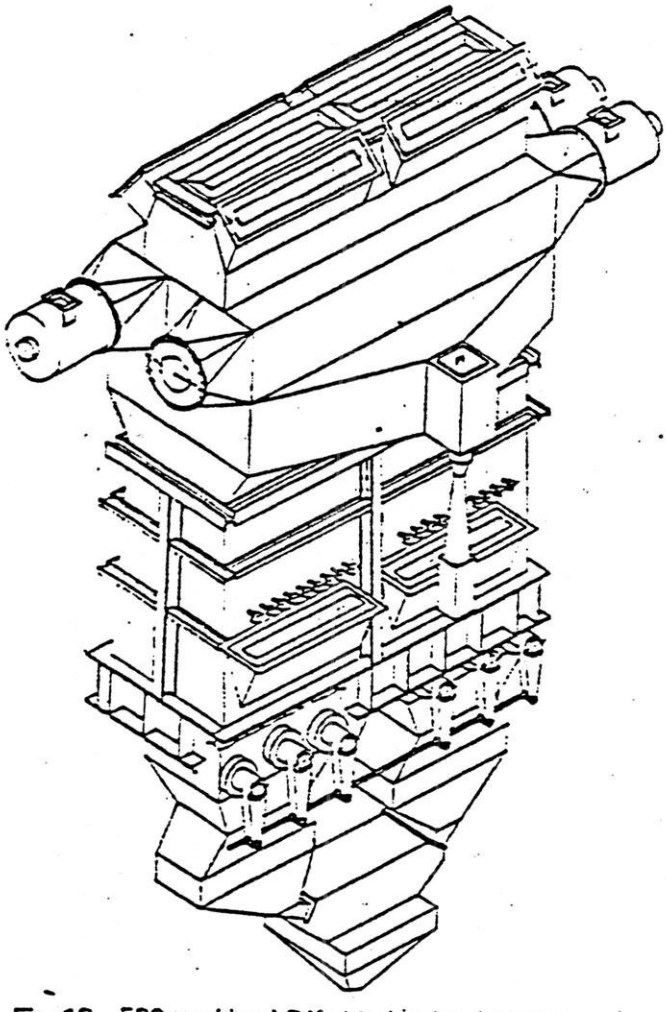


Fig. 13 500 ton/day LDK chlorination furnace

method the chlorination gases were drawn through the dry pellet charge together with the combustion gases. Abraded dust from non-indurated pellets, i.e. cinders, was thus introduced into the waste gas cleaning system. This dust contaminated the liquor and partly dissolved in the hydrochloric acid solution; therefore this solution contained a high percentage of trivalent iron. In the new method the volatilized chlorides are discharged below the induration zone from a region in which the pellets have attained their fired strength and in which practically no abraded dust arises.

(3) As the volatilized chlorides are no longer drawn through the induration zone, and therefore do not come into contact with cold pellets, it would now be possible to charge wet pellets into the furnace, which could result in reduction of operating and capital costs.

The new operating method was used with cinders for which experience had already been gained with the old operating method, as well as with some other cinders. On the basis of the operational results obtained, a larger shaft furnace unit was developed and designed for a rated throughput of 500 ton/day (Fig. 13).

The 100-ton/day pellet chlorination plant had been built not to treat any special type of cinders but to gain experience and to compile data on a commercial scale with various qualities of cinders for the design of even larger units. Table 3 shows the chemical and size analyses for the cinders treated to date. The cinders originated from fluid-bed as well as from multiple-hearth roasters.

Samples of at least 500 tons, but mostly of several thousand tons, were treated in the different test series.

Chemical composition of cinders

The *iron content*, which is unimportant in the volatilization process, was between 47 and 63 per cent Fe. Depending on sulphur and non-ferrous metal contents, it was 2–5 per cent higher in the pellets after treatment.

The *copper content* of the cinders varied between 0·03 and 0·84 per cent Cu. The *zinc content* ranged from 0·08 to 1·86 per cent Zn and the *lead content* from 0·01 to 1·2 per cent Pb.

The total sulphur content of the cinders varied between 1·2 and 3·4 per cent S, two-thirds of which was generally in sulphate form. Only in the case of the pyrrhotite cinders V and VI was the major part of the total sulphur present as sulphides and only about 20 per cent as sulphates.

The *cobalt content* of the cinders was 0·004–0·12 per cent Co, the *nickel content*, as far as it was analysed, reached a maximum of 0·037 per cent Ni. The cinders contained 0·0–1·2 g/t of gold and 2–29·7 g/t silver.

Table 3

	I	II	III	IV	V	VI	VII	VIII	IX
Fe, %	61·0	58·5	63	54·0	55·25	54·3	47·3	59·2	57·5
Cu, %	0·25	0·84	0·39	0·28	0·67	0·72	0·075	0·01	0·83
Zn, %	0·15	0·32	0·50	0·28	0·20	0·08	1·65	1·24	1·86
Pb, %	0·01	0·01	0·10	0·33	0·01	0·01	0·75	1·87	1·01
As, %	0·01	0·01	0·09	0·12	0·04	0·02	0·11	0·12	0·53
Co, %	0·095	0·12	0·02	0·004		0·04	0·005	0·025	0·049
Ni, %						0·0015	0·037		0·005
total, %	1·2	2·0	1·6	3·4	2·15	3·1	1·8	1·25	1·70
S in SO_4, %	0·8	2·0	1·1	2·0	0·45	0·5	1·45	1·10	1·15
SiO_2, %	8·0	5·7	2·3	8·5	11·1	12·4	17·1	3·1	6·15
CaO, %		1·32			1·20	0·65	2·3		0·50
Origin*	FB	FB	FB/MH	FB/MH	FB	FB	FB	FB	FB
Au, g/t		1·0	1·2		0·2	0·3	0·1		1·1
Ag, g/t		5·5	4·1		3·5	5·0	2·0		29·7
Origin†	P	P	P	P	Py	Py	P	P	P
+4 mm			0·7	1·7	0·3		0·8	1·4	2·4
+2 mm			3·1	0·6	1·8	7·7	2·8	3·3	4·3
+1 mm			3·7	0·4	30·2	24·8	3·0	3·5	3·8
+0·5 mm			3·0	0·4	18·0	17·4	3·5	2·6	3·0
+0·25 mm		49·5	15·9	4·4	13·7	12·2	5·9	3·6	13·0
+0·125 mm			25·3	13·8	9·1	8·9	19·2	18·4	18·8
+0·063 mm			18·3	27·1	6·8	7·1	24·7	18·8	14·4
−0·063 mm		50·5	30·0	51·6	20·1	21·9	40·1	48·4	40·3
Blaine number, cm^2/g		150			730		1975	1250	990

*FB and MH indicated fluid-bed and multiple-hearth roasted, respectively.

†P and Py indicate pyrite calcine and pyrrhotite calcine, respectively.

The principal gangue constituents were 3·1–12·4 per cent SiO_2 and 0·5–2·3 per cent CaO. Minor constituents included tin, antimony, magnesium and barium.

Operational results

The numerous factors important in the production of mechanically and chemically satisfactory pellets from the great variety of cinders include size distribution, addition of binding agents, conditions of pellet drying and induration, chlorine consumption and chlorine concentration in the chlorine–air mixture. As it is not possible, within the scope of this paper, to deal with all these parameters, Table 4 gives average operating data and Table 5 contains data on the pellets produced. All these, except the chlorine consumption, are valid for both the old and for the new operating method.

Table 4

Pellet drying conditions	
Blaine number	2800–4500 cm²/g
Bentonite addition	max. 1%
Addition of water in pre-humidifier	about 8%
Moisture of green pellets	12–18%
Pellet size	10–18 mm
Hardness of green pellets	1–2·5 kg/pellet
Hot gas temperature for pellet drying	350–550°C
Moisture of dry pellets	<0·1%
Hardness of dry pellets	10–15 kg/pellet
Shaft furnace operational data, normal practice	
Throughput of cinder (depending on type of cinder)	80–100 t/day
Hot gas temperature	1100–1250°C
H_2O content of combustion gases	5–10% H_2O
Chlorine consumption expressed in multiples of stoichiometrically required amount of chlorine, based on CuCl, $ZnCl_2$, $PbCl_2$	1·3–2 (2–3·5)*
Chlorine concentration in chlorine–air mixture	5–17 vol %
Temperature of heated cooling air	400–500°C
Temperature of discharged pellets	100–200°C
Exit gas data	
Temperature of exit gas at furnace top	200–400°C
Dust losses in exit gas at furnace top	1%
Temperature of outgoing chlorination gases containing volatilized chlorides	800–1000°C

*Old process

The most important parameters influencing the non-ferrous metal volatilization are *induration temperature* and *chlorine consumption*, the influence of which may differ for various types of cinders, as was demonstrated by the tests with cinders II, VII and IX, using the new operating method (Tables 6–8).

Tests 1–6 (Table 6) were performed at almost equal induration temperatures. The resulting pellet strengths were 140–200 kg/pellet. The chlorine consumption was progressively decreased. It appears that in the case of cinder II a chlorine consumption equal to 1·5 to 1·3 times the stoichiometric amount was needed to obtain a low residual copper content of 0·02–0·05 per cent Cu and a low residual zinc content of 0·04–0·09 per cent Zn. Comparison of tests 3 and 7 or 2 and 8, respectively, shows that, with equal chlorine consumptions, pellets of higher strength were decopperized less efficiently than pellets of lower strength (Fig. 14).

Table 5

Data on pellets produced	
Abrasion <0·6 according to Tumbler test	4–8%
Crushing strength	150–300 kg/pellet
Abrasion rates according to Linder	10–13%
Porosity	32–36%
Pellet resistance during reduction (expressed in mm water gauge at 80% reduction)*	6–10
Copper	<0·02% max. 0·05%
Zinc	<0·05% max. 0·25%
Lead	<0·05%
Sulphur	<0·02%
Gold and silver volatilization	>90%

*Carol Lake pellets, 4·0; Wabush pellets, 8·9.

Tests were carried out with cinder II to study the volatilization of cobalt, which may improve the profitability of the chlorination process. As can be seen

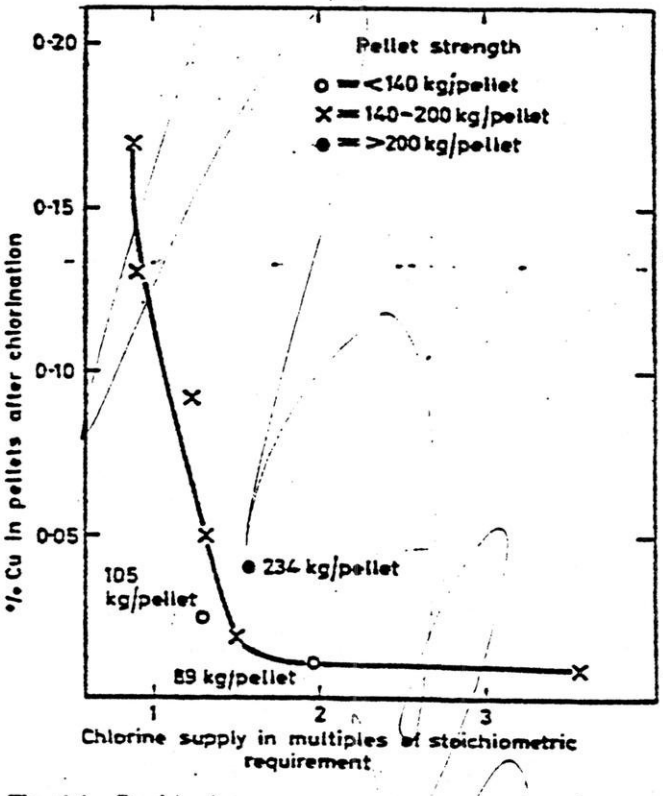


Fig. 14 Residual copper content as a function of chlorine supply

Table 6 Treatment of pyrite calcine II (0·84% Cu, 0·32% Zn, 0·12% Co, 0·01% Pb, 2·1% S) by pellet chlorination

Experiment no.	Chlorine consumption kg/t	× theoretical	Non-ferrous metals in pellets produced % Cu	% Zn	% Co	Pellet strength, kg/pellet
1	34·5	3·58	0·010	0·04	0·042	165
2	14·3	1·50	0·019	0·04	0·087	170
3	12·0	1·32	0·050	0·09	0·11	160
4	11·7	1·23	0·092	0·19	0·10	200
5	8·7	0·91	0·130	0·21	0·12	155
6	8·5	0·89	0·170	0·20	0·11	140
7	12·0	1·31	0·025	0·06	0·085	105
8	15·1	1·58	0·040	0·06	0·11	234

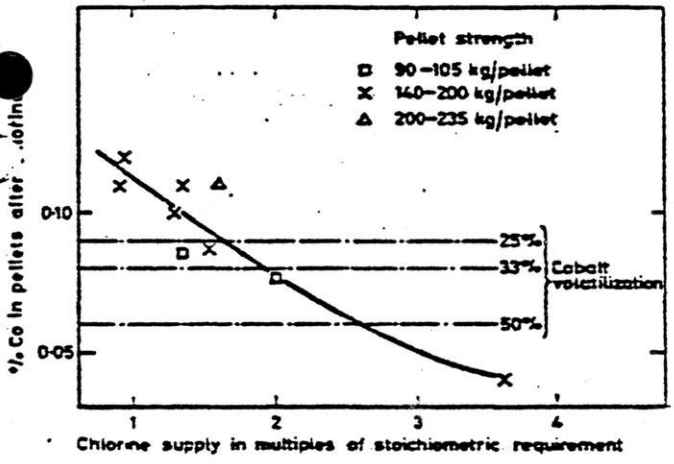


Fig. 15 Residual cobalt content as a function of chlorine supply

of about 50 per cent of the cobalt contained in cinder II.

The results of the tests undertaken with cinder VII, rich in zinc and lead and practically free from copper, are given in Table 7. Tests 1 and 2 show the influence of the induration temperature. With equal chlorine consumptions of approximately twice the stoichiometric requirement, the induration temperature was raised from 1120 to 1150°C. The pellet strength increased from 105 to 244 kg/pellet. The degree of non-ferrous metal volatilization decreased, the residual zinc content rose from 0·1 to 0·27 per cent and the residual lead content from <0·05 to 0·08 per cent Pb.

Tests 1, 3 and 4 show the non-ferrous metal volatilization with respect to chlorine consumption for comparable induration temperatures. With a pellet strength of 105–120 kg/pellet, a chlorine consumption

Table 7 Treatment of pyrite calcine VII (0·075% Cu, 1·65% Zn, 0·75% Pb, 1·8% S) by pellet chlorination

Experiment no.	Hot gas temperature, °C	Chlorine consumption kg/t	× theoretical	Non-ferrous metals in pellets produced % Cu	% Zn	% Pb	Pellet strength, kg/pellet
1	1120	41·2	1·95	0·003	0·10	<0·05	105
2	1150	41·2	1·97	0·013	0·27	0·08	244
3	1135	36·8	1·84	0·011	0·17	<0·05	118
4	1135	29·0	1·45	0·011	0·26	<0·05	111

Table 8 Treatment of pyrite calcine IX (0·83% Cu, 1·86% Zn, 1·01% Pb, 0·05% Co, 1·7% S) by pellet chlorination

Experiment no.	Chlorine consumption kg/t	× theoretical	Non-ferrous metals in pellets produced % Cu	% Zn	Pellet strength, kg/pellet
1	36·0	1·27	0·010	0·06	184
2	34·5	1·22	0·030	0·19	185

From Fig. 15, a high degree of volatilization of cobalt can only be achieved with a considerable excess of chlorine. A chlorine consumption of approximately 2·5 times the stoichiometric amount was needed for the volatilization

equal to approximately twice the stoichiometric requirement was needed to obtain a residual zinc content of 0·1 per cent Zn, i.e. considerably more than, for example, for cinder II.

It is apparent from Table 8, which gives the results of tests with cinder IX with a high non-ferrous metal content, that pellets having a strength of 185 kg/pellet and a low residual non-ferrous metal content (0·01–0·03 per cent Cu, 0·06–0·19 per cent Zn and <0·05 per cent Pb) can be produced. Despite the high non-ferrous metal content of the cinders, chlorine consumption was as low as 1·22–1·27 times the stoichiometric requirement.

Mechanical pellet properties were determined by the pellet behaviour in the cold state and at elevated

temperatures during reduction. The cold crushing strength has already been discussed in detail. The resistance to abrasion according to the ASTM Tumbler test was 4–8 per cent <0·6 mm for the different types of cinders.

To examine pellet strength during reduction a test was developed by Studiengesellschaft für Eisenerzaufbereitung, Othfresen, based on the isothermic testing method given in test sheet Stahleisen No. 1770–64. This yielded figures which largely conform to results obtained in the blast-furnace. In this test method reduction gas is passed through pellets held at 1000°C and under a load of 0·8 kg/cm². Oxygen removal is determined by continuous weighing of the pellet sample. The stability is indicated by the gas flow resistance of the pellet sample. It is known that pellets which show a resistance to flow of less than 15 mm water gauge at a reduction degree of 80 per cent can be described as very suitable for treatment in the blast-furnace.

Table 9 Characteristics of cinder pellets in comparison with iron ore pellets from world market*

Pellet sample	Porosity, vol. %	Velocity of oxygen removal, %/min	Degree of reduction on end of test, %	Differential pressure as indication of resistance during reduction, mm water gauge	
				At end of test	At 80% reduction
Cinder VI					
Sample 1	33·7	0·88	84·6	6·5	6·2
Sample 2	35·5	0·82	84·9	11·8	10·5
Wabush	28·5	0·78	90·6	7·5	8·9
Carol Lake	32·7	0·73	85·3	4·1	4·0

*Pellets of cinder VI: crushing strength = 120 and 135 kg/pellet, respectively.
abrasion (ASTM Tumbler) = 9·6 and 9·3% <0·6 mm, respectively.

This testing method was adopted to examine two samples of pellets from cinder VI. The results, given in Table 9, demonstrate that these cinder pellets are comparable in reduction behaviour with iron ore pellets traded on the world market.

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PROCESSING OF PYRITE CINDERS

by

Sverre Olsen

Paper read at Pyrite symposium, 31st October to 1st November, 1967, organized by the mining engineers' sections, of the NIF and the Norwegian Metallurgical Society, in Norwegian, title: "AVBRAENNSFORDEDLING".

It has already been mentioned that cinders is the substance left after removal of the sulphur. It has also been mentioned that direct use of pyrite cinders as an iron ore is prevented by the other elements present, such as Cu, Zn, S, and As, which are deleterious.

The quantities in which these elements are present depends mainly on the method of enrichment and the roasting conditions but there are very few pyrite cinders which are from the chemical point of view immediately suitable for melting down, before they have passed through some cleaning process or other.

Iron and steel producers impose special conditions as regards the Cu, As, and S content. The requirements for chemically pure iron ores are steadily being tightened and people are now talking already on maximum percentages of 0.03 for copper, for 0.10 for zinc, 0.07 for sulphur, and 0.05% for arsenic in top grade iron ores.

Some of these elements, which in pyrite cinders are detrimental impurities, are by themselves valuable elements, which sometimes can be utilised with advantageous results. We are

thinking here in particular of the copper content. Elements like sulphur, lead, arsenic and the like are of little use in the cinders and can only be regarded as detrimental. This is partly also true for zinc.

The normal procedure for the treatment of cinders is the well known DK process. After roasting, the pyrite cinders are chlorinated by roasting with NaCl, followed by leaching to remove the nonferrous metals. During the leaching stage, iron oxide remains insoluble (purple ore) and after filtering the comparatively pure iron oxide is pelletised and used for producing pig iron.

Deleterious elements such as arsenic and antimony are most conveniently removed during the roasting stage if they present a problem.

The DK process has been in use for very many years and every year about 2 - 3 million tons of pyrite cinders are processed according to this system. This is very large percentage of the total cinders production in Europe. The balance of the cinders is mostly used for direct production of iron without any cleaning process, and some of the cinders is also left unused on account of unsuitable chemical analysis, such as excessive Zn and As content.

The DK process is actually a very good process but it must be pointed out that it is economical only when employed on a large scale of, say, more than 1 million tons per year.

Another important condition for the economy of the process

is a comparatively high content of valuable metals, which help to pay for the cleaning process, a minimum of 0.6 to 0.7% of Cu in the cinders.

Duisburger Kupferhütte require a coarse-grain material for the leaching and filtering stages of the process, in particular also for the sintering of the residue, the purple ore.

The DK process requirements impede the natural development pointing in the direction of more finely grained concentrates, with a poor content of nonferrous metals. This development is due to increasing interest in flotation enrichment and fluidising roasting.

We accordingly have to devise some process for dealing with these new types of cinders.

While the DK process is, generally speaking, a process for the recovery of the individual elements, the new processes can be seen broadly as cleaning processes designed to convert cinders into first class iron ore.

Several such processes have been worked out and their common feature is a chlorinating stage to remove the nonferrous metal from the cinders so as to yield a pure iron oxide. Naturally one also wants to retain the comparatively small quantities of valuable metals if this can be done in an economical manner.

On the laboratory scale there is also another process of a different type, microbial leaching, as mentioned by Mr. Bimhjellen in his paper read at the "Industry Days".

Finally we can mention here the possibility of sulphatising and leaching nonferrous metals like Cu, Zn, Co, a process which

is in actual use at Outokumpu. Sulphatising is a slow process and requires subsequent leaching. It would therefore be expensive and in the case of Outokumpu it is justified by the recovery of cobalt, a valuable metal, which is difficult to recover in other processes.

The cinder processes to be discussed here are all based on selective chlorination in an oxidising atmosphere, using gaseous chlorine or suitable chlorides as chlorinating agents. We obtain reactions of the following types

(12) $MeO(s) + Cl_2(g) = MeCl_2(g) + \frac{1}{2} O_2(g)$

(13) $MeS(s) + Cl_2(g) = MeCl_2(g) + \frac{1}{2} S_2(g)$

where Me stands for the more common nonferrous metals in pyrite cinders (Zn, Cu, Pb).

Metal chlorides have comparatively low boiling points and a corresponding high vapour pressure at moderate temperatures. This means that they can be fairly easily evaporated at temperatures of over about 800° C.

The vapour pressures of some common chlorides are shown in Fig. 7.

While nonferrous oxides can be chlorinated comparatively easily in the presence of oxygen, this is not the case with the iron oxide in the pyrite cinders. Iron oxide is more stable than iron chloride at normal conditions and the great importance of chlorine in the metallurgy of pyrite cinders is just this selective action between iron and nonferrous oxides. We have tried to illustrate this in Fig. 8.

The illustration shows also the equilibrium pressure of chlorine as a function of the temperature (more accurately 1000/T) for the chlorination of iron oxide, copper oxide, and zinc oxide. The resulting chlorides are assumed to be in their reference condition, i.e., a pure molten liquid below boiling point, or gas at a pressure of 14.7 psi above boiling point. The oxygen pressure is also assumed to be 14.7 psi.

For chlorinating and evaporating iron we must have a reducing atmosphere, as for instance in the chlorination of titanium ore (ilmenite) for the production of TiO_2 pigment through titanium tetrachloride.

$CaCl_2$ AS CHLORINATING AGENT

As already mentioned, the chlorinating agent may be either chlorine gas or suitable chlorides. In actual fact there are not many chlorides suitable for this process. They have to meet the following requirements:

1. The chloride must be able to react with the required oxides and sulphides so as to yield the volatile metal chlorides.
2. The nonchlorine constituent of the chloride must not represent a new deleterious impurity for iron ore.
3. The chloride must be a reasonable source of chlorine.

The two obvious chlorides on this basis are calcium chloride, a byproduct of the Solvay process, and sodium chloride (sea salt). These two chlorides can act as chlorinating agents but in the case of sodium chloride we have the unfortunate feature that sodium is undesirable from the point of view of the iron and steel producer. We are left with $CaCl_2$.

We obtain reactions of the type

(14) $Cu_2O(s) + CaCl_2(l) = 2\ CuCl(g) + CaO(s)$

(15) $Cu_2S(s) + CaCl_2(l) + \frac{3}{2}\ O_2(g) = 2\ CuCl(g) + CaSO_4(s)$

(16) $ZnO(s) + CaCl_2(l) = ZnCl_2(g) + CaO(s)$

I shall not go into details of the equilibrium constants of these reactions, but only state that they proceed much more smoothly than one might get the impression from the equilibrium constants. This is due to the binding of calcium as ferrite or silicate.

We should mention here also that NaCl is not suitable as a chlorinating agent for the more common nonferrous oxides because of certain thermodynamic calculations in connection with the reactions corresponding to the equations shown above. Nevertheless sodium chloride does work in practice, but this again is due to the fact that the reaction proceeds in a more complex manner, with formation of, say, sodium sulphate, silicates, and ferrites.

There are some more general advantages and disadvantages in the use of $CaCl_2$ as chlorinating agent. The advantages are its more simple transportation and manipulation, compared with chlorine, we can give each individual pellet the required dose, and reasonable quantities of the chloride act as a binding agent in the pellets.

The disadvantages are the addition of a foreign element (Ca), unless the basic component is specifically required for the production of pellets. Also, there is a danger of inadequate removal of sulphur on account of formation of $CaSO_4$.

$CaCl_2$ is an expensive source of chlorine and it has to be added in excess, perhaps twice the theoretical quantity.

The most important disadvantage is probably that the $CaCl_2$ process is sensitive to water vapour. This means that preferably fuel free from hydrogen should be used.

$$CaCl_2 + H_2O = 2\ HCl + CaO$$

VUOKSENNISKA PROCESS

There has always been some interest in combining the chlorination with pelletising, which is equally necessary. Ordinary sintering is impossible with this finely grained material.

This combination of cleaning and pelletising has been used for the first time, to my knowledge, on a larger scale by Vuoksenniska in Finland. This process has been in use only for a very short time.

More recently, a new combined pelletising and cleaning process has become known, the Kowa Seiko process from Japan.

The Vuoksenniska process was in use for only two years. The installation had a capacity of about 80 to 90 tons per day or about 30 000 tons per year. Quite a lot of money had been invested in this project.

A simplified flow diagram of the process is shown in Fig.9.

Pyrite cinders was pelletised with $CaCl_2$ and sintered in a shaft furnace. During the sintering stage, the volatile non-ferrous chlorides are also driven off. The thermal economy of the process was rather poor. Originally attempts were made to pass the products of combustion into the sintering shaft but the steam content of the blast furnace gas became so high that this had to be discontinued.

Then dry air was heated up in cowpers outside the shaft, but this naturally increased the heat losses. The heat consumption is stated as 1 million kcal per ton of pellets against the usual 250 - 400 000 kcal per ton.

The driving off of some nonferrous elements was also not entirely satisfactory. The table shows the chemical composition of the cinders before and after the combined and sintering and driving off stage.

	Fe_2O_3	Cu	Zn	Pb	Co	S	CaO
	%	%	%	%	%	%	%
Cinders	85.0	1.5	1.9	0.13		2.0	
Pellets	86.0	0.03	0.04	0.01	0.5	0.2	4-5

Elements like Cu, Zn, and Pb are driven off to an adequate extent but the sulphur content in the pellets was too high. It varied generally between 0.1 and 0.3% in the pellet but should have been 0.05% lower in view of the subsequent production of iron and steel.

On account of the difficulty of removing the sulphur, the high CaO content sometimes led to formation of a stable compound $CaSO_4$, which could not be split at temperatures below the softening point of the pellets.

The most important reason for discontinuing this process was the difficulty of recovering the cobalt content of this particular grade of pyrite cinders. The cobalt is now being recovered according to the Kokkola sulphatising process.

The heavy consumption of heat has already been mentioned (80 kg = 175 lb of oil per ton or 1 million kcal per ton).

Among other leading data we can mention here the addition of 6 - 7 % of $CaCl_2$ for dry pellets. This is perhaps a surprisingly low addition of chloride considering the high percentage of non-ferrous metals. It corresponds to twice the theoretical requirements of calcium chloride.

The effective consumption of calcium chloride was even less than this, barely 20 to 25 kg (45 - 55 lb) per ton of pellets. If the calcium chloride was recovered by means of hydrochloric acid gas, all that was needed was limestone, and a little lime in an aqueous medium for forming the calcium chloride.

The subsequent reaction between chlorides and SO_3 gas in the gas cleansing system had also a chlorine saving action. In this way metal sulphates were formed, while the chlorine gas was released and could be returned to the shaft.

Hydrochloric acid gas for recovery of calcium chloride was obtained by hydrolysis of metal chlorides and by taking out one third of the circulating gases and using them as air for combustion for heating the cowpers. Here the free chlorine content of the circulating gas was caught in the water vapour resulting from the combustion of oil (the result being hydrochloric acid gas).

The gas taken out was replaced by dry air in the bottom of the shaft. This air had a cooling action on the pellets and was heated up at the same time.

The cost per ton of pellets were found as 60.- mkr in 1956. This includes the capital costs. The costs of recovering the valuable metals have not been taken into account.

KOWA SEIKO PROCESS

This process, which is now in use in Japan, is basically very much like the Vuoksenniska process. The difference is that the Kowa Seiko process employs a rotary furnace instead of a shaft furnace for sintering and driving off the chlorides. The flow diagram is shown in Fig.9.

The chlorinating reactions are quite fast and the dwell of the pellets in the rotary furnace is only one hour, including 20 minutes at the chlorinating temperature of 300 - 1100° C and 10 minutes for sintering and removal of the sulphur by heating to a maximum temperature of 1250° C in the rotary furnace.

It can be seen that a gas is used which largely consists of CO (70%) as fuel. This is in order to avoid the deleterious water vapour. The gas is obtained from LD converters and contains only 4% of H_2. With this source of heat and using a rotary furnace, Kowa Seiko reckon that it is adequate to use 1.3 times the theoretical quantity of calcium chloride for Pb, Zn, and Cu.

One day per week, the rotary furnace is fired with a mixture of cokery and blast furnace gas containing 24% of H_2, 12% CH_4, and 20% of CO, i.e., a gas with a much higher steam content after combustion.

On this day, 1.5 times the theoretical calcium chloride quantity (worked out for the elements mentioned above) is used. Kowa Seiko say that the same consumption would be applicable when using oil as fuel.

The above figures for the consumption of calcium chloride are much better than those obtained with the Vuohsenniska process and better than those obtained even in the laboratory, using a controlled atmosphere free from water. We found that with dry air it is necessary to use 2 - 3 times the theoretical quantity of calcium chloride.

Kowa's say that the poor yield of calcium chloride in the shaft furnace is due to the disassociation of calcium chloride at low temperatures, with a resulting loss of chlorine. The causes of the various reactions are not yet entirely clarified but it is perhaps permitted to take a somewhat sceptic attitude to the low figures stated by Kowa, in particular in connection with the use of oil fuel.

Both the gas mixtures stated above have a heating value of 2200 kcal/m^3 and it is reckoned that 370 to 400 000 kcal are required per ton of pellets.

Kowa Seiko have an annual capacity of 240 000 tons purified pyrite cinders pellets with the following analysis before and after sintering.

	Cu %	Pb %	Zn %	As %	Au g/t	Ag g/t	S %	Fe %
Dry pellets	0.45	0.10	0.64	0.050	0.94	33.6	0.54	59.15
Sinter pellets	0.04	0.01	0.02	0.048	0.05	7.0	0.02	61.50

The sintered cobalt pellets contain also about 7.5% of SiO_2.

Compared with the pellets obtained by sintering in the shaft furnace, these pellets seem to be of very even quality. Their

compressive strength is stated to be 300 -450 kg (660 - 1000 lb).

1.2 and 1.5 x the theoretical calcium chloride in the form of crystals with 50% of chlorine are required for the pyrite cinders stated here and indicate in fact a consumption of 2.4 and 3% of Ca chloride, respectively, but the consumption is stated as 3 to 5% of the cinders. For the time being there is no means available for recovering the calcium chloride.

The gas from the rotary furnace passes first into a dust chamber, made of steel with a coating of titanium, and lined with acid resistant bricks.

The gas is then cooled down to 70° C while being washed with circulating seawater. Hydrochloric acid, chlorides and sulphates are washed out. After cooling a PVC lining is used for filtering the gas in Cottrell filters with titanium electrodes. The fumes are removed here, with lead salts, before the gas is left to escape in the atmosphere.

It is stated that more than 95% of copper, 60 to 80% of lead, about 90% of gold, and 95% of silver are recovered. It would take us too long to discuss the various recovering methods in detail.

50% of the arsenic is removed during roasting, but as we have seen, the quantity of arsenic reduced during the chlorination stage is insignificant.

A word or two about the sulphur: As a result of the addition of the very large quantities of the calcium chloride, there is a danger of forming $CaSO_4$, a stable compound, with inadequate

removal of sulphur. Our own investigations in this field indicate that an excess of SiO_2 in the pellets facilitates the splitting of calcium sulphate with formation of calcium silicate. It is therefore easy to understand that the Kowa pellets with 7.5% of SiO_2 have a low sulphur content.

CHLORINATING BY MEANS OF CHLORINE GAS

LDK process

There is only one pyrite cinders treatment process in use which uses chlorine directly as a chlorinating agent. This is the LDK process employed by Lurgi and by the Duisburger Kupferhütte hence the name.

The installation in question is a pilot plant with a production of about 100 tons per day. The flow diagram of the LDK process is shown in Fig.12.

Sintering is carried out in a shaft as in the case of the Vuoksenniska. The chlorine is passed in and moves upward in the shaft, and chlorination mainly takes place below the level where the gases for combustion are introduced. The difficulty of this process is that the pellets are sintered before chlorination takes place. Sintering takes place at about 1200° C and there are considerable possibilities for the formation of copper and zinc ferrites. The pellets also shrink very much with a corresponding reduction of the pore volume, which interferes with the essential diffusion of chlorine.

Figs.13 and 14 show the results obtained by us with different pyrite cinders after chlorination of sintered pellets with chlorine

gas.

It can be seen that the porosity of the pellets is a matter of enormous significance in the rate of chlorination and that the various grades of pyrite cinders behave in different ways. It follows that the actual grade of cinders must be carefully investigated before a decision is taken to employ this process.

Lurgi and DK themselves say that the results are governed by the quality of the pyrite cinders, not necessarily its chemical composition, but rather more by the roasting conditions.

It seems that for the time being they are working with a large excess of chlorine in order to reach the required reduction of nonferrous elements, e.g., 2 to 3 times the theoretical quantity of chlorine for cinders with less than 0.5% Cu and 0.5% Zn. It is hoped to reduce the chlorine consumption to 1.3 to 1.5 times the theoretical quantity.

Together with the chlorine concentration, there are 5 to 10% (volume) of air.

Difficulties are obtained not only with varying chemical analyses, but also with lack of uniformity in the quality of the pellets (compressive strength 50 - 400 kg, 110 - 900 lb, per pellet).

The difficulties of the LDK process are due to those generally experienced in reaching a uniform gas distribution over the shaft cross-section. It does not appear that sulphur is going to cause any troubles in the LDK process, and it is interesting to note that a small addition of coke is made to the pellets in order to remove the As.

Cokery gas and town gas with a hydrogen content corresponding to that obtained on combustion of oil is used for the LDK process. The heat requirements are stated to about 500 000 kcal per ton of pellets, supposing that there is 10% of water in the green pellets.

F l u o - c h l o r p r o c e s s

The Fluo-chlor process differs from those discussed above, Vuoksenniska, Kowa Seiko, and LDK, in that the chlorination is not combined with the pelletising process. One might think at first that this is a disadvantage, but in fact it can be shown to be a great advantage.

The laboratory experiments have been carried out by Sintef/ Metallurgisk Institute on instructions issued by the Norwegian Sulphur Pyrite Producers Association and indicate that the chlorination of pyrite cinders in a fluidised bed may be a particularly promising process for the improvement of pyrite cinders.

After this process, the purified pyrite cinders will be present in powder form and can be used directly for making iron sponge or pre-reduced pellets without making the detour via sintered oxide pellets.

The Fluo-chlor process should be carried out directly after roasting so that the heat content of the cinders can be utilised.

The flow diagram of Fig.15 illustrates how it is thought the process can be carried out.

The process equipment is of very moderate dimensions.

A rough calculation for an imaginary installation for the treatment of 100 000 tons of cinders per year shows that the chlorinating reactor should have a bore of 1.2 m (47").

At a gas velocity of 7.5 cm (3") per second in the reactor, at 800° C, the fan should supply (circulate) about 70 m^3 of gas at NTP per hour. The chlorine content of the circulating gas depends on the total content of nonferrous metals in the cinders, but in ordinary flotation concentrates this would be about 5-10% of Cl_2.

The circulating gas is dry and does not yield any special corrosion problems. It would also be at a very low temperature after electroprecipitation.

On account of the small quantity of gas circulated, the metal chloride concentration in the outgoing gas is high, which facilitates recovery.

The most important matter is naturally the chlorine yield. In practice it is limited only by the sulphur content of the cinders, because some gas must be bled to prevent accumulation of SO_2 in the system. On the other hand, it is not impossible that the sulphur content can improve the chlorine yield because reactions can take place with metal chlorides and the $SO_2 + O_2$ gases in the gas cleaning plant. Metal sulphates will be formed in this case and separated out in the electro-precipitator while chlorine is released and returned to the reactor.

(17) $MeCl_2(l) + SO_2(g) + O_2(g) = MeSO_4(s) + Cl_2(g)$

The analysis of the Vuohsenniska process sublimate indicates in fact that the following reactions take place:

Cu	4	-	10	%
Co	0.01	-	0.7	%
Zn	25	-	30	%
Fe	0	-	10	%
S	9	-	14	%
Cl	8	-	30	%

The greatest advantage of the process, if it will keep its promises, is that it can be used even for small roasting plants. The quantity of cinders may be too small to justify a pelletising plant, but pure cinders should be much easier to use than cinders with an average content of nonferrous metals. The sublimate obtained in this process will contribute to a considerable extent to the costs of the cleaning process.

It is probably an advantage both for this and other cinders treatment processes if the cinders is not too finely grained. In the Fluo-chlor process, very finely grained material can create problems in the fluidising stage in the chlorinating reactor.

Chlorinating processes: A survey

Chlorine, either liquid or gas or bonded to calcium as calcium chloride, is comparatively expensive.

Chlorine gas costs approximately 600 nkr per ton carriage free to the reactor, while chlorine in calcium chloride is rather more expensive, say 650 nkr per ton. Calcium chloride contains about 50% of chlorine.

As far as the two nonferrous metals are concerned which use

up most of this chlorine, Cu and Zn, the position is that one unit weight of zinc requires twice as much chlorine as one unit weight of copper.

If we reckon with a chlorine yield of 70%, 1% of zinc in the cinders will cause a direct chlorine cost of nearly 10 nkr per ton of cinders. Similarly, 1% of Cu will cause a chlorine cost of about 5 nkr per ton of cinders.

While $ZnCl_2$ in the sublimate can be regarded as useless, the copper can be said to have a value of 3.50 nkr per kg in this form. 1% of Cu in the cinders, recovered to 90%, will therefore yield a sublimate having a value of 25 nkr per ton of cinders.

This calculation is intended to show that it is realistic to expect the copper to pay for the chlorine if the Zn/Cu ratio is not much worse than 2.

With higher zinc contents in the cinders, it will be a struggle to make the cleaning process pay.

The Zn/Cu ratio is often 2 or worse. It is therefore normally not realistic to regard these cinders treatment processes as profitable methods for the recovery of the nonferrous metals in the cinders. However, they can be justified as processes for the production of first class iron ores from the cinders of moderate impurity content.

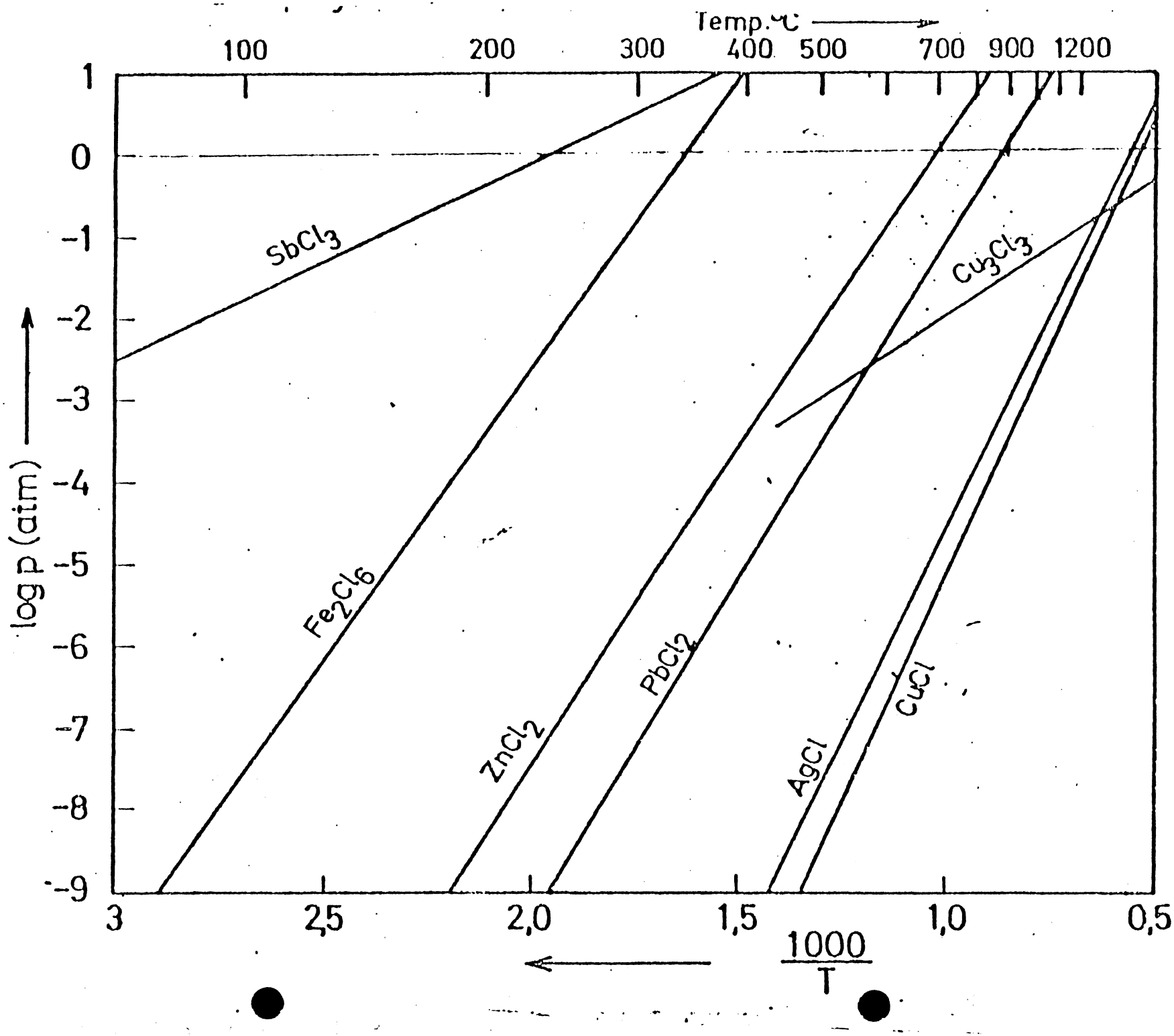
Four different cinders processes have been discussed. The Vuoksenniska process now discontinued, and the comparatively new Kowa Seiko process using calcium chloride as chlorinating agent, and LDK and Fluo-chlor using gaseous chlorine for the chlorination.

The objections to use of calcium chloride have been pointed out, in particular the difficulty of removing the sulphur in the presence of calcium, and the danger of increasing the chloride consumption when using hydrogen containing fuel. If other fuel is available, in particular CO, it is preferable to use it for the treatment of the cinders (see also the Rosenqvist process).

The LDK process is found, in principle, but cannot be regarded as an ideal one after the problem of evening out the sintering in chlorination conditions in the shaft can be controlled.

We have naturally great confidence in the Fluo-chlor process, the one we are ourselves engaged in, but only the future can show whether it can be of any use.

Fig. 7


Temp.°C
100
200
300
400
500
700
900
1200
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
log p (atm)
SbCl3
Fe2Cl6
ZnCl2
PbCl2
AgCl
CuCl
Cu3Cl3
3
2,5
2,0
1,5
1,0
0,5
1000/T

Equilibrium pressure of chlorine in the chlorination of various oxides. Fig 8.

Likevektstrykket av klor ved klorering av diverse oksyder

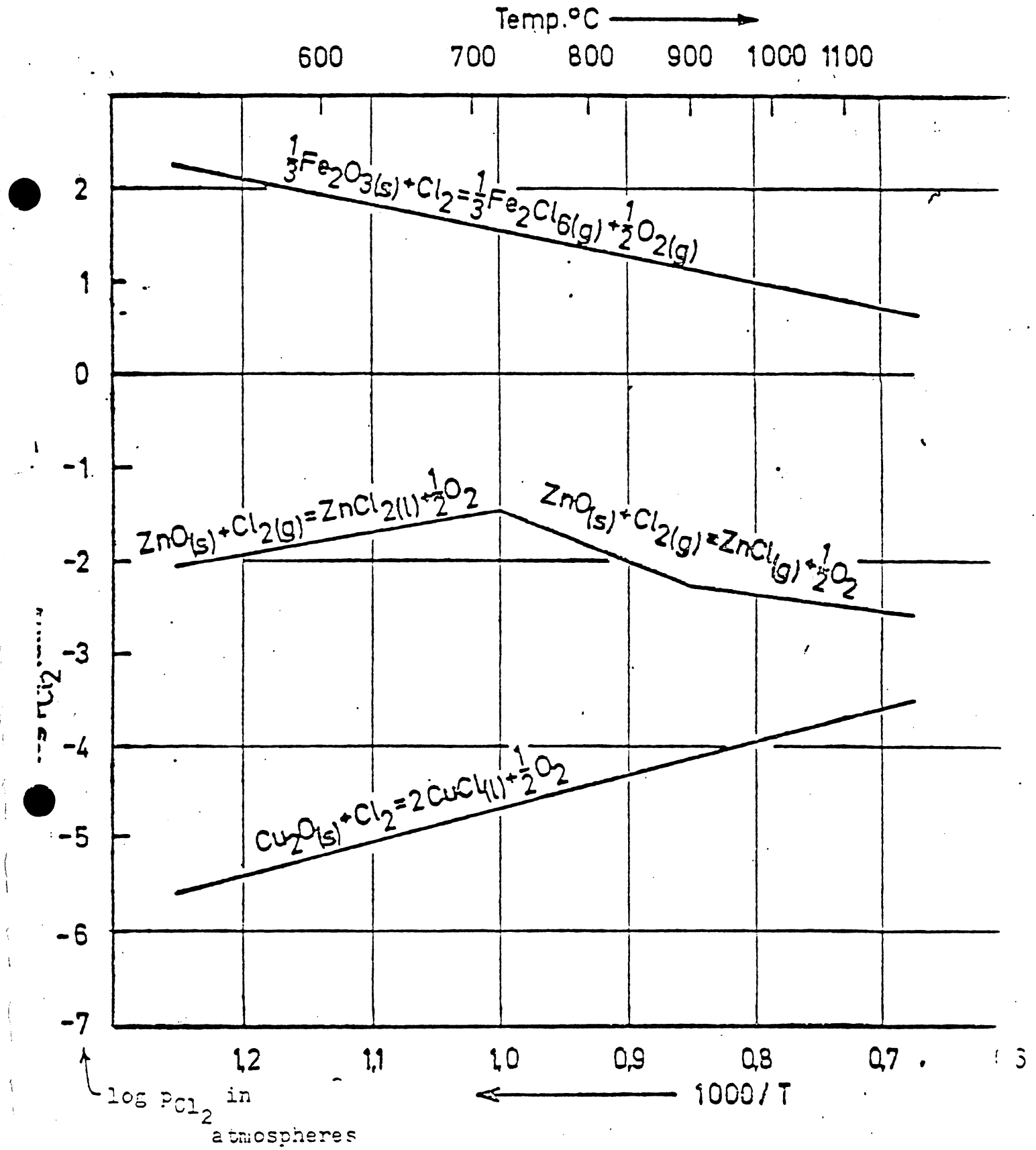
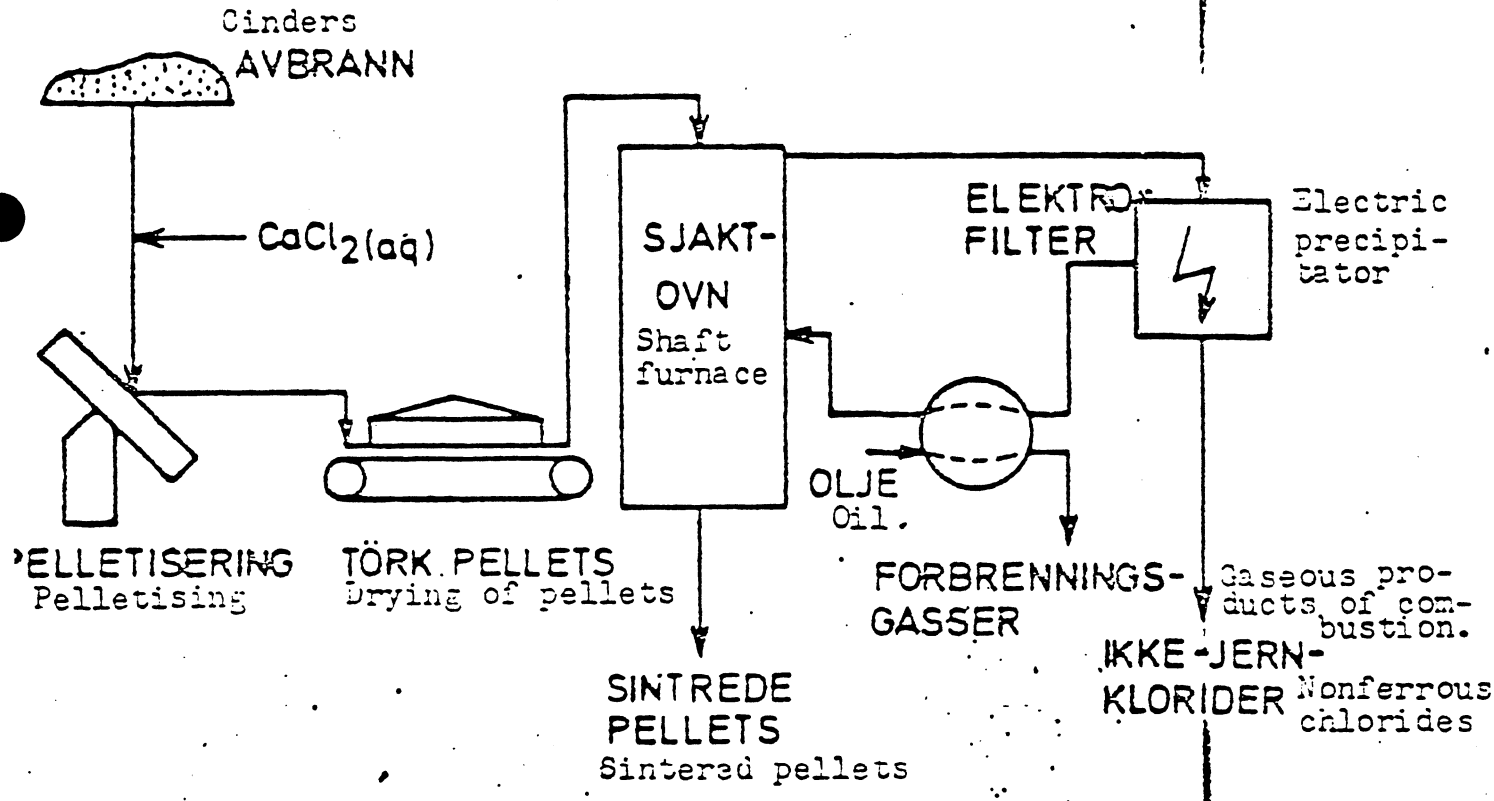


Fig. 9

VUOKSENNISKA. Process

VUOKSENNISKA-PROSESSEN



Kowa Seiko process

KOWA-SEIKO PROSESSEN.

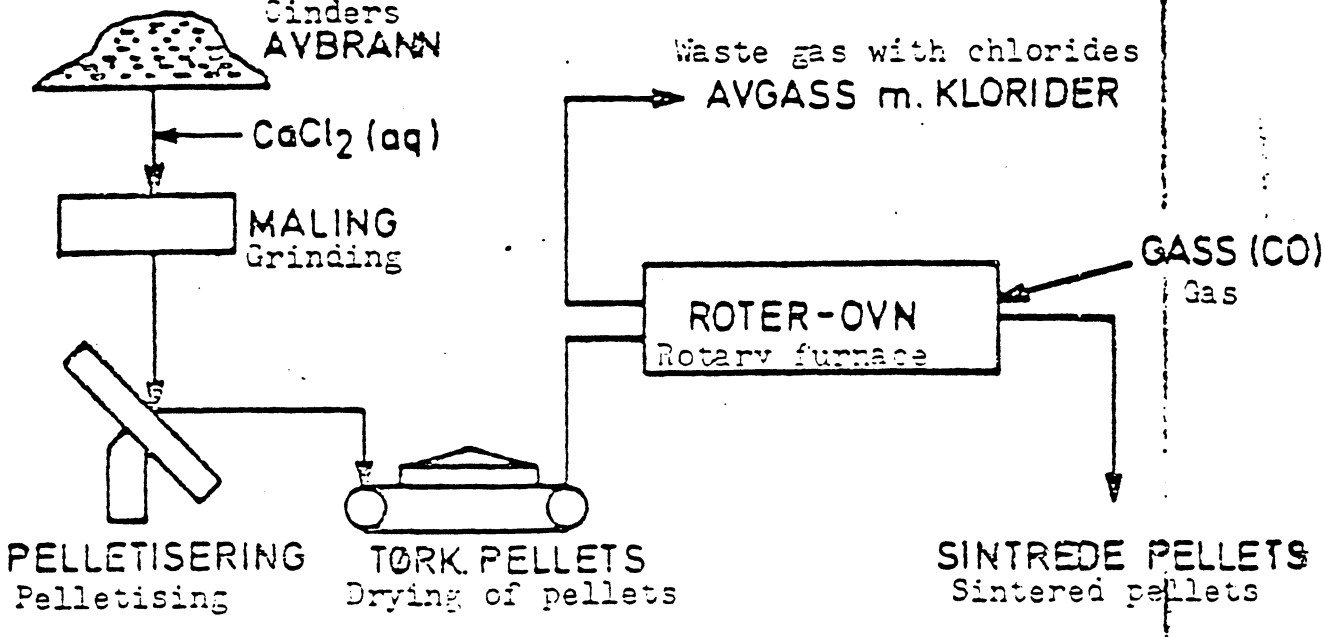
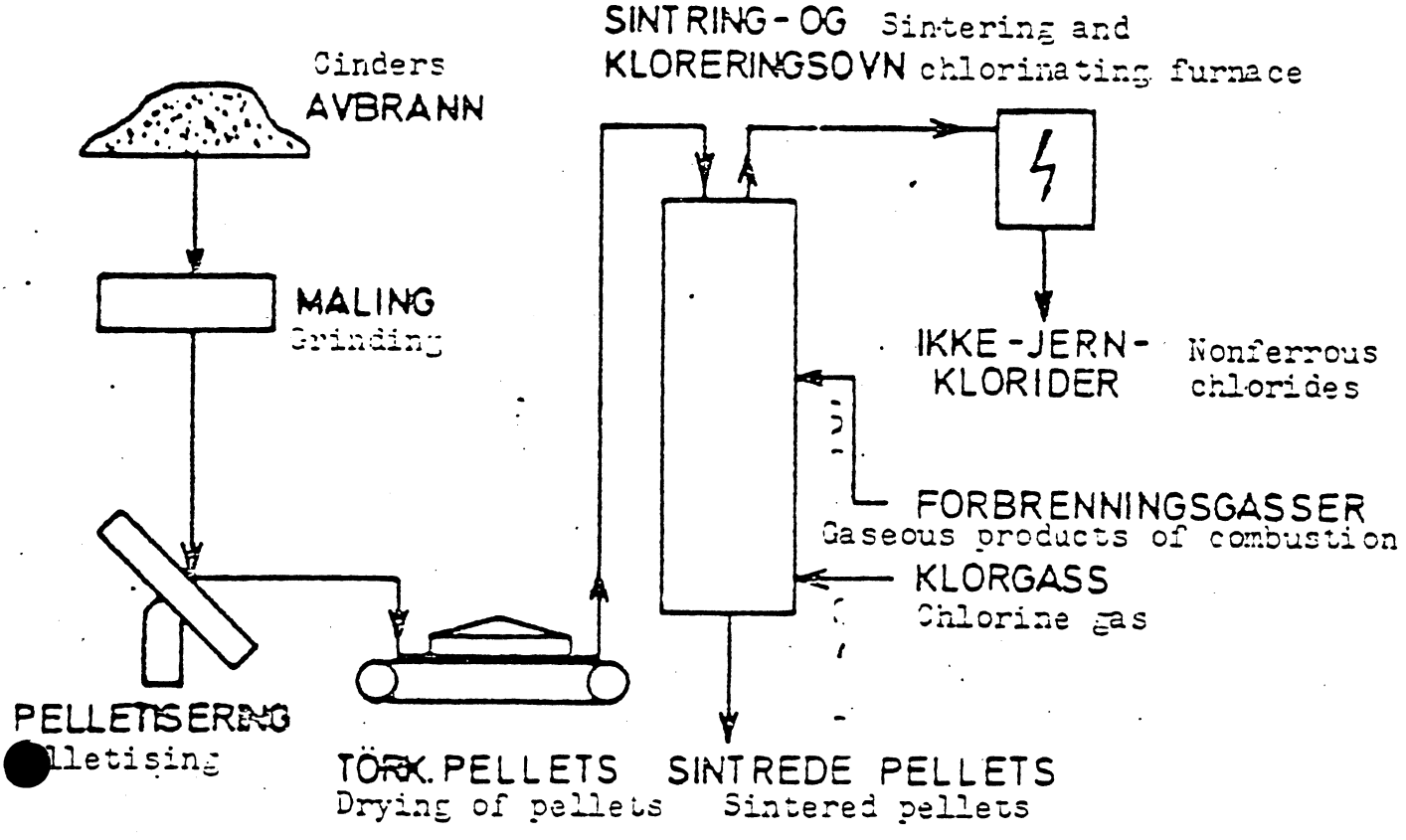


Fig. 12

L DK process

LDK PROSESSEN.



Driving off of Cu and Zn, as a function of time and chloride concentration at 1000° C.

Fig 13

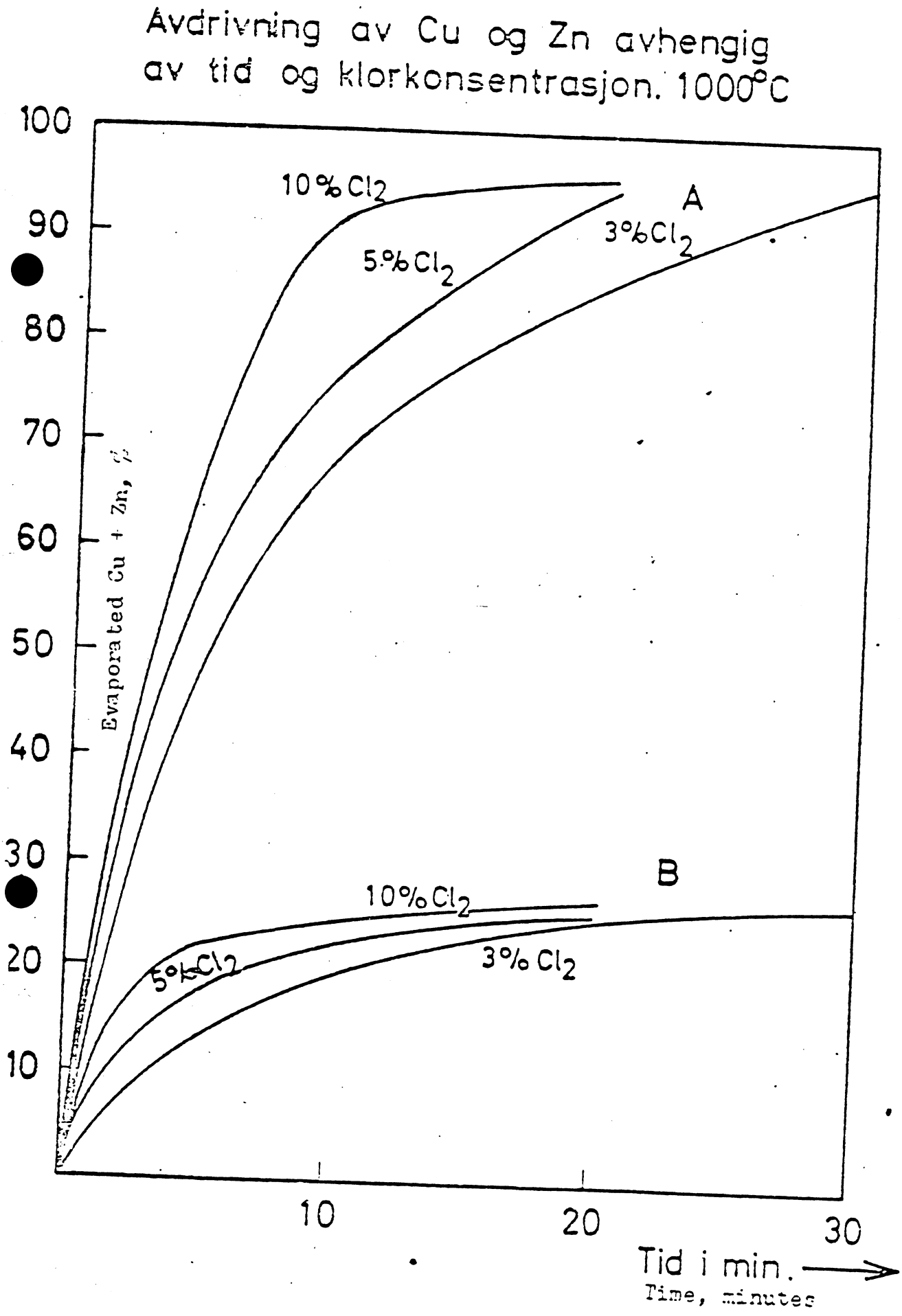


Fig. 14

Importance of porosity in driving off Cu and Zn.

Conditions: 5% (volume) of chlorine gas, chlorination time 10 minutes, 1000° C.

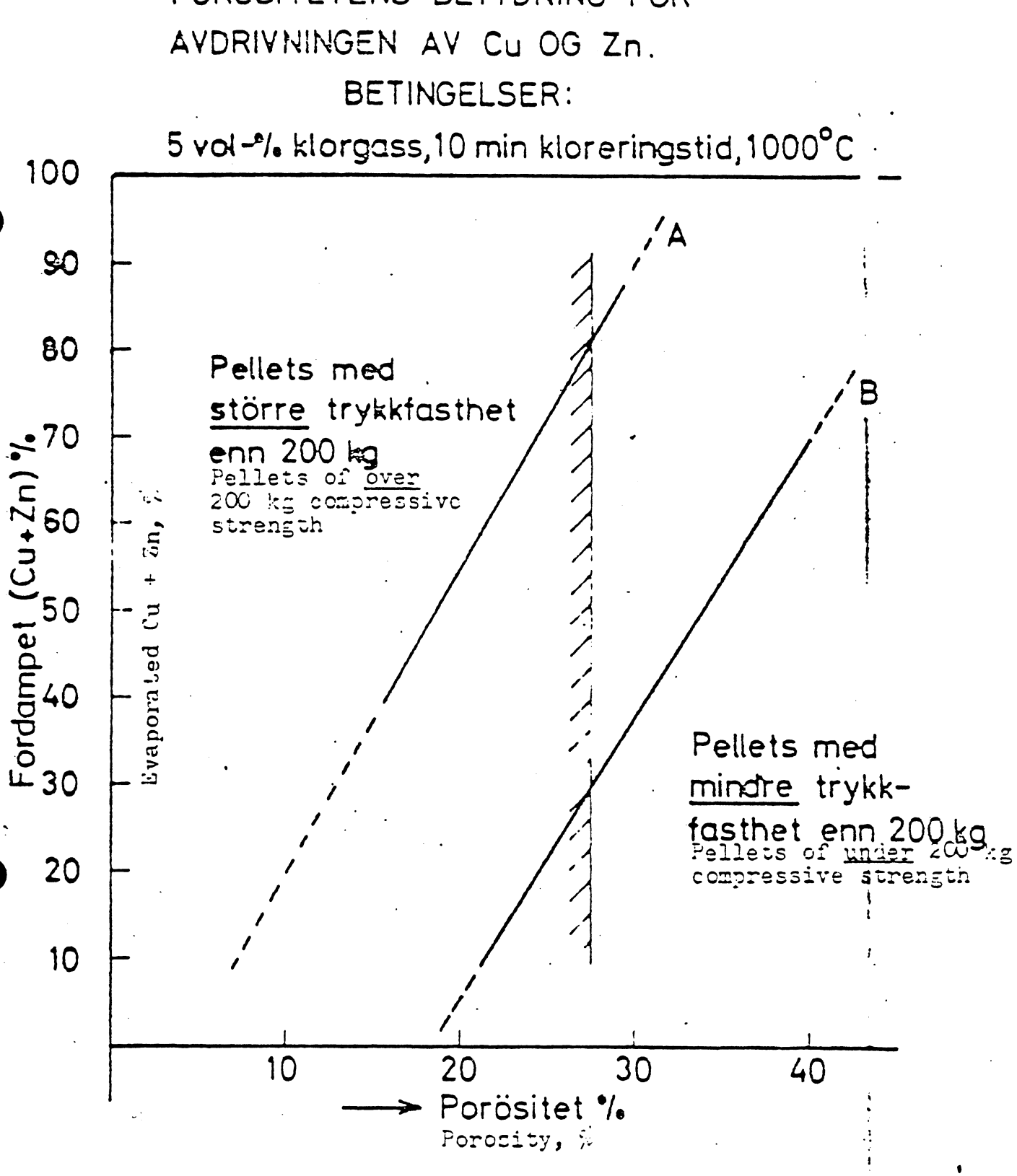
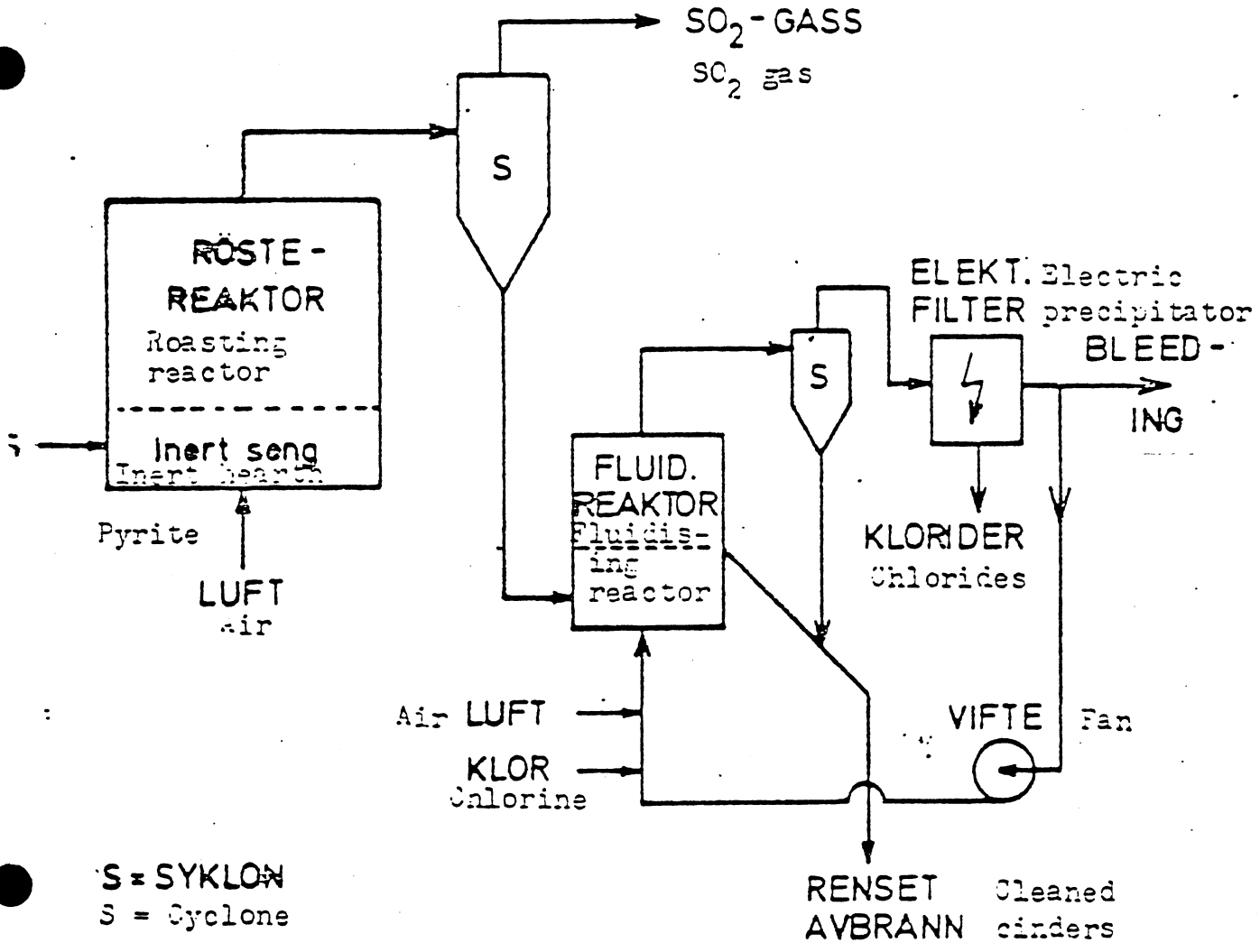


Fig. 15

Fluo-chlor process

FLUO-KLOR PROSESSEN



R. Eggink.

USE OF PYRITE CINDERS IN THE PRODUCTION OF IRON AND STEEL

by M. B. Müller

Paper read at the Pyrite Symposium, 31st October to 1st November, 1967, organised by the mining engineers' sections of the NIF and the Norwegian Metallurgical Society, in Norwegian, title: "Anvendelse av kisavbrann ved jern- og stålfremstilling".

CONTENTS

1. Introduction
2. Chemical properties of pyrite cinders
   2.1 Chemical analysis
   2.2 Gangue
   2.3 Sulphur
   2.4 Metals
   2.5 Degree of oxidation
3. Physical properties of pyrite cinders
   3.1 Granulometry
   3.2 Microporosity and density
4. Utilisation of pyrite cinders
5. Sintering
6. Pelletising
7. Dry reduction
8. Smelting
   8.1 Smelting in blast furnace
   8.2 Use as cooling iron in oxygen converter
   8.3 Melting in electric steel furnace
9. Conclusions

Table 1: Analysis of investigated Norwegian pyrite cinders
Table 2: Pelletising of Norwegian haematitic pyrite cinders without binder

Illustration sheet I Effect of pyrite cinders in the sintering charge
" " II Micropelletising of sintering charge containing pyrite cinders
" " III Reduction of pyrite cinders, laboratory experiments (M. Skeaton)
" " IV Reduction of green pellets
" " V Melting of iron sponge pellets

1. INTRODUCTION

Pyrite cinders is the material left after roasting of iron pyrite and magnetic pyrite and consists substantially of iron oxide. The quality and composition of the cinders is governed partly by the mineralogy of the pyrite, partly by the dressing process employed, partly by the preceding roasting process. In the past this involved quite considerable fluctuations in the analysis and quality of the cinders obtained from the different grades of pyrite.

The considerable progress made by dressing techniques, in conjunction with the economical requirement to utilise the valuable elements contained in the pyrite, mainly copper and zinc, resulted in an evening-out of the quality of the pyrite concentrates produced by reducing their content of gangue and of the sulphides of Cu, Zn, Pb, and As, which make out the most important impurity elements in pyrite. This cleaning of the pyrite during the treatment process is rendered possible by grinding, which is sometimes continued until a very fine substance is obtained. Most pyrite concentrates are therefore very finely ground, with a specific surface in the neighbourhood of 1000 - 3000 cm^2/g.

The roasting process had to be adapted to this development and roasting of concentrates of this kind is now almost entirely carried out in fluidising reactors, mostly arranged for post-combustion in the combustion chamber above the actual hearth. In such reactors there are good possibilities of temperature and analysis control and it is possible to produce cinders of varying oxygen and sulphur content. The cinders are in most cases

oxidised to Fe_2O_3 with a correspondingly low sulphur content but it is also possible to terminate the roasting process at the Fe_3O_4 stage, which presupposes a certain residual content of S. The selection of the process depends on the content of impurity elements, mainly arsenic, and on the nature of the treatment subsequent to roasting.

After roasting, Fe is the only useful element present in the pyrite, and the further treatment of the cinders is accordingly entirely concerned with putting the iron into an industrially suitable condition so that the process is designed to produce iron metal in a suitable shape and in an economical manner.

This is the starting point for my paper, which is also confined to dealing with the treatment of cinders obtained from flotation pyrite cinders roasted in the conventional manner in fluidised bed reactors.

2. CHEMICAL PROPERTIES OF PYRITE CINDERS

2.1 Chemical analysis

All evaluations of pyrite cinders in the metallurgy of iron have to be based on the characteristic chemical and physical properties of the cinders.

The composition of the cinders is governed by the analysis of the pyrite and the conduction of the roasting process. If we disregard magnetising roasting of arsenic containing pyrite, the iron mineral is mainly present in the form of haematite. The trend is that the contents of non-ferrous and non-ferrous metals is continuously falling on account of the improvements in

the flotation dressing of pyrite concentrate. Table 1 shows a list of the chemical analyses of some Norwegian cinders. It shows in particular the S, Cu, and gangue contents. If the roasting process is properly conducted, the residual sulphur can be kept down to 0.1 - 0.2%.

2.2 Gangue

A gangue content of up to 8%, mostly in the form of SiO_2, is quite acceptable in the production of pig iron, where the quantity of slag should preferably be about 300 to 400 kg per ton. The cinders of flotation pyrite concentrates have a lower gangue content but this does not involve any economic advantage in this connection.

If the cinders is used directly for making steel, without a preceding melting process, the position is quite different. The gangue must have in this case a high basicity ($\%CaO/\%SiO_2 > 2.0$), which requires large quantities of lime, yields large quantities of slag, consumes energy and reduces furnace productivity. These additional expenses must be compensated for in the price of the cinders.

If we take figure of 100 kg (220 lb) of slag per ton of steel as reasonable, this corresponds to about 20 kg (45 lb) of SiO_2 per ton of Fe, or 2%. This involves a maximum of 1.3% of SiO_2 in the cinders. For an SiO_2 content higher than this, we shall expect a reduction in the price of cinders. The lime content is acceptable. Pyrite from Joma has the advantageous feature that it can be used directly for the production of steel, as it contains about 1% of CaO and about 0.5% SiO_2, but this

presupposes careful removal of sulphur and arsenic.

2.3 S u l p h u r

Practically the whole of the sulphur disappears on sintering and oxidising of the pellets so that this does not interfere with quality of the iron.

With increasing restrictions as regards pollution of the atmosphere, however, the sulphur content is sometimes a serious hindrance in the sale of pyrite cinders in areas where air pollution is already high.

In the reduction of the cinders to metal without a preceding oxidising treatment, the sulphur content in the iron sponge or in the liquid metal can be taken as rather high. This requires considerable quantities of slag for cleaning, in the same way as the gangue. Cinders with a high sulphur content will therefore also tolerate a higher gangue content. According to Sven Eketorp (Lit.Ref.1) the sulphur content can be reduced by 50 - 75% by mixing lime into the reducing agent during the production of iron sponge according to the Höganäs method. It can be assumed that this also applicable to other methods for reduction of briquettes or pellets, but not to reduction of powder with gas.

A rough calculation shows that a sulphur content of over 0.1% in reduced iron lessens to a considerable extent the possibilities of using the iron directly for making steel. This is on account of the unfavourable sulphur balance. The sulphur content should be less than 0.05% in the iron, corresponding to less than 0.03% in the cinders, for a steel charge of 100%.

When using the cinders for making pig iron, the sulphur balance is less critical because the distribution of sulphur between slag and metal is quite favourable (about 50/50), the quantity of slag is very much higher and also because sulphur can easily be removed from pig iron.

2.4 Metals

All metals actually present in the cinders will be almost quantitatively reduced in the blast furnace process, but apart from this they behave all in different ways.

Zinc is present after reduction as a gas at a temperature of over 913° C and it follows the other gases upwards in the furnace. As they are enriched with CO_2, the metal is re-oxidised to zinc oxide, which is present as a solid, but finely divided, forming a white smoke. Some oxide will leave the furnace, but most of it will be caught by the charge above it and returned in this way to the reduction zone. We have accordingly constant circulation and accumulation, resulting in scaffolding and other operational disturbances. The maximum content of zinc in the charge must consequently be kept down to 0.20% and this is usually accepted at the current prices of cinders. In high grade cinders the zinc content would be expected to be substantially lower. Since pyrite cinders is always mixed with other ores, there is no danger of excessive accumulation. Maximum zinc contents of 0.1% in the cinders should be acceptable for all conditions.

Lead remains liquid in the range from 327 to 1755° C. It does not mix with liquid iron and forms accordingly its own liquid

phase in the bottom of the furnace, where it tends to penetrate through cracks and joints in the lining, and contributes to the gradual deterioration of the lining. In the case of furnaces regularly used for roasting lead containing charges, arrangements should be made for periodically tapping off lead. In other furnaces no lead-containing charges should be used.

Copper remains quantitatively in the iron and cannot be removed from it. It will therefore have some effect on the quality and utilisation properties of the steel eventually produced. A certain copper content is quite desirable for certain purposes because copper increases the durability of the steel and impedes its corrosion. However, steel with a high copper content is hot short, so that it is subject to heat checking in billets and slabs, as a result of penetration of a low melting point phase rich in copper between the grain boundaries. This deleterious effect is amplified by tin, if present, even in very small percentages such as 0.01% Sn.

Up to, say, 0.10 - 0.30%, copper in itself is not very dangerous, but the problem must be assessed in relation to the copper content of commercial scrap iron, which tends to be rather high and exhibits a rising trend. The copper content of cinders should therefore be reduced to below 0.05% and preferably more so that it can be accepted as a high grade ore with not more than, for instance, 0.02% of copper.

Arsenic also remains quantitatively in the iron and cannot be removed from it. Since arsenic accompanies a number of iron ores, it accumulates in the scrap iron and reduces the limit of tolerance for arsenic in new iron. The action of arsenic

is the same as that of phosphorus, except that it is stronger. Already very small arsenic contents, below 0.05%, increase the strength and reduce the ductility. Most serious is a possible increase in the age brittleness of mild steel. For instance, an increase of the arsenic content from 0.015 to 0.050% reduces the impact test results in artificially aged mild basic Bessemer steel from about 12 to 4 kg/mm^2 if there is 0.025% of phosphorus in the steel. Arsenic containing pellets should therefore be used only for soft structural steel if the resulting total arsenic content can be limited to 0.02%. The other negative effects of arsenic become acute at only at over 0.20% of As and can therefore be disregarded here.

2.5 Degree of oxidation

The intention of the magnetising roasting process is usually to remove arsenic as a volatile trioxide during the roasting process. If it is desirable to remove the copper content of the cinders by bacterial leaching, the roasting process must also be carried on till the magnetite stage. This involves a higher sulphur content.

For direct reduction to metal without preceding oxidising treatment, a low degree of oxidation is an advantage because this "artificial" magnetite is easily reducible. For all other purposes, the haematite cinders process is the simplest and cheapest one.

3. PHYSICAL PROPERTIES OF PYRITE CINDERS

3.1 Granulometry

The screen analysis of pyrite cinders is more or less the

same as the screen analysis of the pyrite concentrate used. It seems accordingly that the individual pyrite grain retains its shape and size during the roasting process.

The effect of the free crushing process varies considerably for the various pyrites but even the finest grained pyrites can now be subjected to selective preparation. The degree of fineness of the ground pyrite is also raised on account of increasing purity requirements for the product and the high Cu+Zn yield.

We have shown the screen analysis of four Norwegian cinders in Table 1 (Lit.Ref.2). This table shows also the chemical analyses.

The specific surface does not include here the internal surface of individual grains resulting from the removal of the sulphur, and producing a skeleton shape structure of the individual grain.

3.2 Microporosity and density

The individual grain retains its shape and size during the roasting process so that the iron atoms retain the same molar volume as in the pyrite mineral. This is

$$V_p = (1/\varrho_p) \times (FeS_2/Fe) = (1/4.87) \times (120/56) = 0.440 \cdot cm^3/g\ Fe$$

Natural haematite ore has compared with this a molar volume of

$$V = (1/\varrho_h) \times (Fe_2O_3/2Fe) = (1/5.12) \times (160/112) = 0.275\ cm^3/g\ Fe$$

The difference is represented by the microporosity of the cinders, with the following volume part:

$$\varepsilon_m = (0.44 - 0.275)/0.44 = 0.375$$

This relation governs the density (weight per volume) of the cinders.

If we assume that natural magnetite or pyrite concentrate and pyrite cinders, all stored in the usual way, loosely, have the same packing density corresponding to an interstice factor of 0.55, the appropriate densities are

Magnetite concentrate: $4.8 \times (1-0.55) = 2.16$ t/m³

Pyrite cinders : $4.8 [1-(0.55+0.375 \times 0.45)] = 1.34$ t/m³

In actual fact, the density of pyrite cinders is about 10% lower, which is presumably connected with the fact that the skeleton shaped grains can not be packed just as tightly as concentrate grains.

With a density of the order of magnitude of ½ of that of oxide concentrate, and a water absorption many times higher, pyrite concentrate is a fairly inconvenient material to handle. The storage capacity is poorly utilised and in the Norwegian climate it would be inconvenient to store the material in the open. Freight, transportation, and handling become more expensive on account of the poor utilisation of the capacity of the equipment while the dust becomes a distinct nuisance.

For these reasons, pyrite cinders should be palletised and it should be sintered at the earliest possible stage in the treatment process.

4. UTILISATION OF PYRITE CINDERS

Alternative possibilities for using pyrite cinders

The use of pyrite cinders in the metallurgy of iron presupposes a treatment covering several stages, either individually or in combination:

a. Purification by chlorination, to remove deleterious elements, mainly S, Cu, Zn, and Pb.

b. Grinding to break down the skeleton structure of the cinders.

c. Mixing with other ores, dust, and/or ballast or aggregate

d. Aggregation by pelletising, briquetting, or moulding under high pressure.

e. Sintering or oxidising hardening by burning

f. Reduction with solid or gaseous fuel

g. Melting to form pig iron or steel.

The selection of a suitable combination of processes depends on the nature of the cinder, its quantity and quality in relation to the available production equipment, primary material, and requirements for the finished product. There is hardly any point in using pyrite cinders unless there is full compensation for any misfortunes or shortcomings as regards the economy, process technology, and quality of the product. This has had partly the result that the price of pyrite cinders is very low, compared with oxide ore competing with it, and partly that the possibilities of selling the cinders have been limited to a small number of firms. In certain fields, however, pyrite cinders have properties making it more convenient than ordinary oxide ore as a primary material in the production of steel. All other conditions remaining the same, this should increase the price. These factors now will have to be considered in more detail in the evaluation of the pyrite cinder plant.

The actual process combinations are mainly:

I. Production of pig iron, using stages c, e, and f above, sometimes combined with stage a.

II. Production of quality pellets, using stages a, b, d, and e, and perhaps also stages c and f.

III. Production of quality scrap iron, using stages a, b, d, and f for melting in the electric furnace or converter.

IV. Production of sintered powder products using stages b, f, and d (we are not dealing with this aspect in the present paper).

5. SINTERING

The great majority of pyrite cinders charges have been put into the blast furnaces as part of sintered charges. It is therefore convenient to discuss this alternative first.

The action of adding increasing proportions of pyrite cinders to sinter charges has been investigated by Sven Eketorp (Lit.Ref.1). He used conventional, fairly coarse grained Swedish pyrite cinders of a screen analysis between those of Mofjellet and Sulitjelma cinders (about 38% less than 325 mesh).

Fig.1 shows the value of the production and of the returned material for varying mixtures of Hørnefors pyrite cinders and ordinary magnetite concentrate. This is partly coarse grained Stripa concentrate (two grades) and partly finely grained Strassa material. The experiments were carried out in a small experimental sintering pan (about 8 kg = 18 lb capacity) at KTH and showed a production maximum with an admixture of 10% of pyrite cinders and an acceptable output up to 20%. These good

results are partly contradicted by the next illustration, Fig.2, obtained from operational experiments at Norrbotten Järnverk, where Rönnskär pyrite cinders was mixed into the normal sinter charge for pig iron for both open-hearth steel and basic bessemer steel. It can be seen that the production falls immediately on addition of pyrite cinders. The fall in production roughly corresponds to the percentage of pyrite cinders present.

With a finely grained charge of sinter, e.g., concentrate with a specific surface of 500 - 1500 cm^2/g, production can be increased by micropelletising. Fig. 4 shows the sintering productivity of coarse Tuolluvaara concentrate (Kst) with unpelletised and micropelletised charges, respectively, plotted against rising percentages of pyrite cinders. For finely grained Tuolluvaara concentrate (K_S), we can see that pelletising improves productivity more than coarse dust. However, productivity falls considerably and immediately on application of pyrite cinders, even if this is kept at a reasonable level of 20 - 30% in the mixture.

The explanation of this may be that the cinders are put into the charge without first breaking down the skeleton structure by grinding. This results in very porous, weak pellets, while at the same time the large addition of water for pelletising may reduce permeability and cause collapse of the structure as a result of recondensation of evaporated water in the lower part of the sintering furnace. If the cinders are first ground down there is no reason why pyrite cinders-containing sinter charges should not give the same high production, when micropelletised, as pure concentrate charges.

In order to maximise the permeability of the sinter charge, when using pyrite cinders, the addition of water must be increased. The water consumption is particularly high in micropelletised sinter charges. Fig.3 of Eketorps experiments shows this. Here, too the consumption of water can be greatly reduced by first grinding the material.

The disadvantages in the use of pyrite cinders in sinter charges for blast furnaces and electric furnaces for pig iron can be reduced by a. cleaning, b. grinding, c. micropelletising. This is an expensive matter and is still not fully effective in turning cinders into a material of the same high quality as a good dust. For instance, the consumption of coke for sintering will be higher. One should therefore seriously investigate other alternatives for a more economic use of cinders.

6. PELLETISING

Possible markets are the production of pig iron in blast furnaces and in electric pig iron furnaces, or the use of this material for cooling and refining in steel furnaces; we are thinking here mainly of oxygen converters and using this material as a raw material for the production of iron sponge. The main point here is that a high-grade ore with a wide range of uses must be obtained which does not require mixing with better ores in order to yield an acceptable grade of pig iron or steel.

This presupposes a purifying process designed to considerably reduce the content of nonferrous metals. Suitable maximum limits would be 0.02% Cu and 0.10% Zn, perhaps with traces of lead and arsenic. The sulphur content should preferably remain

below 0.03%.

It also seems that regrinding in the ball mill must be acceptable as an essential condition for economic pelletising. In the pelletising of magnetite concentrate much attention is paid to the moisture content, which should be about 9% H_2O, corresponding to a cavity proportion of about 33%. If the grains are assumed to be tightly packed, the cavity proportion of pyrite cinders is (see our calculations above):

$$\varepsilon = 0.33 + 0.375(1-0.33) = 0.58$$

This yields 0.58 x 1.0 g of water and 0.42 x 5.0 g of iron oxide, corresponding to 21.7% of H_2O. Actual measurements show a water percentage of about 24, irrespective of the grain size. Grinding experiments yielded for actual Norwegian cinders the results listed in Table 2.

The table shows clearly the importance of regrinding for the compressive strength of the pellet in its raw, dried, or sintered condition. At the same time the water content drops by 40 to 50% to a level acceptable for the process, but it is still about 40% higher than for ore dust. Compared with pellets of oxidic concentrate we have here in particular a higher compressive strength of dry pellets, if they have been reground for a sufficiently long time, the compressive strength may be 3 to 4 kg and higher. This is a matter of great importance for reduction of the green pellets without preceding sintering.

The hardening of the pellets can be carried out on an ordinary Dwight-Lloyd machine, but the machine capacity should be about 50% compared with that for magnetite pellets on account of

the longer drying time so that the pellets remain in the combustion zone for a longer period. The heat consumption is also correspondingly higher. Roller furnace hardening is also suitable. It should be noted here that magnetising roasting of the cinders creates considerable problems in the sintering of pellets since the oxidation of the magnetite to haematite takes place in this case at 250 to 300° C, compared with 900 to 1000° C for natural magnetites. This makes it impossible to exploit the heat of oxidation for any useful purpose.

It should also be noted that the density of the pellets of cinders increases during the burning process, and it increases the more, the more finely grained the initial material. The resulting density of the burnt pellets is still just as dependent on the grinding time as their strength.

If the material is properly treated, it seems possible to reach very strong and dense pellets from most pyrite cinders, which will be fully equivalent to commercial concentrate pellets. However, pyrite cinders pellets can be made of adequate strength without addition of binders. By adding 1 to 2% of slaked lime, the strength can be increased even more. Other binders are less effective.

7. DRY REDUCTION

The reduction of pyrite cinders with gas takes place at a kinetic reaction very quickly when the material is powdered, and the temperature can then be kept quite low. The higher microporosity has in this case a very advantageous effect.

S. Eketorp (Lit.Ref.1) has reduced various pyrite cinders and oxidic concentrate with hydrogen at 600° C; the result is shown in Fig.5. The most easily reducable material was magnetite cinders (Iggesunds black), which is due to its lower oxygen content and higher proportion of fines. Reduction to an oxygen removal of 95% from the cinders takes place during half the reduction time for natural oxide ores. There is at present no technological method available for controlling the reduction of so light and finely grained powder materials, so that there is no point in discussing this alternative any further.

Reduction of burnt pellets is a technically feasible method and can be carried out according to quite a number of different processes. Experiments were carried out by S. Eketorp (Lit. Ref.1) with pellets of ½" to 5/8" diameter, made of pyrite cinders and concentrate reduced by means of hydrogen at 900° C. The result is shown in Fig.6. For an oxygen removal of 95%, magnetite concentrate requires 3 to 4 times as much time for its reduction as pyrite cinders. Kjell Haesje (Lit.Ref.3) found in his dissertation dated 1966 a difference not quite as large. For instance, a removal of 95% of the oxygen had been achieved after 25 minutes in the case of pellets made of Mofjellet pyrite cinders, and after 50 minutes in Rana pellets supplied by A/S Norsk Jernverk. The same problem has been dealt with by J.A. Aune (Lit.Ref.4) in a relevant dissertation. It seems here that the reduction takes place more slowly than stated above, for pyrite cinders, which is certainly due to the greater density of the pellets after the preceding regrinding operation. In this case reduction is carried out by barelling with an excess of

coal or coke in rotary furnaces at 1000° C and yields very dense and good pellets reduced to a considerable extent.

Burning of pellets as a preliminary treatment for a reduction stage, however, is a very expensive process, difficult to turn into something yielding a finer product on an economic basis. Much more interesting are the new methods for direct reduction of crude, wet pellets in rotary furnaces, without the preceding hardening process.

K. Haesje (Lit.Ref.3) reported the following results obtained by reduction of green pellets in Lindner equipment. The green pellets were mixed with coke and the burden was heated without rotation to 750° C. Then barelling started by adding a reducing gas containing 35% of CO and 65% of N_2. The reduction was completed after 3 hours at 1000° C.

	Pellets from Sulitjelma cinders	Pellets from A/S Norsk Jernverk
Degree of reduction	51.1%	63.5%
Crushed to below 3 and over 1 mm	0%	0%
Crushed to under 1 mm	7.0%	100%
Compressive strength of reduced pellets	59.2 kgf	0

The experiments were repeated in a larger rotary furnace by J. A. Aune (Lit.Ref.4). A metallised shell was formed round the pyrite cinders pellets by quickly heating the charge. This shell prevented further pulverising of the charge. However, it is too early to incorporate these results in a general assessment.

K. Meyer and associates (Lit.Ref.6) discussed the SL/RN process for the production of iron sponge. No details are given but they mention that green magnetite pellets are advantageously used in the flow sheet shown in Fig.8 (Fig.7 shows the same process in greater detail). If this is possible with oxidic concentrate, the conditions must be even better for pyrite cinders, according to our own investigations, and the cost of transforming pyrite cinders pellets into iron sponge must be lower than those of transforming concentrate pellets, on account of the shorter reduction times and higher reduction effect. A diagram showing the distribution of the costs in the production of iron sponge is shown in Fig.9 (Lit.Ref.5).

U. Kalla and coworkers discussed in great detail (Lit.Ref.6) the economics of producing iron sponge according to the better known processes, such as SL/RN, and the value of iron sponge in the production of steel. The following equation can be obtained from his graphs for the calculation of the production costs of iron sponge from green pellets in an SL/RN installation at Rotterdam:

Production costs = 155.- nkr + 3.5 x fuel cost in nkr/g-cal.

For a price of fuel oil of, say, 120.- nkr per ton, the production cost is according to this equation about 200.- nkr per ton. We are assuming here a price of 75.- nkr per ton, cif, of [illegible] ground down to pelletising fineness and iron sponge containing 95% Fe, 0.04% S, and 0.1% C. This must be regarded as a fairly reasonable price for scrap iron and the economic

results should be even better for pyrite cinders.

However, much work has still to be done before an economic reduction process for green pyrite cinders pellets has been fully worked out but the prospects of an advantageous result can be regarded as extraordinarily good.

8. SMELTING

8.1. Smelting in blast furnace

The use of prereduced pellets in the blast furnace is regarded at present as a very interesting subject, in particular in the United States. The results which can be achieved as regards increased production and reduced consumption of coke are shown in Fig.10 (Lit.Ref.5) according to experiments carried out in the experimental blast furnace at Bruceton, P. The method is particularly interesting if the degree of reduction is low, and the gangue and/or sulphur content is high, or their dilution is desirable on account of a high copper content or the like. It can be assumed that the cost of these methods is comparatively low.

8.2. Use as cooling iron in oxygen converter

The reduced, heavy pellets are extremely suitable for use as cooling iron in oxygen converters. They are suitable for bin storage, automatic weighing and charging, so that they contribute in this way to better control of the process. The quality requirements are on the whole the same as for iron used for melting in an electric steel furnace.

8.3. Melting in electric steel furnace

When using iron sponge pellets instead of scrap iron as the charge for electric furnaces, a very advantageous change can be carried out with this process, by replacing batch charging by continuous charging and melting. In this way continuous control of the bath temperature and analysis is ensured, and the melting times and in particular the refining times can be greatly shortened. We have shown in Fig.11 (Lit.Ref.5) the saving in the charging time by comparing batch charging and continuous charging, as a function of the proportion of iron sponge pellets in the charge of a 25 ton furnace.

In the latest issue of JISI, J. G. Sibakin et al. (Lit. Ref.7) had a detailed paper on the production of steel in the electric arc furnace with continuously charged iron sponge pellets in accordance with experiments carried out by the Steel Company of Canada. The arrangement for the charging of the furnace is diagrammatically shown in Fig.12. The energy consumption, as a percentage of the energy consumption for 100% of scrap iron, is shown in Fig.13 as a function of the proportion of iron sponge pellets and of the SiO_2 content in the iron sponge. We have also shown a bar diagram of the charging time distribution for ordinary scrap iron charges and with continuously added sponge iron charges. The most important conclusions of this paper are:

1. Continuous charging with iron sponge pellets in quantities from 15 to 100% can be carried out quite easily.

2. The charging time is reduced on omitting conventional refining periods so that the productivity is increased by 45% and there is a considerable reduction in the charging time.

3. The energy consumption is largely governed by the proportion of acid gangue in the iron sponge and can be below or above the consumption for scrap iron charges.

4. The optimum content of residual oxygen in the iron sponge is 0.9%, which yields a maximum rate of production.

5. The consumption of refractory material falls by more than 40%, the electrode consumption remains unchanged, and the consumption of ferro alloys is slightly higher compared with the corresponding figures for scrap iron charges.

It can be assumed that the development sketched out here will greatly stimulate the use of iron sponge as a charge material for electric furnaces, in particular in countries where electric power is cheap. Pyrite cinders have important advantages over iron concentrate in the production of iron sponge on account of the greater reduceability of the cinders. Development work should therefore be started for the improvement of pyrite cinders for this purpose. The main problem in this connection is reduction of the sulphur content of the cinders, because this varies considerably in the various types of pyrite.

9. CONCLUSIONS

Quantitatively seen, pyrite cinders form an almost negligible proportion of the ore requirement for the total world production of pig iron and steel, and constantly new sources of oxidic ore

are discovered and keep down the prices charged by ore producers.

We accordingly cannot expect that very great endeavours will be put under way by the iron producers for developing the use of pyrite cinders to the production of iron and steel. This work must necessarily be done by the pyrite producers.

In the past their attitude in this field has been a rather passive one, they merely tried to sell the product unchanged, at a price discount required by the iron works as compensation for the unavoidable difficulties made by this material.

Another alternative, which from the industrial point of view is much more interesting and from the economic point of view more advantageous is now everywhere coming to the fore. It is based on the idea that pyrite cinders should be used as a primary material in those fields where its use brings with it technological and economic advantages, compared with competitive iron ores.

Pyrite cinders is always less suitable than oxide ore, when added to a sinter charge for the production of pig iron. When used for oxide pellets, the cinders can in many cases (but not always) be as useful as iron ore concentrate and should help to spread the pyrite producers' costs.

If pyrite cinders is used for the reduction of iron sponge for direct smelting in the electric furnace or converter, the conditions are right for a more economical production method compared with oxide concentrate because the transformation costs are lower.

The use of concentrate in conjunction with cinders presupposes partly a considerable removal of sulphur, copper, and other deleterious accompanying elements, and partly far-reaching research and development on reduction processes. We hope that both the pyrite producers and the NTNF will contribute more in this direction.

Finally I wish to add that a successful development of the process in these fields will also render it desirable or even necessary to carry out certain structural changes in production and transformation of pyrite and cinders in order to establish a basis for Norwegian processing work in this field.

TABLES

Table 1

Analysis of investigated Norwegian pyrite cinders

Cinders	Mofj.-Bleikvassli	Sulitjelma	Joma	Skorovass
Chemical analysis,%				
Fe (tot.)	64.5	66.1	67.4	67.8
S (")	0.59	0.55	0.84	0.50
Cu	0.22	0.03	0.24	0.16
Zn	0.63	0.53	0.53	0.36
Pb	0.33	-	-	0.04
As			0.07	0.07
SiO_2	3.51	2.21	0.51	1.02
CaO	0.70	0.27	1.02	0.26
Fe_2O_3	88.2	91.2	89.1	90.7
Fe_3O_4	3.8	3.2	7.0	6.0
S-(sulphate)	0.11	0.30	0.51	0.32

Screen analysis, %				
+ 147 µ	2.4	13.2	0.6	0.4
- 147 + 104 µ	6.8	11.8	2.2	1.2
- 104 + 74 µ	19.0	25.0	7.2	2.2
- 74 + 43 µ	23.6	21.0	16.2	19.4
- 43 + 10 µ	46.4	29.0	72.7	79.6
- 10 µ	0.8	Traces	1.1	Traces
Density, g/cm^3 = (specific gravity)	4.82	4.73	5.08	5.10
Specific surface, cm^2/g	1560	900	3130	3330

Table 2

Pelletising of Norwegian haematitic pyrite cinders without binder.

A : Bleikvassli - Mofjellet

B : Sulitjelma

D : Joma

F : Skorovass

Grinding time, minutes	0	20	40	60	80
	Specific surface, cm^2/g				
A	1560	4050	5740	6920	
B	900	2050	3060		3690
D	3130		7460	8560	8750
F	3330		9750	11300	
	Moisture content of green pellets, % H_2O				
A	23.4	17.4	14.7	12.9	
B	24.0	16.0	11.6	-	9.8
D	24.2	-	16.4	13.5	13.1
F	24.7		17.0	15.6	

Compressive strength of green pellets, kgf					
A	0.38	0.77	1.40	2.50	
B	0.35	1.35	1.67	-	2.25
D	1.18	-	1.61	2.56	3.33
F	0.96		1.48	2.56	
Compressive strength of dry pellets, kgf					
A	0.10	0.75	1.98	3.08	
B	0.40	1.52	3.60	-	5.50
D	0.55	-	1.82	2.78	4.25
F	0.46		1.99	3.41	
Compressive strength of sintered pellets, kgf (1385° C)					
A	48	153	240	376	
B	41	128	204	-	266
D	131	-	340	385	
F	164		290	494	
Increase of tightness on burning (1385° C) g/cm³					
A	1.53-2.34	1.93-2.91	2.22-3.70	2.40-3.91	-
B	1.74-1.93	2.22-2.62	2.64-3.33	-	2.67-3.53
D	1.75-3.02	-	2.23-3.82	2.45-4.00	2.79-
F	1.76-3.23		2.23-4.03	2.45-4.45	

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1. S. Eketorp : Järnoxid ur Svavelkis - en ny järnravara. (Iron oxide from sulphur pyrite, a new primary material for iron). J.K.A. Vol.149, 1964, p.316-333.

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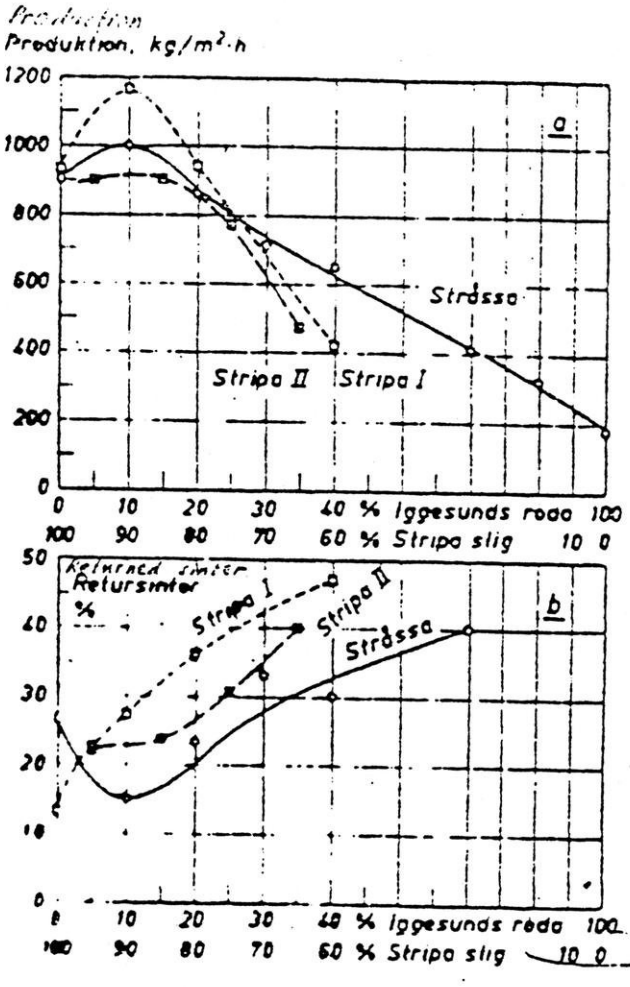
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6. U. Kalla & al.: Vergleich der technischen Kennzahlen und der Wirtschaftlichkeit bei der Herstellung und Verarbeitung von Eisenschwamm. (Comparison of technological characteristics and economics of production and processing of iron sponge). St.u.E. 87 (1967) No.9, p.534-542.

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Sheet I

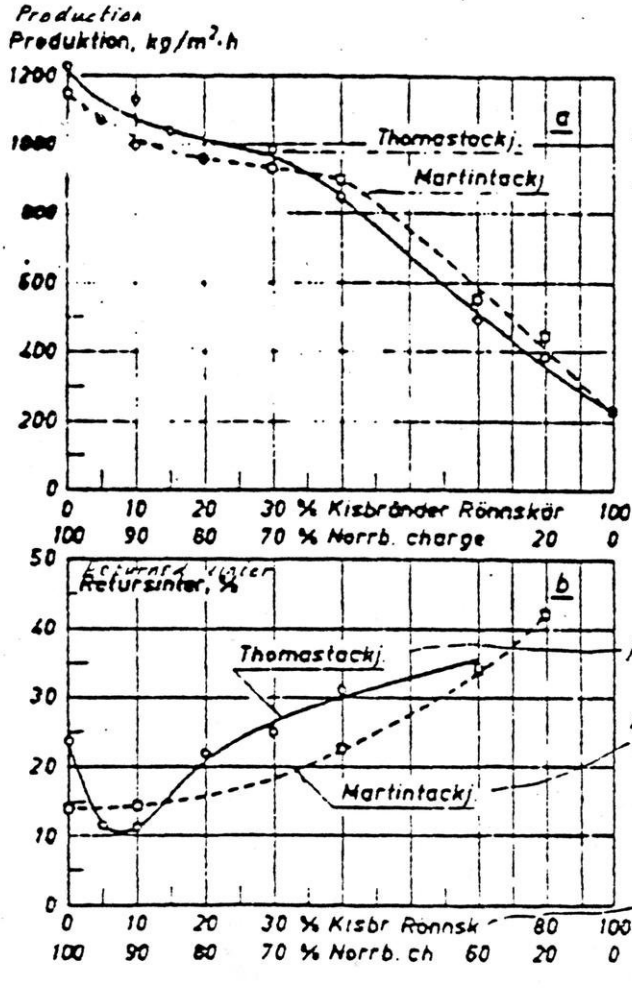
Effect of pyrite cinders in the sintering charge (S. Dietorp)

Fig. 1

Production results of normal concentrates mixed with pyrite cinders; the mixture is sintered

Iggesund red

Stripa concentrate



Pig iron f. basic Bessemer steel

Pig iron f. open-hearth steel

Fig. 2

Rönnskär pyrite

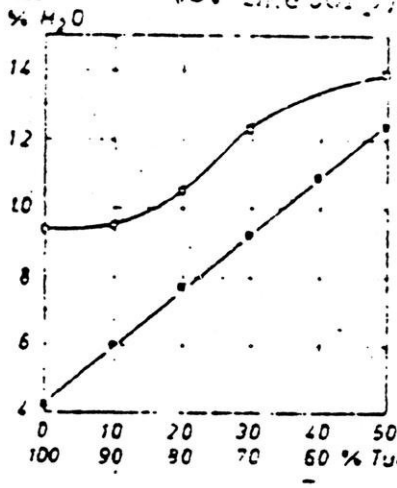
Pig iron for basic Bessemer steel

Pig iron for open-hearth steel

Corresponding results obtained at Norrbottens Järnverk AB

Rönnsk. pyrite

. Sheet II - Micropelletising of sintering charge containing pyrite cinders (S. Ekeberg)



Water content at optimum permeability in pelletised and non-pelletised charges

Fig. 3

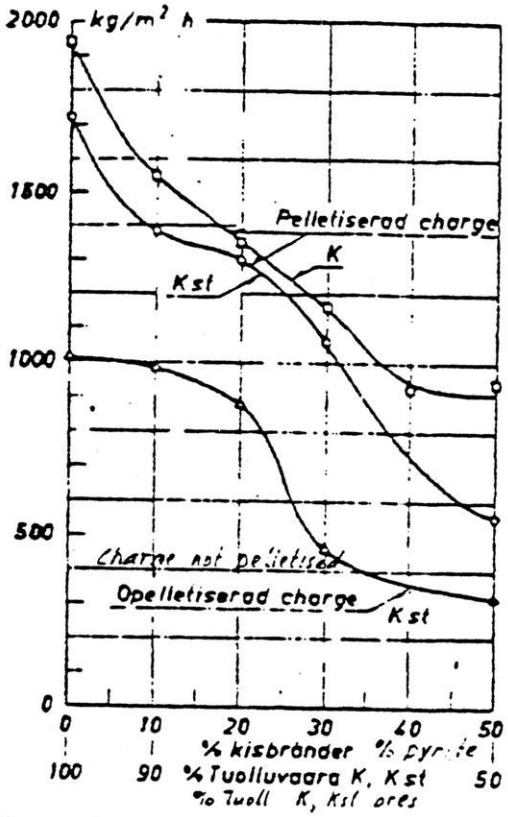


Fig. 4

Sinterproduktion vid pelletiserad och opelletiserad charge. Grov och fin slig: Tuolluvaara Kst respektive K.

Production results for pelletized and non pelletized charge. Coarse and fine concentrates, Kst and K, respectively

Sheet III - Reduction of pyrite cinders, laboratory experiments (S. Eketorp)

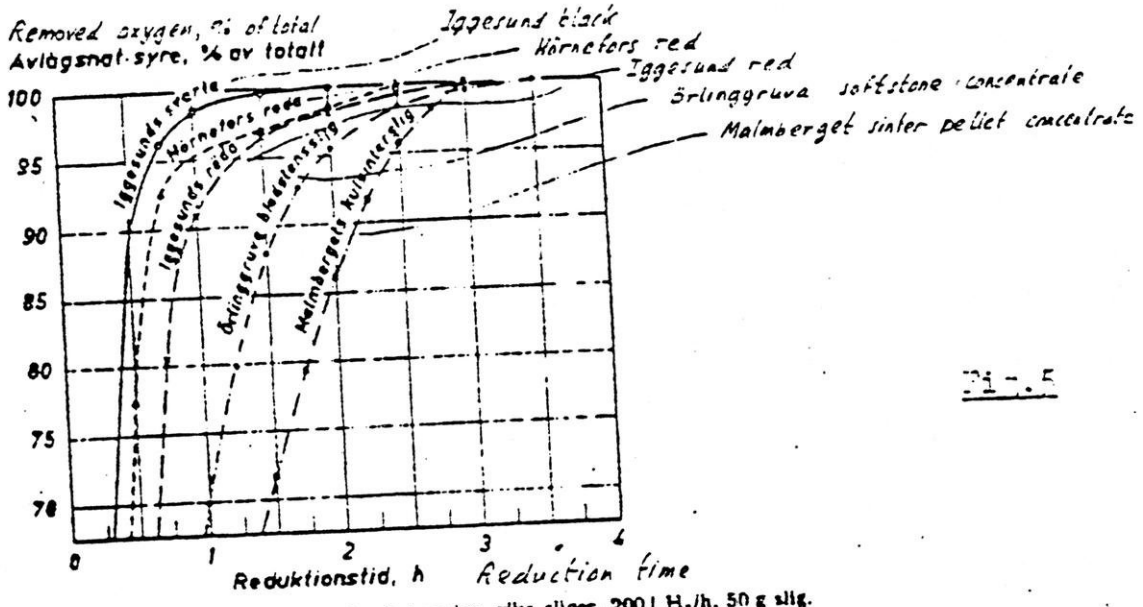


Fig. 5

Reduktion med väte vid 600°C av olika finkorniga, rika slig. 200 l H_2/h, 50 g slig.

Reduction with hydrogen at 600°C of rich concentrates of different grain size (Iggesund and Hörnefors are pyrite cinders).

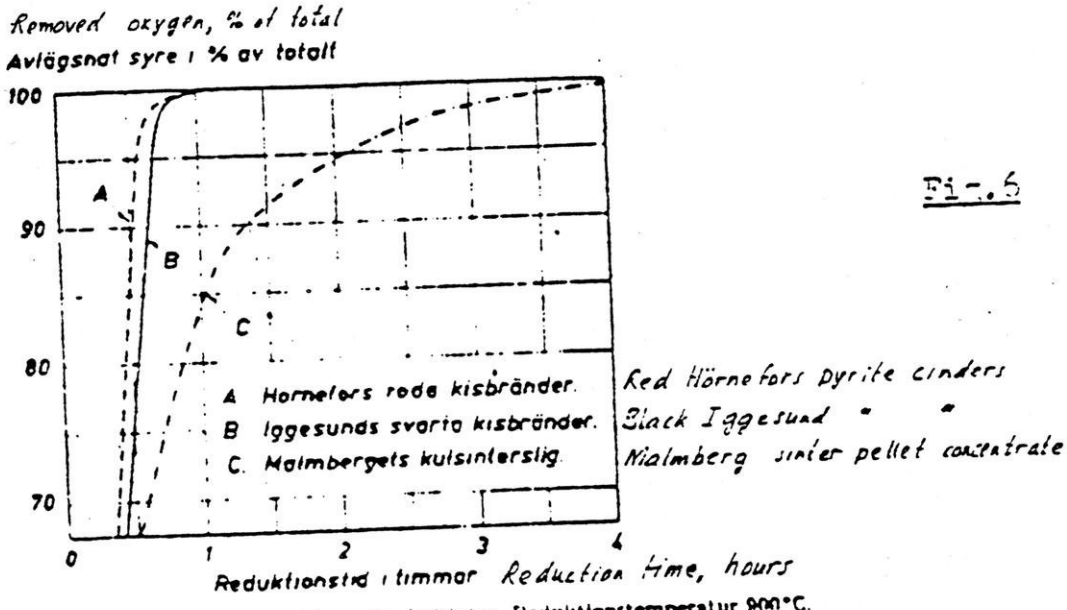


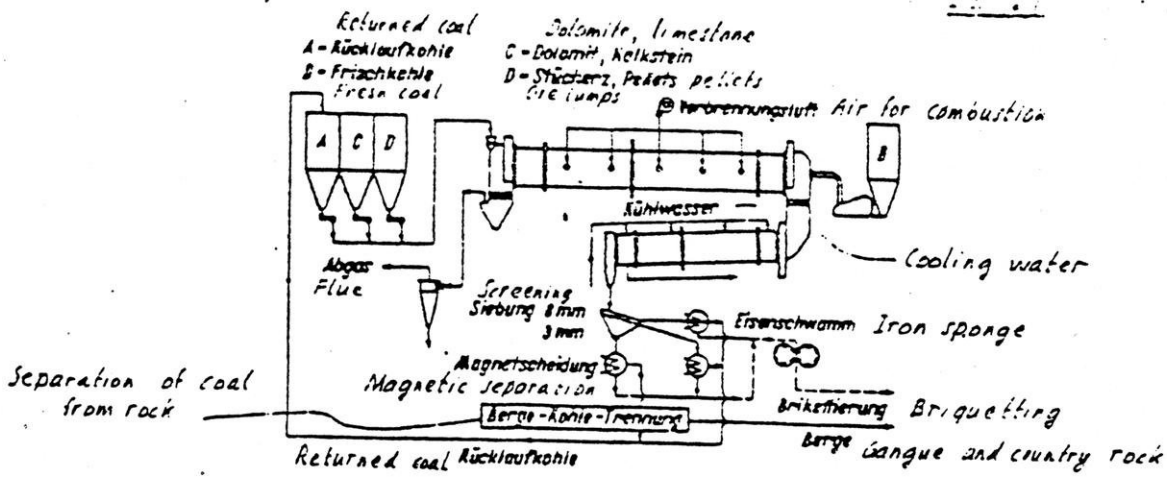
Fig. 6

Reduktionsprov med väte av olika sorts kulsinter. Reduktionstemperatur 900°C. 200 l H_2/h, kulstorlek 12–15 mm.

A med 1 % bentonit + 10.6 % $Ca(OH)_2$; 1250°C.
B med 10.6 % $Ca(OH)_2$; 1250°C.
C med 2 % $CaCl_2$; 1250°C.

Reduction with hydrogen at 900°C of pellets. A with 1% bentonite and 10.6 % $Ca(OH)_2$; 1250°C. B with 10.6 % $Ca(OH)_2$; 1250 °C. C with 2 % $CaCl_2$; 1250°C. Pellet size 12–15 mm.

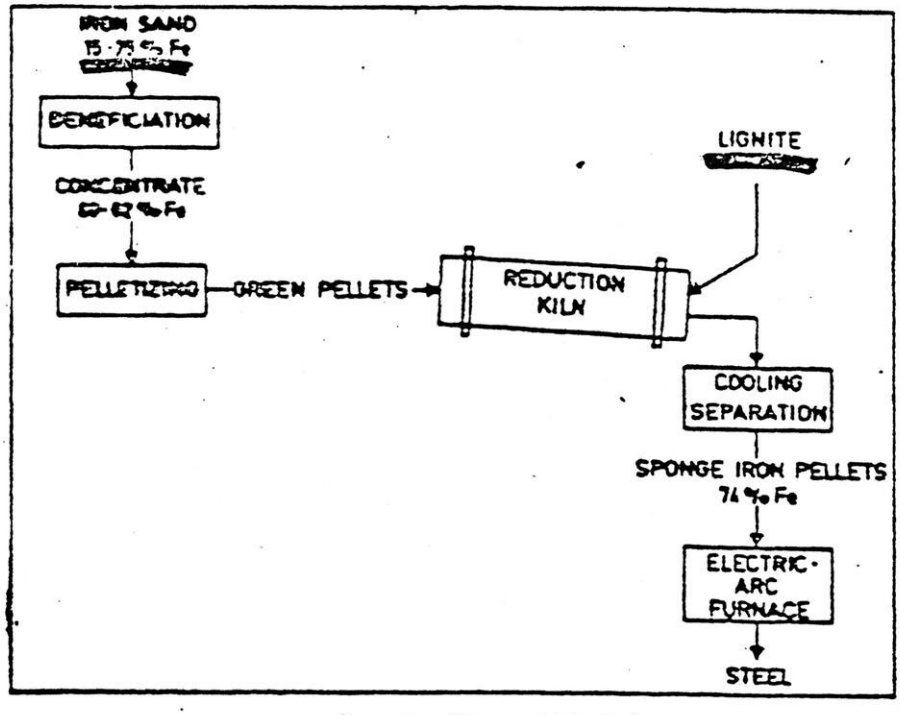
Fig. 7



Schematischer Aufbau einer SL/RN-Großanlage

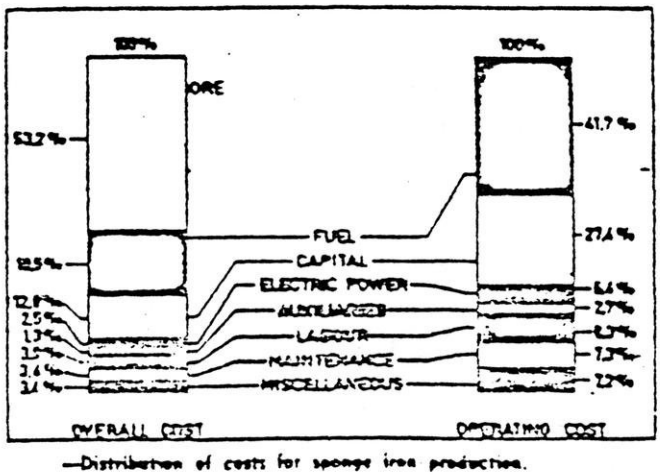
DIAGRAM OF LARGE SL/RN INSTALLATION

Fig. 8



–Processing of iron sand into steel.

Fig. 9



–Distribution of costs for sponge iron production.

Sheet IV

Reduction of green pellets

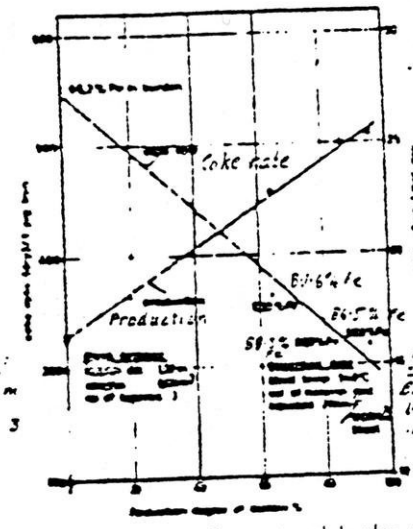


Fig. 10—Influence of pre-reduced burden on coke rate and pig iron production.

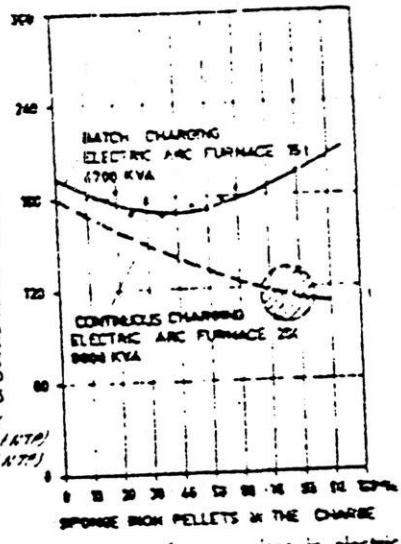
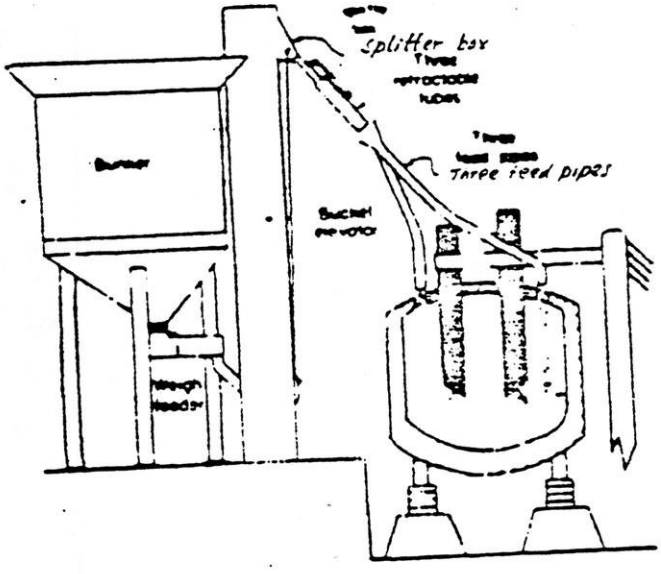
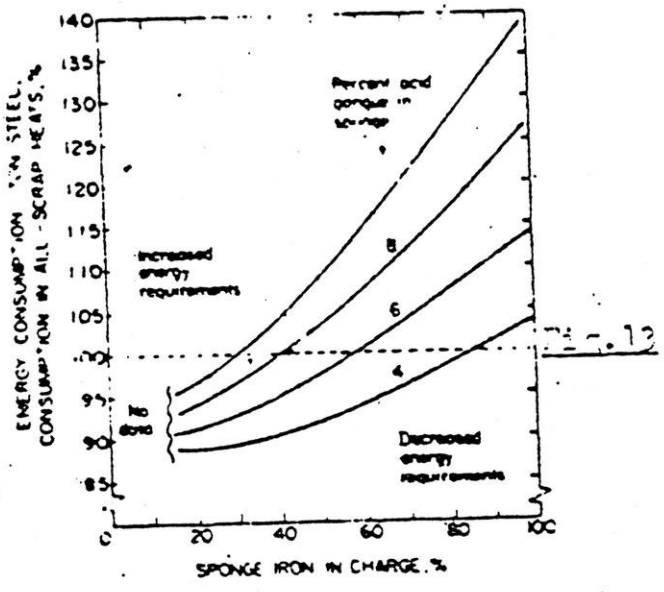


Fig. 11—Melting of sponge iron in electric arc furnaces.



Continuous charging apparatus

Fig. 12

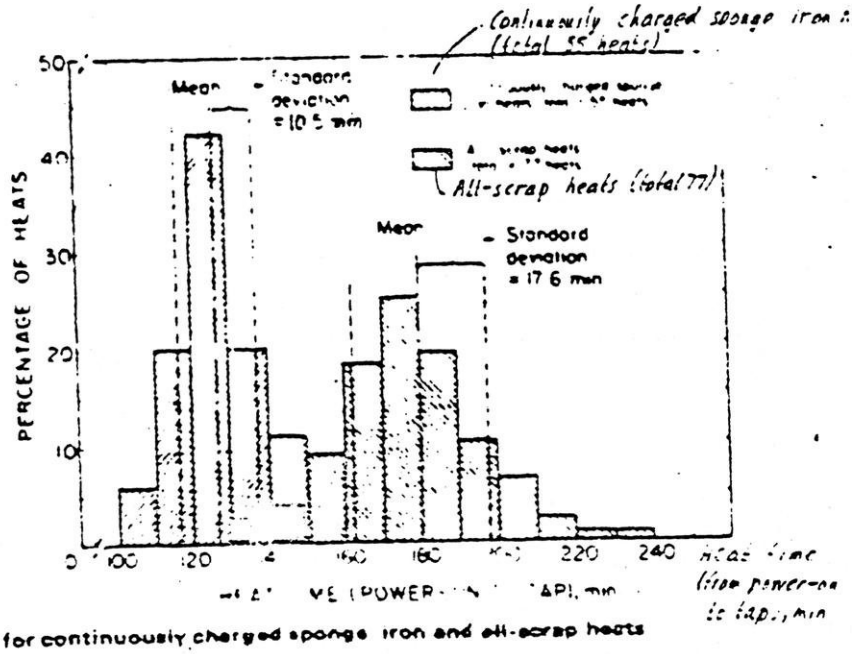


Effect of sponge iron percentage and gangue content on energy consumption

Fig. 13

Sheet V

Melting of iron sponge pellets



Heat time histograms for continuously charged sponge iron and all-scrap heats

Fig. 14

622.3C6.1 CF

R. Lagesen.

PROCESSING OF PYRITES

by

Sverre Olsen

Paper read at Pyrite Symposium, 31st October to 1st November, 1967, organised by the mining engineers' sections, of the NIF and the Norwegian Metallurgical Society, in Norwegian, title: "Kisforedling".

INTRODUCTION

Iron pyrites are mainly a sulphur mineral and sulphur (in its elementary form or as iron pyrite) is mainly a primary material for the production of sulphuric acid. The production of sulphuric acid in Norway is on a comparatively moderate scale compared with our production of pyrite so that we have to export the major part of our pyrite in an unprocessed condition. The iron pyrite used in Norway is processed to sulphur dioxide, sulphuric acid, and pyrite cinders but there is no further processing of pyrite cinders in Norway into first class iron ore or iron.

Pyrite is a fairly wide concept. The most common types of concentrates are:

1. Fine pyrite concentrate prepared according to a gravimetric method.
2. Sulphide concentrate, also called bulk concentrates, and
3. Pyrite concentrates prepared by selective flotation.

These types of concentrates differ in their chemical analysis and in their granulometry, and present metallurgists with different

problems in their further processing.

A chemical description is most conveniently presented in the form of a table (see Fig.1). The table shows the composition of some typical Norwegian pyrite concentrates. The main mineral in iron pyrite is FeS_2 and the percentage content of the main element, sulphur, depends on the enriching method employed. The highest content is naturally that of the most finely ground concentrates obtained by selective flotation, and is about 50 to 52%. The sulphur content of fine pyrite concentrates shows larger variations and is often in the neighbourhood of 42 to 48%. The iron content is closely connnected with the sulphur content and requires here no further comments.

The most common nonferrous metals in Norwegian pyrite deposits are copper, zinc, and lead. The arsenic content is reported as low compared with that found in many foreign deposits.

Even the most enriched pyrite concentrates contain some gangue. The gangue is often of an acid kind so that it is mainly composed of SiO_2, but other gangue minerals are also found. The most important nonsilicious mineral in the gangue is limestone, in the case of the Joma deposit.

The dressing of pyrite comprises processes applied to both pyrite and pyrite cinders until the final product is obtained, but the word is often used in a somewhat narrower meaning, among Norwegian pyrite producers and pyrite metallurgists, meaning simply the production of elementary sulphur from sulphur pyrite. For the past 10 to 15 years, much attention has also been paid to the recovery of the valuable metals in the pyrite by carrying

out a specific pyrite process. At present this does not seem to be very important because most Norwegian pyrites can be treated only by selective flotation, which is a method of enrichment with which the metallurgist cannot easily compete.

As regards the treatment of pyrites, we have already mentioned that this treatment is only concerned with the cinders and it covers the cleaning and pelletising processes designed to convert pyrite into a high grade iron ore. This may sometimes also include processes for the recovery of nonferrous metals.

The entire processing of iron pyrite from mining and through concentration to the recovery of individual elements involves a number of possible subprocesses and the result which is the best possible from the point of view of economics depends on how these various part processes are compounded to form the entire processing system.

The profitability of the process combination naturally depends mainly on the number of given circumstances, for instance, the possibilities of local sales of sulphuric acid. This means that there is no generally valid solution for the processing of pyrite.

This paper is intended to illuminate existing processing methods, with special reference to the possibilities available for the production of sulphur from pyrite, in other words, the iron pyrite dressing process in the narrower sense of the word. We shall also discuss in more detail the methods available for the treatment of pyrite cinders.

ELEMENTARY SULPHUR FROM IRON PYRITE

Production of elementary sulphur from iron pyrite is, strictly speaking, carried out along a detour. However, with few exceptions, this sulphur ends up as SO_2 gas and sulphuric acid.

If nevertheless Norwegian pyrite people are interested in these processes, this is because our sulphuric acid requirements are comparatively moderate compared with the level of our present and potential pyrite production.

The full utilisation of pyrite in Norway would accordingly involve either export of sulphuric acid or of elementary sulphur. Sulphuric acid is transported nowadays in large tankers but elementary sulphur is a more suitable product for sale both as regards storage and transportation.

The first aim in the treatment of pyrite is to carry out the reaction

(1) $2\ FeS_2(s) + \frac{3}{2}\ O_2(g) = Fe_2O_3(s) + 4\ S(s)$

Then this iron oxide has to be purified.

In connection with this general reduction, it is interesting to note that

$$\Delta H_{298} = -112 \text{ kcal}$$
$$\Delta G_{298} = -80 \text{ kcal}$$

This implies that the equilibrium of the reaction is well over to the right hand side, in other words, that iron oxide and sulphur are the stable components at room temperature in an oxidising atmosphere.

We should also note that the reaction is an exothermic one,

it gives off heat, so that it can be carried out without admission of heat from the outside.

The industrial process which comes most closely to the ideal one is pressure oxidation of pyrite in an aqueous medium. Pressure oxidation has been tried but is found to take place very slowly. One important disadvantage is also that the iron oxide obtained is almost colloidal and requires additional steps for conversion into a solid form.

On paper there are also other "autogenous" pyrite processes, which in theory do not require any additon of energy. The most important one of these are the chlorine processes and the Halvorsen process.

Chlorine processes

These processes consist of two stages, chlorination and oxidation.

During chlorination, the metal sulphides react with chlorine gas and yield metal chloride and free sulphur.

(2) $2\ FeS_2(s) + 2\ Cl_2(g) = 2\ FeCl_2(s) + \frac{1}{2}\ S_2(g)$

(3) $2\ CuS(s) + 2\ Cl_2(g) = 2\ CuCl_2(s) + \frac{1}{4}\ S_2(g)$

(4) $2\ ZnS(s) + 2\ Cl_2(g) = 2\ ZnCl_2(l) + \frac{1}{4}\ S_2(g)$

Ferrous chloride forms the bulk of the residue and melts at 670° C ($CuCl_2$ at 620° and $ZnCl_2$ at 283°) so that one would naturally try to keep below this temperature.

During oxidation, the chloride is exposed to oxygen in air and the iron chloride is converted into trivalent iron oxide while chlorine is released and can be pumped back to the chlorination

stage:

(5) $2\ FeCl_2(s) + \frac{3}{2}\ O_2(g) = Fe_2O_3(s) + 2\ Cl_2(g)$

Nonferrous chlorides are more stable than the corresponding oxides and are not attacked. They can be washed out of the iron oxide or removed in some other way.

The corresponding reactions release heat and in theory it should not be necessary to add energy.

The process is accordingly very promising but there are some difficulties in practice on account the formation of trivalent iron chloride (boiling at 315° C), which is present as a gas during the actual reaction temperatures between 350 and 650° C.

Trivalent iron chloride can be formed during the two stages of the process, but is mainly formed during the oxidation stage

(6) $6\ FeCl_2(s) + \frac{3}{2}\ O_2(g) = Fe_2O_3(s) + Fe_2Cl_6(g)$

In the chlorination stage we have

(7) $2\ FeCl_2(s) + Cl_2(g) = Fe_2Cl_6(g)$

Any recovery of chlorine on oxidation of the trivalent iron chloride must take place in the gaseous phase, which is much more difficult to carry out than the oxidation of the solid ferrous chloride. An important disadvantage is also the finely grained nature of the iron oxide formed in the reactions in the gaseous phase as this oxide can be recovered and utilised only with difficulty.

However, it would take us to far to enter into the comparatively intricate reactions taking place in the formation of ferrous and ferric chlorides and their significance in this process.

Chlorine processes have been very thoroughly investigated by several independent companies and research establishments, such as Comstock & Westcott and the Texas Gulf Sulphur Co., who were probably the first, also by Outokumpu of Finland, Mitterberg Kupferbergbau of Austria, and the A/S Norsk Bergverk/Kisforedlingen in Norway. These activities have been particularly intensive during the 1950's.

The alternative process, rather more promising, is that developed by Mitterberg-Kupferbergbau; see the flow diagram of Fig.2.

The Mitterberg process takes into account the unavoidable formation of ferric iron chloride and employs this substance (Fe_2Cl_6) as the chlorinating agent for the pyrite

(8) $FeS_2(s) + Fe_2Cl_6(g) = 3\ FeCl_2(s) + \frac{1}{4}\ S_8(g)$

The process was operated on a small, pilot scale but discarded for one reason or another. This is perhaps due to the difficulties encountered in recovering the more valuable metals. The process may perhaps be more interesting in connection with pure pyrite concentrates.

Halvorsen process

The principle of another of the autogenous pyrite processes appears from the equation

(9) $3\ FeS(s) + 2\ SO_2(g) = Fe_3O_4(s) + \frac{5}{2}\ S_2(g)$.

This is the basis of the well known Halvorsen process, which was very thoroughly investigated during the first half of the 1950s.

Equilibrium investigations showed that 3 - 4 (by volume) of

sulphur vapour was obtained in a gaseous mixture of S_2/SO_2 in equilibrium with magnetic pyrite and magnetite at 900 to 950° C, provided that time is allowed for the equilibrium to adjust itself.

The flow diagram as originally imagined for the Halvorsen process is shown in Fig.3.

On account of the low equilibrium content of sulphur in the gas mixture it is clear that large quantities of SO_2 have to circulate in the system. This appears from the total equation for the reaction, which can be written

(10) $4\ FeS_{1.1} + 3\ O_3 + 75.5\ SO_2 = 2\ Fe_2O_3 + 2.2\ S_2 + 75.5\ SO_2$

The reaction should take place at the highest possible temperature towards 950° C, in order to yield the highest sulphur content in the gas. It is quite clear that the large quantities of flue gas will contain correspondingly large quantities of heat. Autogenous operation presupposes that this quantity of heat is used for the preheating of the incoming gas. The heat exchangers are of enormous dimensions on account of the large quantities of gas.

Large dimensions quite generally characterise the process equipment because of the circulating SO_2 gas.

Duisburger Kupferhütte in Germany built a pilot plant for a modified version of the Halvorsen process during the first half of the 1950s. The sulphur production in the pilot plant was 1 ton per day. As an acide we can mention here that the original Halvorsen process has never been used on any scale whatever.

DK (Duisburger Kupferhütte) did not attempt to operate an autogenous process by utilising the heat content of the flue gas for the preheating of the incoming gas. The major part of the heat content of the outgoing gas was used for producing steam.

The required addition of heat to the incoming gas was admitted in a gas preheater, presumably by burning about 200 kg (440 lb) of coal per ton of sulphur produced.

The Halvorsen/DK process requires industrially pure oxygen, i.e., 95 to 98%. Air cannot be used because the gas volume in the process is already large enough as it is.

Even when using industrially pure oxygen, the nitrogen content gradually builds up so that a part of the gas has to be bled. This involves also removing a certain quantity of SO_2 from the system. One can accordingly count with a sulphur production of 80 - 90% in the form of elementary sulphur. The SO_2 would either have have to be used up locally for processing into sulphuric acid, or can be compressed and transported as liquid SO_2.

DK operate with pyrite lumps or pellets in a shaft furnace. It was found that a long dwell in the furnace (about 15 hours) is needed. Since the shaft furnaces are of limited size, this requires something of the order of magnitude of 100 shaft furnaces for processing about 200 000 tons of pyrite per year.

It is stated that DK spent about 3 million DM on development work but the process had to be discontinued because it did not pay at the prices paid at the time for iron pyrite and elementary sulphur, and it is not very likely that the conditions are more favourable today.

As already mentioned, theoretically speaking the Halvorsen process is an autogenous one, but in the one modification in which it has been tried out, the DK process, it was necessary to add energy. It was also found that all other known methods of treating pyrite require admission of energy in some form or another. This inevitably results in increase of the heat excess of the process, which either can be used for producing steam or can be lost. Under the conditions prevailing in Norway there is no special need for steam and an increase of the heat excess of the process would therefore be regarded as a weakness of the process.

The energy can be admitted to the pyrite process in different ways:

1. By adding coke, carbon monoxide, or oil for the reduction of SO_2 gas,
2. By adding oil or electric power for removing the first sulphur atoms from the pyrite.

Orkla process

In the old Orkla process (see Fig.4) the pyrite lumps were mixed with coke and slag forming agents, quartz and limestone, and all this was melted down in a water jacket furnace. One of the sulphur atoms of the iron pyrite was given off in the top part of the furnace, and the resulting iron sulphide continued downward in the furnace and was oxidised in the combustion zone to FeO and SO_2. The SO_2 gas rose upward in the furnace and met the coke on its way. The coke acted here as a reducing agent, not as a fuel, but nevertheless it represented the most

important method of adding energy to the process. The SO_2 gas was reduced to form free sulphur and SO_2, an exothermic reaction yielding the energy required for splitting off the first sulphur atom.

FeO reacted with quartz and limestone to form fayalite, i.e., iron silicate and hedenbergite, which is a calcium iron silicate. The copper, mostly bonded to sulphur, formed with the rest of the iron sulphide a copper matte with 12 - 14% of copper.

The characteristic feature of this process was the recovery of 80% of the sulphur in the form of elementary sulphur. The balance was mostly obtained from the matte. As already mentioned, the copper content was recovered in the form of copper matte.

The process was technologically very well worked out, but had to be discontinued early in the 1960s on account of rising coke prices and falling prices of sulphur, which made the process everywhere unprofitable. It can also be said to suffer of the weakness that the iron content of the pyrite was slagged away and lost.

Rosenqvist process

Fig.5 shows another example of a process with reduction of SO_2 gas. This is the Rosenqvist process, which exists only on paper, but may well be applied industrially when it has been developed a little. The process has been proposed as a result of joint development work by Rosenqvist, Elektrokemisk, and Kisforedlingen.

In this case CO gas is used as the reduction agent. Since 1956, much attention has been paid in Norway to the uses of CO gas because serious plans were drawn up for a Norwegian cokery and the possible applications of the cokery gases.

It is known that the gas of Norsk Koksverk is used for different purposes but the idea of utilising CO gas for the reduction of SO_2 gas is still very topical in Norway. We only have to think of a large quantities of CO formed in Norwegian metallurgical works and which are partly left to go to waste. The utilisation of CO gas from the smelting furnaces requires the furnaces to be closed and it is known that in this case we cannot utilise CO gas for smelting with ferrosilicon.

Ferrosilicon furnaces must be open for reasons which we cannot discuss here, but one could imagine that in future materials will be found which enable even ferrosilicon furnaces to be closed, and then we shall have vast quantities of CO available.

It is generally thought that this process would be carried out in a shaft furnace. It can be seen that the shaft furnace will have to be subdivided into several zones:

I. Preheating zone, where the pyrite is heated to 650° C in counterflow with the rising gas. At the same time a number of secondary reactions take place in the gas, in particular conversion of CoS with SO_2.

II. Pyrite splitting zone, 650 - 900° C. The FeS_2 is here split into FeS and at the same time the main reaction between SO_2 and the added CO gas is taking place here.

This reaction is an exothermic one and meets the heat requirement for the splitting of the pyrite.

III. Then we have the roasting zone, 900 - 950° C. Here FeS is roasted to form $Fe_3O_4 + 3O_2$. In this zone excess heat is developed. We require accordingly a circulation system for the gas with cooling of the gas outside the furnace.

IV. In the sulphating zone the copper and zinc content of the pyrite is turned into sulphates.

V. In the cooling zone the material is cooled down in counter-flow with the incoming cold air.

The Rosenqvist process is thermically speaking an excess removal process as shown in the illustration where we can see that a part of the gas has to circulate through a cooler in order to remove the excess heat.

The Rosenqvist process can also be visualised as being carried out in fluidising furnaces. The reaction then has to take place in two separate stages:

1. Splitting of iron pyrite. The heat requirements recovered by the reaction between SO_2 gas of the following stage and the admitted CO gas or some other reducing agent.

2. Roasting of pyrrhotite (FeS), preferably to form magnetite (Fe_3O_4). The pyrrhotite is obtained in stage 1.

Kokkola process (Outokumpu)

The reaction

(11). $2\ FeS_2 = 2\ FeS + S_2$

is strictly speaking a basic reaction in the pyrite processing technology. It is accordingly one entering into several of the processes above (Orkla, Halvorsen, Rosenqvist). The reaction requires added heat and represents a stage in the process where the energy can be added. The reaction can easily be carried out on an industrial basis and several processes or more accurately speaking process propositions have been considered particularly for the recovery of the first sulphur atom as elementary sulphur. The other sulphur atom can be used for SO_2 gas to make sulphuric acid or for reduction by means of carbon or CO, as mentioned before.

In the Pyror process, which was operated on a pilot scale by Orkla-Grube AB the pyrite was smelted electrically in an electric furnace and in this way the first sulphur atom was driven off. The remaining FeS matte was then dissolved in sulphuric acid solution with development of H_2S. The H_2S gas can quite easily be converted into sulphur and in this way the entire sulphur content was recovered in an elementary form. However, the process was never employed on an industrial scale because it was found difficult to sell one of the main products, electrolytic iron, at market prices.

The only pyrite process at present in commercial operation is that operated by the Finnish Outokumpu Co. in Kokkola. The installation was built in 1961 to 1962 (see Fig.6).

The pyrite, which has a water content of 5 - 6%, is dried in an oil-fired rotary furnace before it is blown into the reverberatory furnace. The reverberatory furnace is charged with about 60 tons of pyrite per hour and uses up in the same period 9 tons

of oil. The air for combustion is preheated.

The admission of heat is adequate for splitting and melting the sulphur pyrite.

More than half of the sulphur content of the pyrite leaves the reverberatory furnace as a gas (S_2, H_2S, COS, SO_2) and can be recovered as elementary sulphur in the same way as in the Orkla process. The heat content is used for generating electric power by means of steam.

The iron sulphide is removed from the furnace in a liquid condition, granulated, and roasted. The cinders can be purified by chlorinating with chlorine gas in a small shaft furnace, as required.

The roasted granulate is of ideal grain size for ordinary sintering and is a valued iron ore.

It is difficult to state accurate production figures as the process is steadily being developed but one can say that nearly 400 000 tons of pyrite concentrates per year are being processed in this way. The production of elementary sulphur is nearly 100 000 tons, and sulphur in the form of SO_2 gas is produced at a rate of about 95 000 tons. Together with this, 200 000 tons of granulated Fe_2O_3 and 250 million kW-h are obtained.

SURVEY OF PYRITE PROCESSES

The chlorine process is in principle an autogenous one and should not require much addition of energy but in practice we have to reckon with a certain loss of chlorine. A loss of chlorine of 5% corresponds to a chlorine consumption of about 30 kg (66 lb)

per ton of pyrite. Converted into Norwegian kroner, this is about 16.- nkr.

The Halvorsen process is also in principle an autogenous one but can hardly be operated in this way. Also it is always dependent on a supply of industrial oxygen, roughly 140 m^3 (5000 ft^3) at NTP per ton of pyrite. The price of oxygen depends considerably on the quantities produced. For treating 200 000 tons of pyrite per year, the price of oxygen is about 0.07 nkr per m^3 at NTP, corresponding to 10 nkr per ton of pyrite.

In the DK modification heat is admitted for the preheating of the incoming gases, probably about 100 kg (220 lb) of coal per ton of pyrite. The cost of this coal corresponds to nearly 12 nkr.

In the old Orkla process about 100 kg (220 lb) of coke were added per ton of pyrite, corresponding to about 13 nkr.

In the Rosenqvist process cheap excess reduction gas is used, e.g., from electric smelting furnaces but one also visualise the direct use of low grade coke. One would require 130 kg (290 lb) per ton of pyrite, costing about 13 nkr.

For electric smelting without the use of excess heat from later production stages as in the Pyror process, one can reckon with about 800 kW-h per ton of pyrite, 0.03 nkr per kW-h, so that the cost of energy per ton is 24.- nkr.

One can visualise the use of electric power for heating, by means of plasma burners. In this case one could do without smelting and utilise some excess heat from the subsequent roasting stage. First one can then make do with about 300 kW-h per ton

of pyrite but this power is rather more expensive, on account of the plasma equipment, it would cost, say, 0.05 nkr per kW-h, so that the total cost will be 15 nkr per ton of pyrite.

In the Kokkola process nearly 150 kg (350 l) of oil are added per ton of pyrite concentrate. This is bunker "C" oil, at 0.10 nkr per kg so that we have here 15 nkr per ton of pyrite.

All this can be summarised in the following table:

Process	Added	Costs
Chlorine process	Chlorine	nkr 18
Halvorsen/DK	Oxygen and coal	" 10 + 12
Orkla	Coke	" 18
Rosenqvist	Coke	" 18
Pyror 1st stage	Electric power	" 24
Kokkola 1st stage	Oil	" 15

These costs are naturally not of very great importance in the evaluation of the different processes. A number of other costs must be added to them, in particular the capital costs, which may be quite different.

The processes yields also different products and must also be assessed from this point of view.

The addition of energy is acceptable if the resulting energy excess can be utilised in a reasonable way. This will present some problems under Norwegian conditions.

The Kokkola process is in many ways interesting but we must bear in mind that only about half the sulphur is recovered in elementary form. The balance must be processed further to sulphuric acid. The reduction of SO_2 gas of the roasting stage

will hardly produce a large excess of energy in the process for subsequent generation of steam.

The use of steam for producing electric power is reasonable in Finland, where a kilowatt hour costs 0.8 - 0.10 mkr, but hardly in Norway at the low local cost of electric power.

An open question is whether Kokkola granulate with a higher copper and zinc content than Pyhasalmi pyrite concentrate can be satisfactorily chlorinated in a shaft furnace.

The Orkla and Pyror processes have certainly be thoroughly assessed by the Orkla Grube Company and there is little we can add here.

If there is a demand for sulphuric acid or steam, the chlorinating process according to Mitterberg Kupferbergbau or Rosenqvist seems to show the greatest advantages.

The chlorination process still requires much pioneering work and the formation of dust by the $FeCl_3$ gas may present considerable problems.

The Rosenqvist process is technologically speaking the one which can most easily be applied on a commercial scale. It seems particularly promising if heat reduction gas is available but it may also be advantageous if it is necessary to use up coal or low grade coke as the reducing agent. It is probable that the process is not suitable for shaft furnaces because in this case problems arise in connection with the production of pyrite pellets of acceptable quality. I feel that we should consider again whether the process can be developed as a two-stage fluidising treatment.

Tab. 1

Chemical analysis and granulometry of different Norwegian iron pyrites.

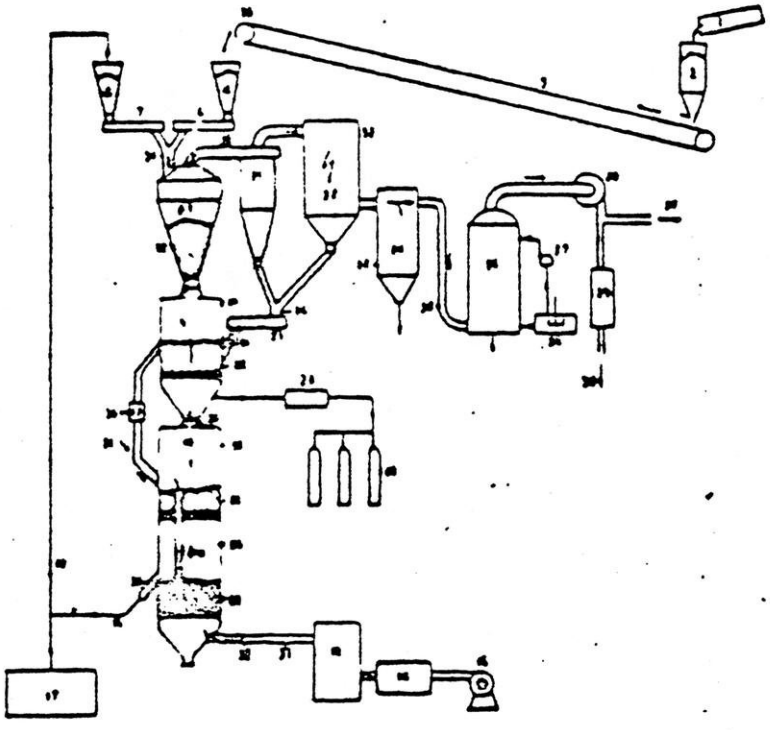
Type of pyrite	Chemical composition							Granulomet
	S	Fe	Cu	Zn	Pb	As	Gangue	0-200 Mesh %
Grua fine pyrite	41	37	2.00	1.20	0.06	0.05	13.8	
Sterovas fine pyrite	45		1.40					
Killingdal flotation pyrite	48	45	0.60	3.10			2.7	29
Sulitjelma flotation pyrite	51	45	0.03	0.25		-0.09	2.7	72
Nord-Norge A/S	51	47	0.27	0.90	0.30			52
Tosdalen A/S	49	44	0.50	0.02			4.4	39
Joma A/S	52	46	0.15	0.25	0.01	0.08		95

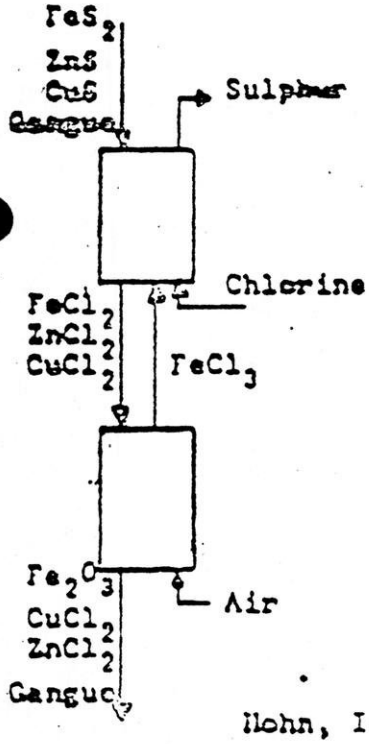
Fig. 2.

Chlorine process

KLORPROSESSEN

Mitterberg Kupferbergbau





Chlorination stage

Kloreringstrinn:

$$4\ FeS_2 + 4\ Fe_2Cl_6 = 12\ FeCl_2 + S_8$$

$$8\ CuS + 8\ Fe_2Cl_6 = 16\ FeCl_2 + 8\ CuCl_2 + S_8$$

$$8\ ZnS + 8\ Fe_2Cl_6 = 16\ FeCl_2 + 8\ ZnCl_2 + S_8$$

Oxidation stage

Oksydasjonstrinn:

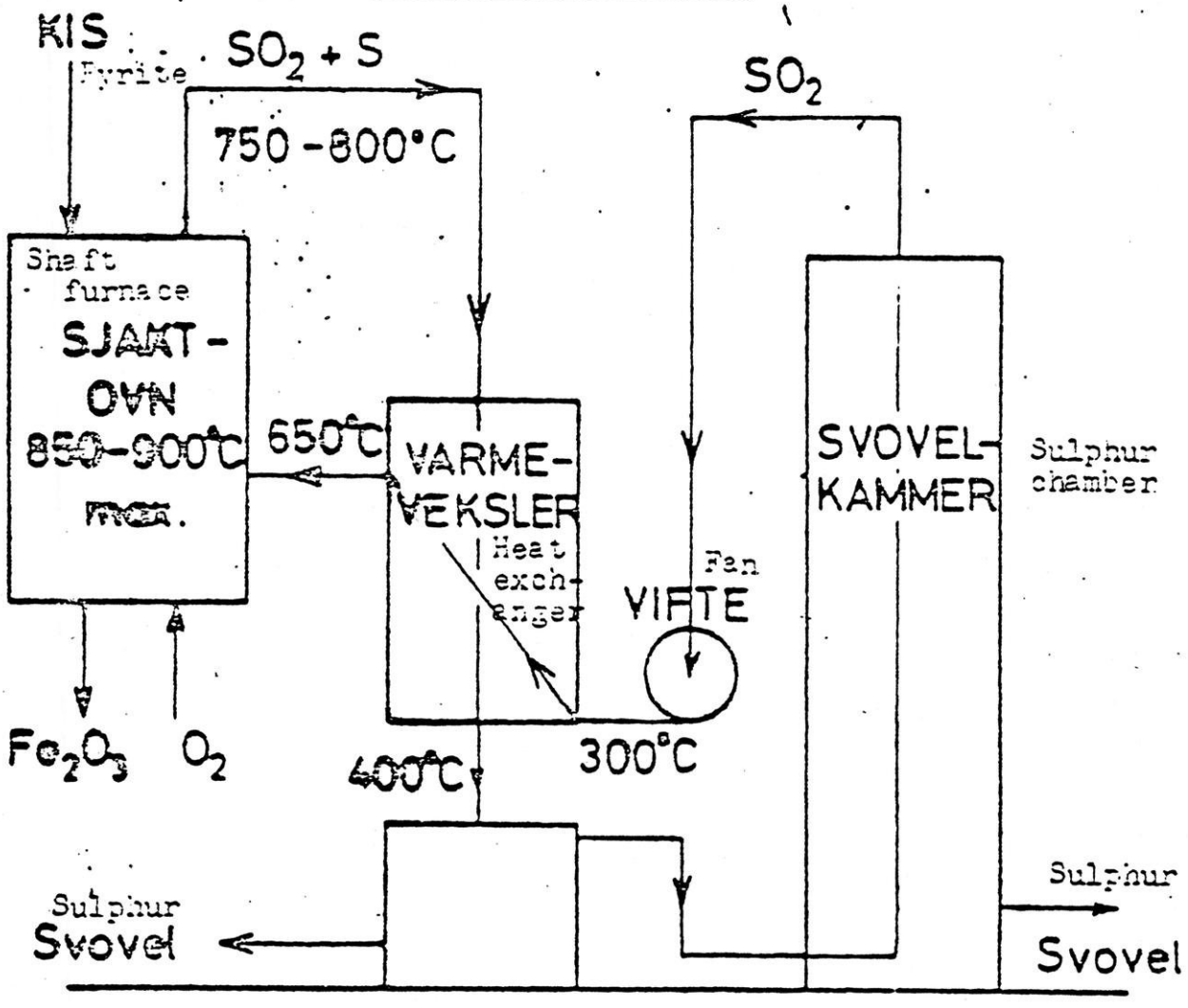
$$12\ FeCl_2 + 3\ O_2 = Fe_2O_3 + 8\ FeCl_3$$

Mohn, International Min. Dress. Congr., Stockholm 1957.

Fig 3

Halvorsen process

HALVORSEN - PROSESSEN



1. $2\,FeS_2 = 2\,FeS + S_2$

2a. $FeS + SO_2 \rightarrow Fe_3O_4 + S_2$

2b. $FeS + O_2 \rightarrow Fe_2O_3 + SO_2$

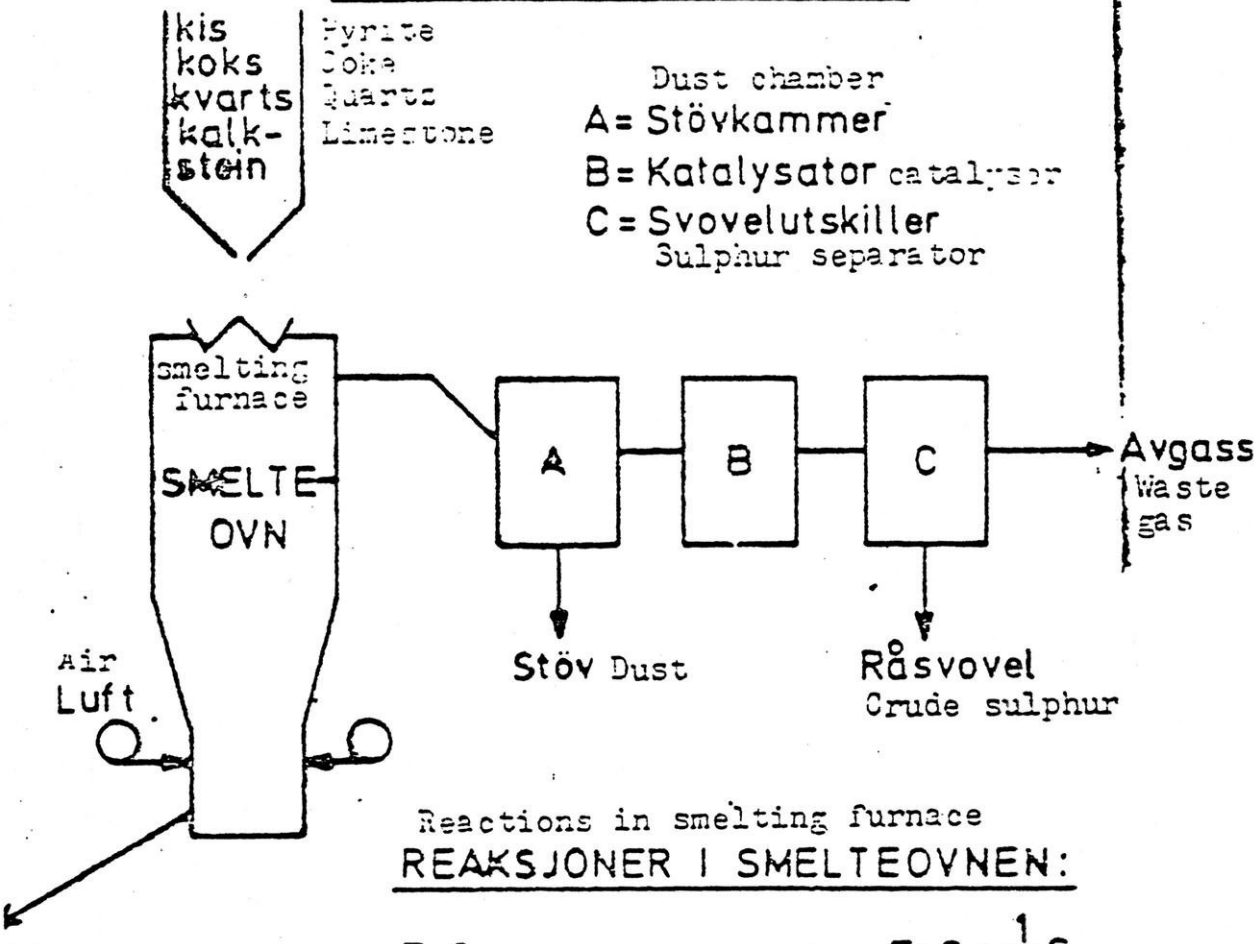
2c. $Fe_3O_4 + O_2 \rightarrow Fe_2O_3$

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2. $FeS + O_2 \rightarrow Fe_2O_3 + S_2$

Orkla process

ORKLA-PROSESSEN



Reactions in smelting furnace

REAKSJONER I SMELTEOVNEN:

$$FeS_2 \longrightarrow FeS + \tfrac{1}{2}S_2$$

$$SO_2 + C \longrightarrow CO_2 + \tfrac{1}{2}S_2$$

$$FeS + O_2 \longrightarrow FeO + SO_2$$

$$FeO + SiO_2 + CaO \longrightarrow \text{Slagg slag}$$

$$FeS + CuS \longrightarrow \text{Skjærsten Matte}$$

Reactions in catalyser

REAKSJONER I KATALYSATOR:

$$SO_2 + 2\,H_2S \longrightarrow 2\,H_2O + 3S$$

$$CS_2 + 2\,SO_2 \longrightarrow CO_2 + 3S$$

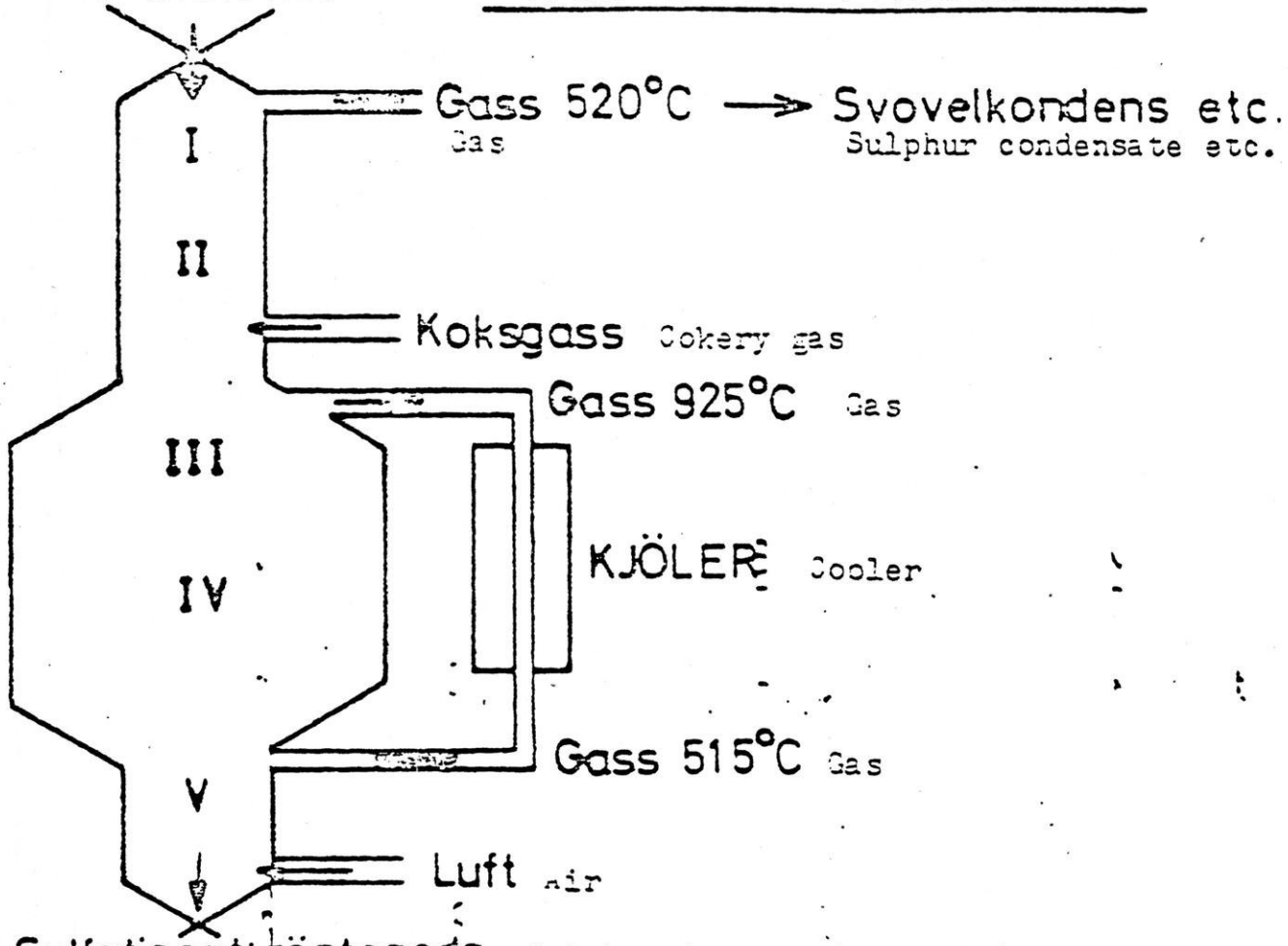
$$2\,COS + SO_2 \longrightarrow 2\,CO_2 + 3S$$

Fig. 5

Pyrite briquettes — Rosenqvist process

Kis-briketter

ROSENQVIST - PROSESSEN



Sulfatisert röstegods — Sulphated roasted material

Sone I : Forvarming av kisen til 650°C

Sone II: Pyrittspaltesone 650°-900°C

$$2\,FeS_2 \longrightarrow 2\,FeS + S_2$$

$$SO_2 + CO \longrightarrow CO_2 + \tfrac{1}{2}S_2$$

Sone III: Röstesone 900°-950°C

$$3\,FeS + 5\,O_2 \longrightarrow Fe_3O_4 + 3\,SO_2$$

Sone IV: Sulfatisering av kisens Cu-og Zn-innhold. Ca. 600°C

Sone V: Avkjölingssone

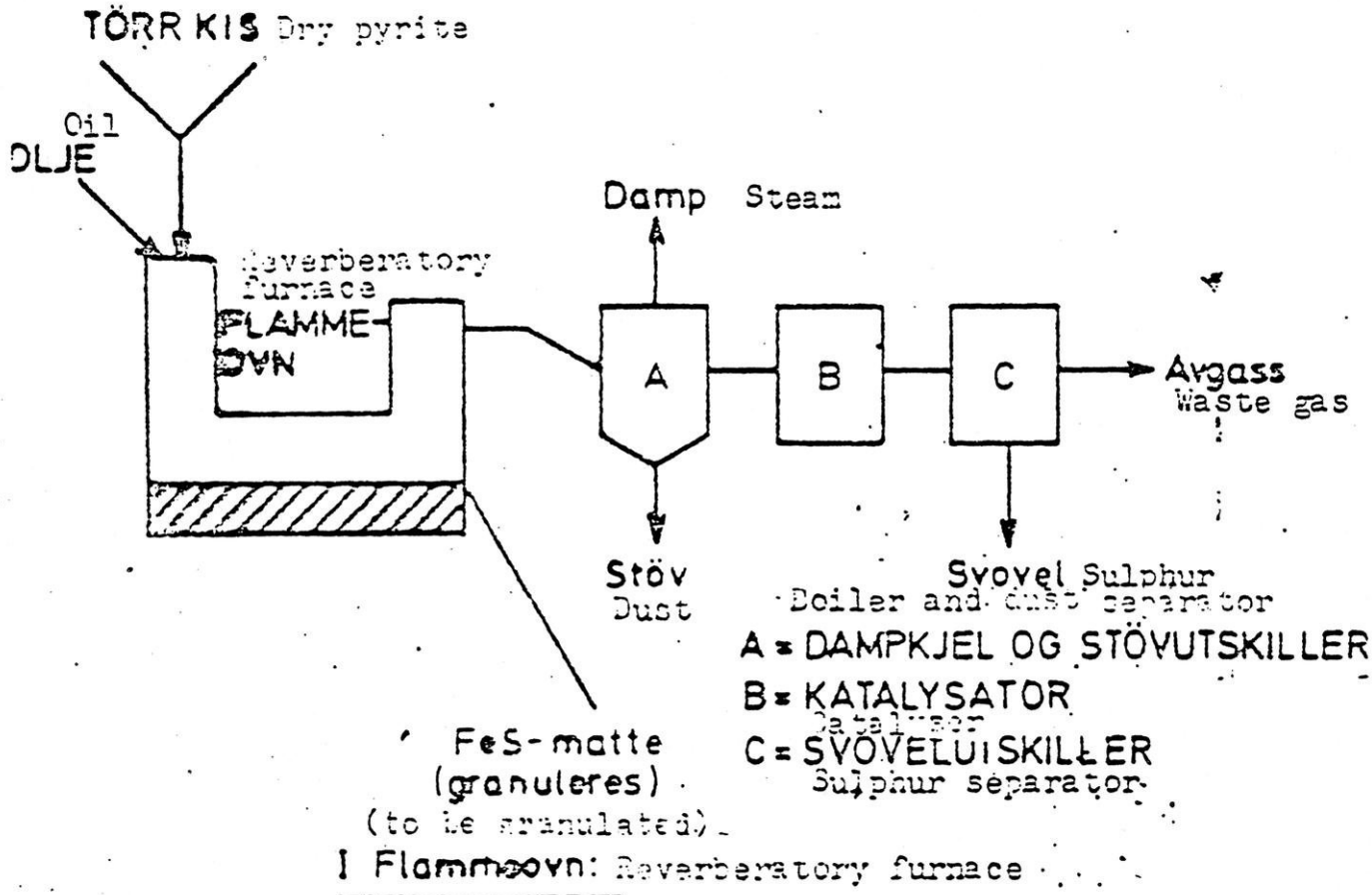
Zone I : Preheating of pyrite to 650° C
" II : Pyrite decomposition zone
" III : Roasting zone
" IV : Sulphating of Cu and Zn contained in pyrite
" V : Cooling zone

Fig. 6

Kokkola process

KOKKOLA-PROSESSEN

(OUTOKUMPU)



I Flammeovn: Reverberatory furnace

$$FeS_2 \longrightarrow FeS_{(l)} + \frac{1}{2}S_2$$

I Katalysator: Catalyser

$$SO_2 + 2\,H_2S \longrightarrow 2\,H_2O + 3S$$

$$2\,COS + SO_2 \longrightarrow 2\,CO_2 + 3S$$

Sherritt Gordon Process for Production of Elemental Sulphur and Iron from Pyrites

THE conventional procedure for the treatment of pyrites and most sulphide ores involves roasting the material in air to produce either a metal or a metal oxide and sulphur dioxide. The oxide-containing cinders are then used to produce the appropriate metal, usually after treatment to remove and recover the small amounts of precious and semi-precious metals that are often present. The sulphur dioxide is either used for sulphuric acid production or vented to atmosphere depending on plant location and market conditions. The economics of any process depend to a great extent on the full utilization of the materials available and obviously the venting of the sulphur dioxide does little to enhance the economics of the metal production. Even if sulphuric acid is produced, it frequently has to be transported to the market areas and the high cost of movement of the acid has to be offset against the allowable credit in the metal manufacturing process. The advantages of co-producing elemental sulphur are many indeed, viewed in this context.

With the exception of the flash-roasting process developed by Outokumpu Oy in Finland, none of the roasting and leaching processes currently in use produces appreciable quantities of elemental sulphur, and it is reported that the cost of the elemental sulphur produced is well above current sulphur prices. It is, therefore, not surprising that there has been considerable interest in hydrometallurgical pressure techniques in ammoniacal and acid media that can produce sulphur in an elemental form.

In Canada, Sherritt Gordon Mines Ltd. has carried out considerable work using this approach for the treatment of pyrites, zinc, nickel, cobalt, lead and copper sulphide concentrates. The process for pyrites has been studied in great detail on a laboratory scale and a tentative scheme has been proposed for a large scale unit, together with a detailed cost analysis. The following is a summary of the work with pyrites; the processes for the other minerals will be dealt with in a subsequent issue of *Sulphur*.

In a patent granted to Sherritt Gordon in 1962, the oxidation of pyrrhotite (FeS) to iron oxide and elemental sulphur in an aqueous medium was shown to be possible. Other work indicated that both natural and artificial pyrrhotite were about twenty times more reactive than pyrite and would oxidize virtually completely to iron oxide and elemental sulphur. Two process schemes have now been developed by Sherritt Gordon, the first to process a 'clean' or relatively pure pyrite and the second to treat a "dirty" pyrite containing assorted non-ferrous metal impurities. It is the latter that is considered here, since the 'clean' pyrites process merely bypasses several of the stages that would otherwise be used. The process involves the thermal decomposition of pyrite into artificial pyrrhotite and elemental sulphur, followed by the oxidation of the pyrrhotite in an aqueous acid medium to iron oxide and elemental sulphur. The iron oxide is leached with sulphur dioxide-sulphuric acid and the resulting ferrous sulphide solution is purified and hydrolysed under oxidising conditions. The basic iron sulphate that is precipitated is calcined and reduced to iron metal.

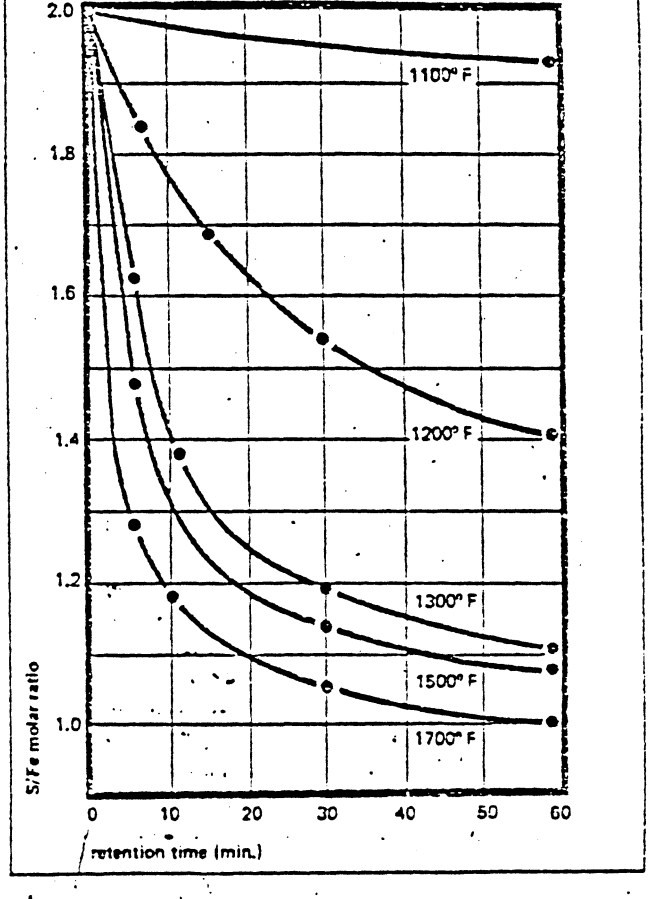
Thermal Decomposition of the Pyrite

The principal reaction that occurs at this stage can be represented by the following equation:

$$FeS_2 \longrightarrow FeS + S$$

although in the presence of steam, several other reactions can occur to form sulphuric acid, hydrogen sulphide, hydrogen, sulphur dioxide etc. It was shown, however, that at the relatively low temperatures and steam concentrations used, only minor quantities of impurities and side products were found in the exit gas. In the initial experimental work, an atmosphere

Fig. 1. SHOWING THE TEMPERATURE RATE OF SULPHUR REMOVAL RELATIONSHIP

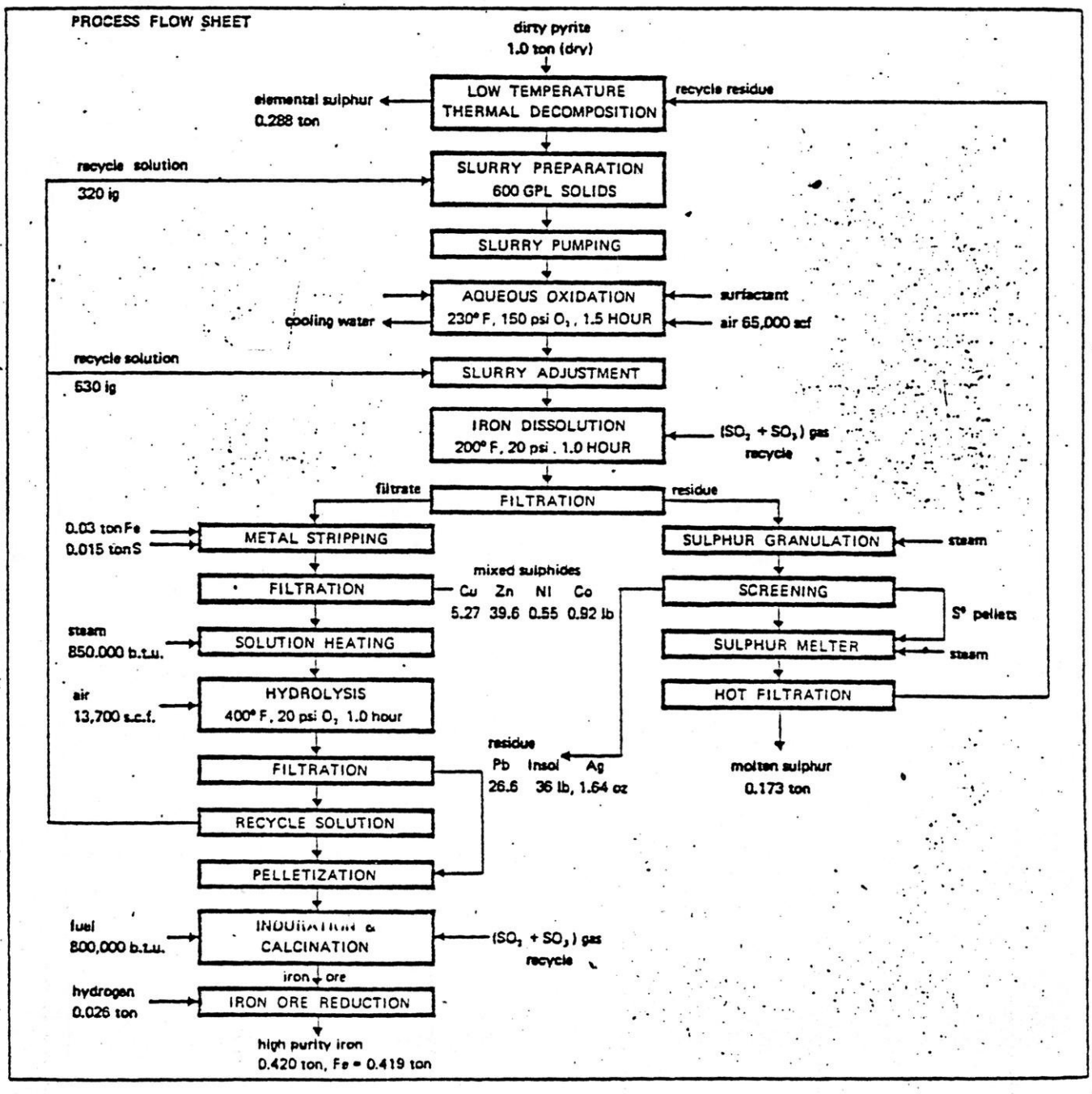


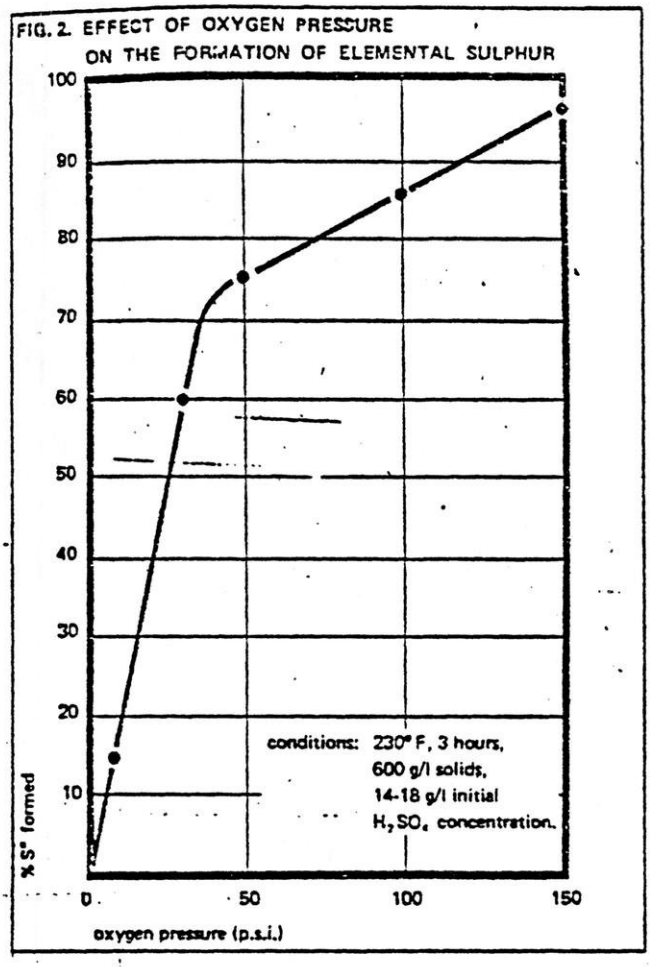
typical of completely combusted natural gas was used in the reactor, although it is proposed to use Bunker C fuel oil as the heat source in any large scale application. The effects of temperature, rate of gas flow and particle size of the feed material on the rate of sulphur removal were investigated and it was shown that temperature was the most important variable. Fig. 1 shows the temperature/rate of sulphur removal relationship.

A sulphur-to-iron molar ratio of 1.2:1.0 was established as being sufficient for the subsequent aqueous oxidation treatment and this condition was readily obtainable at 1,300°F with a 30 minute retention time. Tests showed that during the thermal decomposition, 40–45% of the total sulphur was removed, of which 85% was in the form of elemental sulphur. Of the remainder, 10% was as sulphide sulphur and 5% as sulphur dioxide.

In the scheme for an actual plant, it is proposed that the pyrites would be initially dried in a fluidized-bed dryer before being combined with unreacted sulphides from the aqueous oxidation step and fed to the thermal decomposition reactor. This will be of a fluidized-bed type, and because of the endothermic nature of the reaction, additional heat has to be supplied by the direct combustion of fuel oil or natural gas in the fluidized-bed. The solids discharging from the reactor are fed into a slurry tank where they are mixed with a recycle solution before being introduced into the aqueous oxidation autoclave.

The gases from the reactor contain elemental sulphur together with small quantities of other sulphur compounds such as hydrogen sulphide, sulphur dioxide and carbonyl sulphide if any carbon monoxide is present. It is proposed that after passing the gases through cyclones, a waste heat boiler and an electrostatic precipitator, a catalytic converter unit will convert





the sulphur dioxide and hydrogen sulphide to elemental sulphur which will be recovered in a sulphur condenser.

Aqueous Oxidation of Pyrrhotite

This reaction takes place in a dilute sulphuric acid solution or, alternatively, a recycle leach solution inside a steel autoclave equipped with mechanical agitators.

$$2FeS + 3H_2O + 1\tfrac{1}{2}O_2 \longrightarrow 2Fe(OH)_3 + 2S$$

The autoclave is charged with solution, heated to the desired temperature and oxygen admitted. Investigations showed that the most important factor controlling the oxidation was the mass transfer of oxygen from the geasous phase to the surface of the pyrrhotite. Thus both the application of higher oxygen pressures and improved agitation increase the amount of elemental sulphur produced in unit time. The effect of the oxygen pressure is shown in Fig. 2 and it can be seen to be more pronounced between 0 to 50 p.s.i. than between 50 and 150 p.s.i.

The optimum temperature for the reaction was about 245°F, i.e. below the melting point of sulphur, but 230°F was taken as being the oxidation temperature to ensure that no localized melting of the sulphur occurred. Exposure of the leach solution to temperatures above 245°F for even a short period of time, adversely affected the rate of oxidation, the probable explanation being that the solid particles become coated with sulphur. Initially, sulphuric acid is required to start the reaction, but this is regenerated by a subsequent reaction and the process becomes self-sufficient. Recycle leach solution containing about 20 g/l. H_2SO_4 was found to be a successful substitute for the sulphuric acid. The effect of various surface active agents on the rate of sulphur formation was also investigated and it was shown that the amount of sulphur formed after 1 hour was up to 20% more if an additive was used. Over a longer period of time, the effect was less pronounced, but still significant.

The studies carried out indicated that the optimum conditions occurred when the reaction temperature was 230°F, the oxygen partial pressure 150 p.s.i. and the slurry contained 40% of solids initially. Recycling of the leach solution was also found to be important. Under these conditions, a very rapid initial oxidation takes place, and after 1 hour 70% of the sulphide sulphur is oxidized to an elemental form. Removal of the sulphur formed by flotation and by granulation was considered, with the latter being shown to give superior results. The technique involved heating the slurry after the oxidation to a temperature above the melting point of sulphur, then cooling with agitation to form granules of sulphur.

In practice, a three-compartment autoclave made from carbon steel with a lead and acid-proof brick lining has been proposed, the vessel being similar to one already in service with Sherritt Gordon for the acid leaching of nickel-cobalt concentrates. The iron monosulphide slurry is pumped into the autoclave by special high pressure pump, together with air at 800 p.s.i.g. to provide the required oxygen overpressure. The air compressor is driven by a gas turbine and a waste heat boiler on the gas turbine exhaust generates all the process steam requirements. To prevent the temperature inside the autoclave from rising above 230°F, cooling coils made from titanium are incorporated in the design to remove the heat of reaction.

Separation and removal of the sulphur can be achieved by heating the slurry from the reactor to about 260°F, then flash-cooling it under controlled conditions when pellets of elemental sulphur together with unreacted sulphide are formed. A 28-mesh screen separates the sulphur pellets from the solution and hydrated iron oxide. A purification circuit then melts the sulphur pellets in hot water at 300°F to form a slurry which is filtered in a pressure filter to recover about 95% of the elemental sulphur present as a pure product. The residue from the hot filtration stage is ball-milled and recycled to the thermal decomposition stage since unreacted pyrite, pyrrhotite and some elemental sulphur are present. This is the technique used for clean pyrites; however, if the pyrites contain contaminants, a different method — outlined below — is adopted which allows the recovery of these materials.

Dissolution of the Iron Oxide

The hot slurry from the autoclave is flashed to atmospheric pressure and diluted with recycle liquor from the subsequent hydrolysis stage. The diluted slurry is then introduced into the iron dissolution tower which is a countercurrent sieve plate column constructed from mild steel and lined with rubber and acid-proof brick. Sulphur dioxide gases from the subsequent calcination stage react with the iron and totally dissolve it as ferrous sulphate whilst the other components remain unattacked, and can be removed by

FIG.3. EFFECT OF COST OF DIRTY PYRITE ON % GROSS RETURN

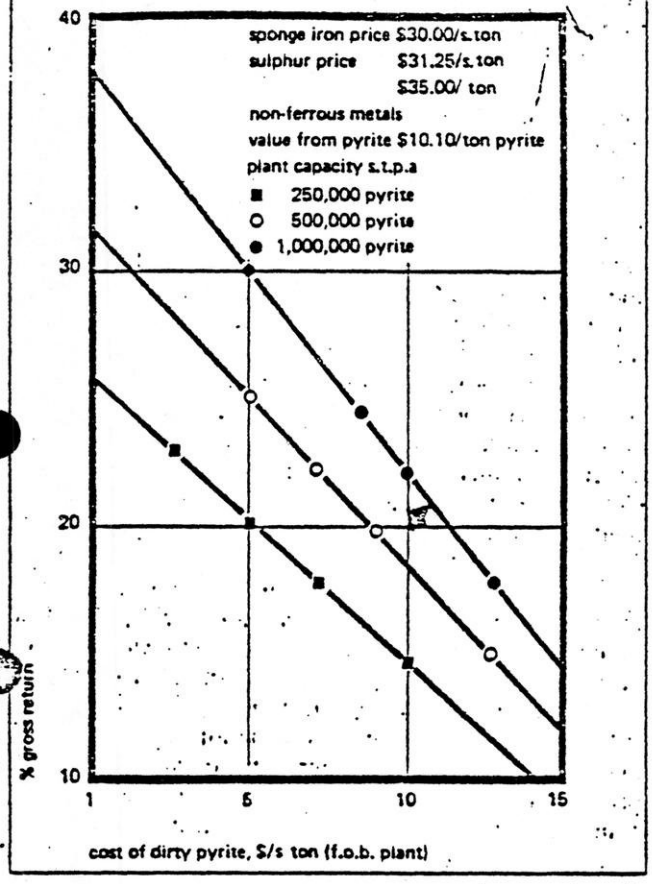
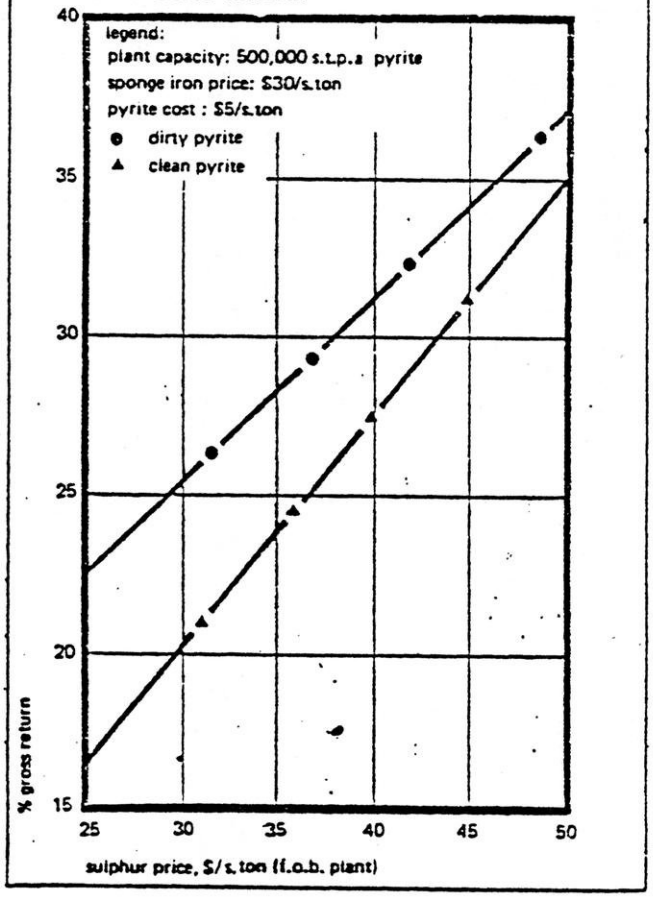


FIG. 4. EFFECT OF SULPHUR PRICE ON % GROSS RETURN



filtration. The residue containing the sulphur is then heated to 300°F, i.e. above the melting point of the sulphur, flash-cooled and screened to recover unreacted sulphides and elemental sulphur. The latter is in a pellet form which is treated in the manner described above, to recover the sulphur. The remaining solids, after this treatment, contain all the lead as lead sulphate, precious metals and gangue, all of which can be utilized in a lead smelter.

The filtrate contains a solution of iron, together with the zinc, cobalt and copper content of the ore. The zinc is removed as the sulphide and the copper nickel and cobalt by the addition of divided sponge iron.

$$3\,Fe + Cu^{++} + Ni^{++} + Co \longrightarrow 3\,Fe^{++} + Co + Ni + Cu$$

$$Zn\,SO_4 + H_2S \longrightarrow ZnS + H_2SO_4$$

After pressure filtration to remove these semi-precious metals, the iron is hydrolysed at 400°F in a lead and acid proof brick lined tower. The presence of air converts the ferrous iron to ferric acid and a mixture of basic ferric sulphate and hydrate iron oxide is precipitated.

Calcination and Reduction

The hydrated iron oxide from the 'clean' pyrite or the mixture of oxide and sulphate from the 'dirty' pyrite is calcined at 1,800°F to remove any remaining sulphur prior to conventional treatment for reduction to sponge iron. It was found that the best results were obtained if the hydrated iron oxide from the aqueous oxidation stage was pelletized prior to calcining.

Economics

A study of capital and operating costs has been made, based on pre-pilot plant data and several pre-determined design variables. Three sizes of plant were considered as well as units for clean and dirty pyrite. A summary of capital costs and direct operating costs are given in the table below.

TABLE 1

Summary of Cost Estimates

Plant Capacity (s.t.p.a. Pyrite)	Type Of Pyrite	CAPITAL COST: Thermal Decomposition Cost ($)	CAPITAL COST: Aqueous Oxidation Cost ($)	CAPITAL COST: Total Capital Cost ($)	DIRECT OPERATING COST: Thermal Decomposition Plant ($/Year)	DIRECT OPERATING COST: Aqueous Oxidation Plant ($/Year)	DIRECT OPERATING COST: Total Direct Operation Cost ($/Year)
250,000	Clean	3,200,000	13,400,000	16,600,000	650,000	2,600,000	3,250,000
	Dirty	3,200,000	17,500,000	20,700,000	650,000	3,200,000	3,850,000
500,000	Clean	5,200,000	24,400,000	29,600,000	1,100,000	4,900,000	6,000,000
	Dirty	5,200,000	30,700,000	35,900,000	1,100,000	6,100,000	7,200,000
1,000,000	Clean	8,300,000	43,100,000	51,400,000	2,000,000	9,000,000	11,000,000
	Dirty	8,300,000	55,100,000	63,400,000	2,000,000	11,600,000	13,600,000

They are based on a battery limit plant, together with offsite facilities for a grass-roots plant, but exclude process development costs and royalties. A hypothetical site in the Great Lakes area of Canada is assumed. The direct operating costs do not include the the cost of pyrite, depreciation and interest or the sales revenue from the iron and sulphur products.

The success of any industrial venture is usually reflected in the return of capital that can be obtained; in a process such as this one, the value assigned to the numerous products together with the cost of the pyrites influences the yield to a very large extent. Fig. 3 shows the effect of the cost of the pyrite on the gross rate of return and Fig. 4 the effect of the selling price of the sulphur for a 500,000 t.p.a. plant. This size of plant or larger, and the use of 'dirty' pyrite would be favoured for an economically attractive project in conjunction with raw material and low cost energy availability. In addition, markets for sponge iron and sulphur must exist. The satisfaction or partial satisfaction of these conditions should allow the successful operation of a plant using this process. Sherritt Gordon Mines is presently constructing a pilot plant to verify this experimental evaluation and the result of this work should be of great interest.

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Mehta, B. R. *et. al.* Economics of Iron and Elemental Sulphur Recovery from Pyrite using Low Temperature Thermal Decomposition and Aqueous Oxidation.

Both papers were presented at the CIMM Conference of Metallurgists, held at Kingston, August 1967.

World Carbon Disulphide Supply — continued from page 27

t.p.a. plant at Huidiya at the beginning of this year, which is integrated with rayon staple and fibre capacity at the same location. In Indonesia, a 150 t.p.a. unit is to start production this year, and will mainly supply a cellulose research laboratory where investigations could lead to the establishment of a rayon industry.

Several major developments have occurred in Argentina where Industrias Quimicas Argentinas Duperial S.A.I.C. replaced older plants with a 14,000 t.p.a. unit at San Lorenzo in 1962, based on the FMC methane process, and this remains the only example of the utilization of a hydrocarbon process in the developing world. Sociedad Nuevas Industrias Argentinas Fibras Artificiales, a rayon and cellophane manufacturer, formerly dependent on an external supply of carbon disulphide, commissioned its own 2,000 t.p.a. plant this year, and Partenopea Argentina SA. recently restarted the operation of its 26-year-old 2,400 t.p.a. facility.

The only other recent CS_2 plant construction in the developing world has taken place in India where Baroda Rayon Corp., Indian Rayon Corp. and South India Viscose Ltd. installed new plants with a total capacity of 5,800 t.p.a. between 1960 and 1963. In spite of the 30,000 t.p.a. level of demand for carbon disulphide in India, the structure of the Indian rayon industry — small-scale and geographically diverse — is unlikely to favour the construction of a large methane-based unit capable of supplying the whole market.

Oxygen-enriched Air for Kennecott Copper Converters

By 1969 the Utah Copper Division of the Kennecott Copper Corp. plans to use oxygen-enriched air in its copper smelter near Salt Lake City, Utah, U.S.A. Some of the advantages offered by this innovation include greater process flexibility, higher throughput, reduced air pollution and higher concentration of the by-product sulphur dioxide, used subsequently in sulphuric acid production. The plant will use 250 t.p.d. oxygen piped from a nearby air-separation unit that is currently being built by the Linde Division of Union Carbide Corp. and is scheduled to be on-stream by early 1969. The idea of using oxygen enriched air in copper converters has been under consideration for some time, but it has been reported that Kennecott will be the first U.S. copper company to employ the concept in a commercial-scale application.

In Kennecott's present process, copper concentrates are smelted in a reverberatory furnace to form a matte of copper, iron and sulphur, which consists of a eutectic mixture of cuprous and ferrous sulphides. This matte is processed in a converter through which air is bubbled so that the ferrous sulphide is oxidized and combined with silica to form a slag. The temperature in the converter is kept below 1,230°C to avoid damage to the refractory lining. As well as the slag, the other two products obtained in the converter are sulphur dioxide and blister copper. The oxidation takes about 10 hours, after which the slag is skimmed off the molten copper and returned to the reverberatory furnace to recover any remaining copper, while the sulphur dioxide-containing gases from the converters are subsequently used in Kennecott's nearby sulphuric acid plants.

By increasing the oxygen content of the feed air to the converters by 10% to about 31% by volume, Kennecott anticipates that the reaction in the converter will be more rapid and intense, with the result that the liberation of heat will be faster and that some of the raw copper concentrate may be added directly to the converter thus cutting down the use of the reverberatory furnaces. In this way it is envisaged that the copper output from each converter will be increased from 65 to 75 or 80 tons per batch and that greater flexibility will be effected. By reducing the use of the reverberatory furnaces the amount of sulphur dioxide escaping to the atmosphere will be reduced.

Oxygen-enrichment also means that the sulphur dioxide content of the gases used as feed for sulphuric acid manufacture will be increased from 4% to 6% or more, resulting in more efficient acid production. In many processes for the manufacture of sulphuric acid from gases containing sulphur dioxide, the optimum SO_2 content is around 7½%.

As a result of the scheduled innovation, it is expected that Kennecott's sulphuric acid capacity will be increased from 1,400 s.t.p.d. to 1,700 s.t.p.d. with minor equipment changes. This increased acid capacity will be partly taken up by the company's ore-leaching operations and also by surrounding industry; the higher price of by-product acid has also been an added incentive.

Boliden process for roasting arsenical pyrite

THE introduction of the fluidized bed roaster into the sulphuric acid industry has brought about many changes including lower capital costs than other types of conventional roasters, and higher specific throughputs. There were, however, some disadvantages that occurred and probably the most significant was the inability of the fluidized bed roaster to run on a pyrites feed high in arsenic and produce a cinder with a low residual arsenic content. Lead and antimony removal was also a difficulty. One approach to solving this problem was described recently in some detail, both from the theoretical and the practical point of view in *Sulphur*.* The BASF two-stage process uses two fluidized bed roasters in series, the first allows limited roasting of the pyrites to the monosulphide and at the same time, the volatilization of virtually all the arsenic present in the feed. The second stage roaster allows the oxidation to proceed further and yield ferric oxide (haematite). In a conventional fluidized bed roaster, the pyrite is oxidized almost entirely to haematite which can react with the oxidized arsenic present to form a stable, non-volatile iron arsenate.

$$As_2O_3 + O_2 + Fe_2O_3 \longrightarrow 2Fe\,AsO_4 \qquad (1)$$

The controlled oxidation in the BASF process allows the arsenic to volatize before the iron is fully oxidized to haematite and so prevents the contamination of the cinders.

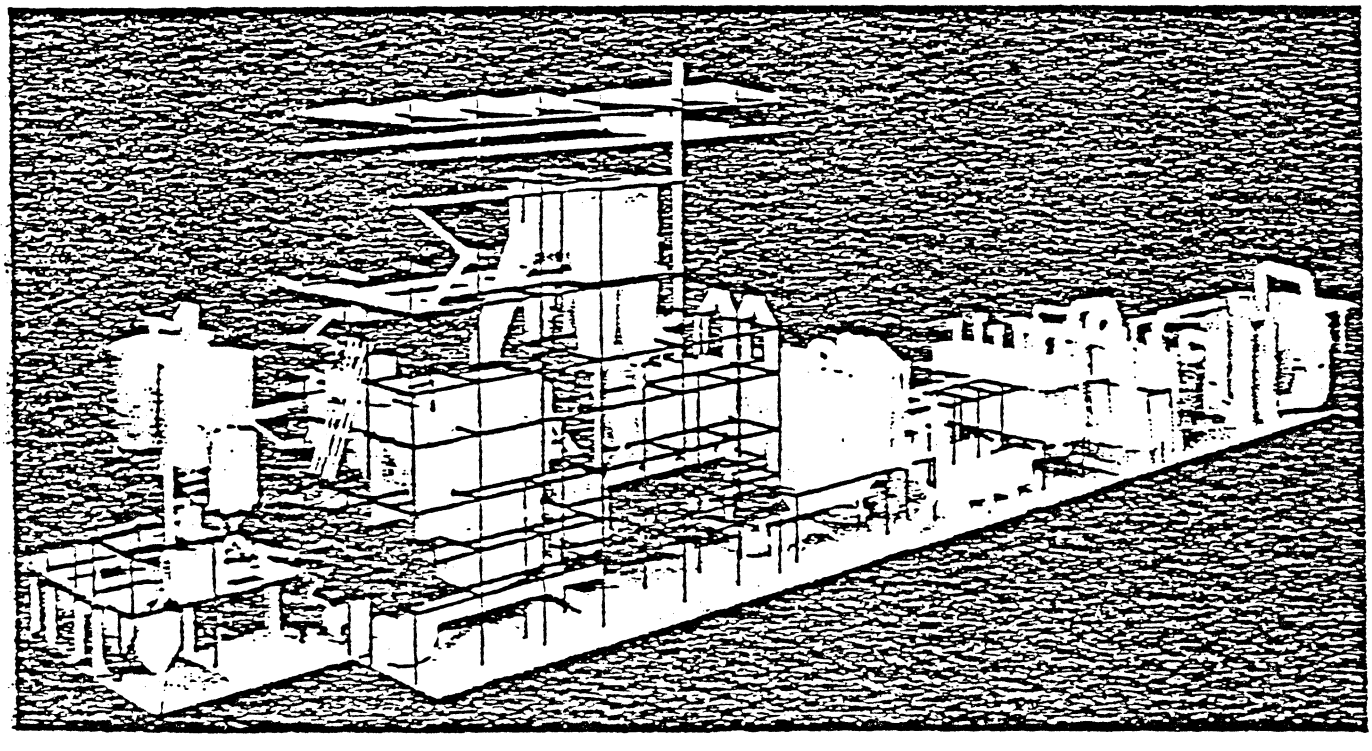
Existing plants

The Swedish company, Boliden Aktiebolag, has developed a one-stage process for use with arsenical pyrites and currently operates a 175,000 t.p.a. H_2SO_4 plant at Hälsingborg in Sweden using this technology. A further unit rated at 250,000 t.p.a. came on-stream in September of this year, and a third unit, also of 250,000 t.p.a., is in the planning stage. Outside Sweden, a considerable amount of interest has been shown in the process, and at least two plants are currently under construction including a single-stream 420,000 t.p.a. unit being built in Australia.

Theory of process

The Boliden process utilizes the fact that the formation of the undesirable iron arsenate complex only occurs in the presence of excess oxygen, as indicated by equation 1. Sufficient oxygen is required not only to oxidize the pyrites to ferric oxide and the arsenic to arsenious oxide initially, but to allow the formation of arsenate. The effect of the oxygen concentration is clearly shown in Fig. 1 which shows the thermodynamically calculated demarcation zones for the existence of iron arsenate ($FeAsO_4$) ferric oxide or haematite (Fe_2O_3), ferrosoferric oxide or magnetite (Fe_3O_4) and ferrous sulphide (FeS). These are expressed as a function of the log of the partial pressure of oxygen, in atmospheres, and the temperature. In effect,

* See *Sulphur* No. 78, September/October 1968, pages 20-25.



Model of acid plant utilizing the Boliden process

iron arsenate will be formed and is stable under any of the conditions above the line *a*; likewise magnetite is formed when the prevailing conditions occur below the line *c*. Since the partial pressure of oxygen is related to the concentration in the gas phase, it follows that at high oxygen concentrations, haematite and iron arsenate will be formed, whilst at the other extreme, the oxidation will only proceed as far as the monosulphide.

It follows therefore, that if the roasting of pyrites takes place at a temperature and partial pressure of oxygen below the curve *a*, the cinders produced will be essentially arsenic free. If the conditions lie between curves *a* and *b*, the most of the iron will be in the form of haemite, or if the conditions are below the curve *c* the iron will predominantly be in the magnetite form. Below curve *d*, then monosulphide will be formed as is the case in the first stage of the BASF process. In all these instances, the arsenic will be volatilized mainly as the sulphide As_2S_3 and/or oxide As_2O_3. It is this controlled oxidation during the roasting process that is the basis of the Boliden process.

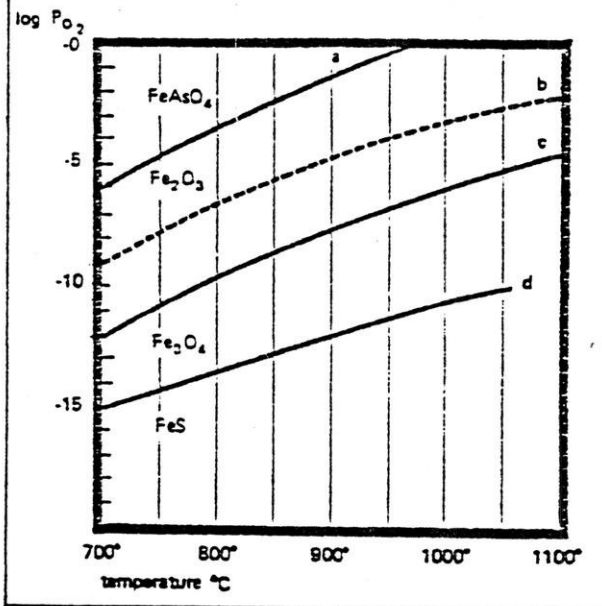
The roasting must, therefore, be carried out well below curve *a* to prevent arsenic retention, and also well above curve *d* to minimize formation of the monosulphide. In practice, the conditions lie below curve *c*, which means that most of the iron in the cinders is in the form of magnetite (Fe_3O_4).

In all these cases, the establishment of equilibrium conditions is mainly a function of the grain size of the pyrites feed, and the retention time in the bed. In the case of a very fine feed, such as a flotation concentrate, the equilibrium is established very rapidly but the retention time is short since the fine dust is rapidly carried away in the gas stream. With larger size articles, i.e. up to 5 mm. in diameter, the establishment of equilibrium is a much slower process, but to compensate for this, the material is present in the reaction zone of the fluidized bed for a much longer period of time, since the cinders are removed from the bed itself.

Although an arsenic free cinder has been obtained by using an oxygen deficient atmosphere, the gas stream leaving the roaster is highly contaminated with cinders and volatile impurities such as arsenic and sulphur.

Cinders removal is easily effected in a cyclone, and in the absence of cinders, it is possible to increase the partial pressure of oxygen and allow the arsenic to become oxidized to the trioxide, and the sulphur to

FIG. 1. BOLIDEN PROCESS



sulphur dioxide. Subsequent cooling of the gases allows the removal of the contaminants by conventional means.

Plant design

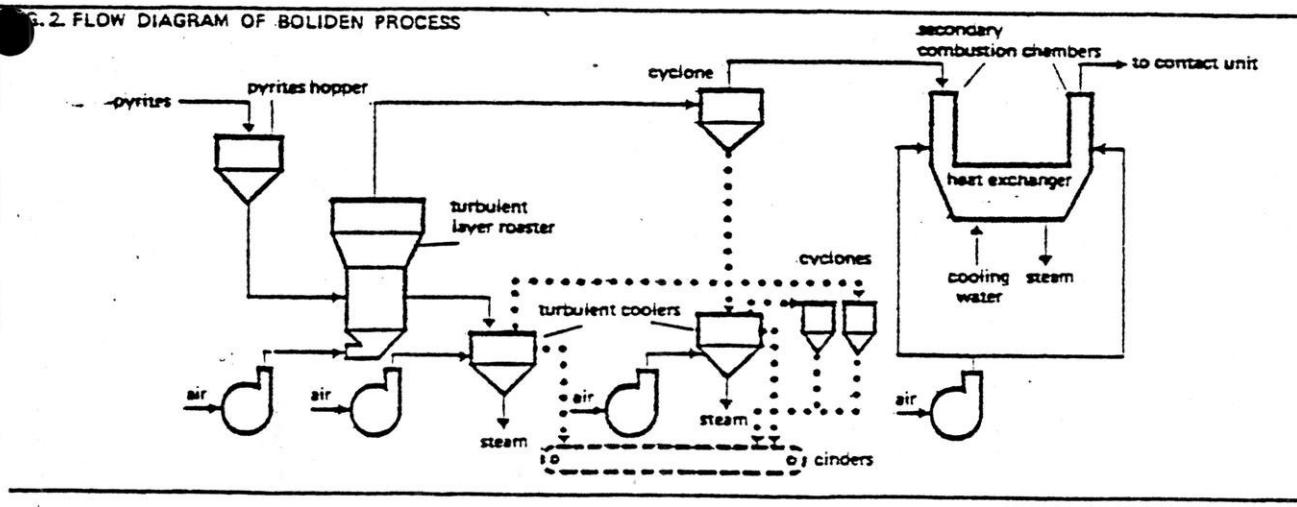
A simplified flow diagram of the Boliden roasting process is shown in Fig. 2. The feed used by Boliden at Hälsingborg is flotation pyrites, and contains comparatively small amounts of zinc and copper. A typical analysis is as follows:

Iron	46%
Sulphur	51%
Zinc	0.20%
Copper	0.04%
Lead	0.05%
Arsenic	0.40%

Roasting

Whereas the BASF roasting system makes use of two fluidized bed roasters linked by a fairly intricate system of seals to prevent arsenic contamination from

FIG. 2. FLOW DIAGRAM OF BOLIDEN PROCESS



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the first roaster entering the second, the Boliden process uses a single unit. Of critical importance to the process is the atmosphere inside the roaster for the reasons explained earlier. The oxygen deficient atmosphere is obtained by using a reduced air flow into the base of the bed and it is of interest to compare the relative air inputs of the BASF and the Boliden process. For each tonne of pyrites input per hour, the Boliden process requires an air input of approximately 1,970 Nm^3/hr whereas the first stage of the BASF process needs 840 Nm^3/hr and the second stage 1,450 Nm^3/hr. These air inputs correspond to the following reactions:

Boliden $3FeS_2+(8-2n)O_2 \longrightarrow Fe_3O_4+(6-2n)SO_2+nS_2$

BASF

1st Stage $FeS_2+O_2 \longrightarrow FeS+SO_2$

2nd Stage $4FeS+7O_2 \longrightarrow 2Fe_2O_3+4SO_2$

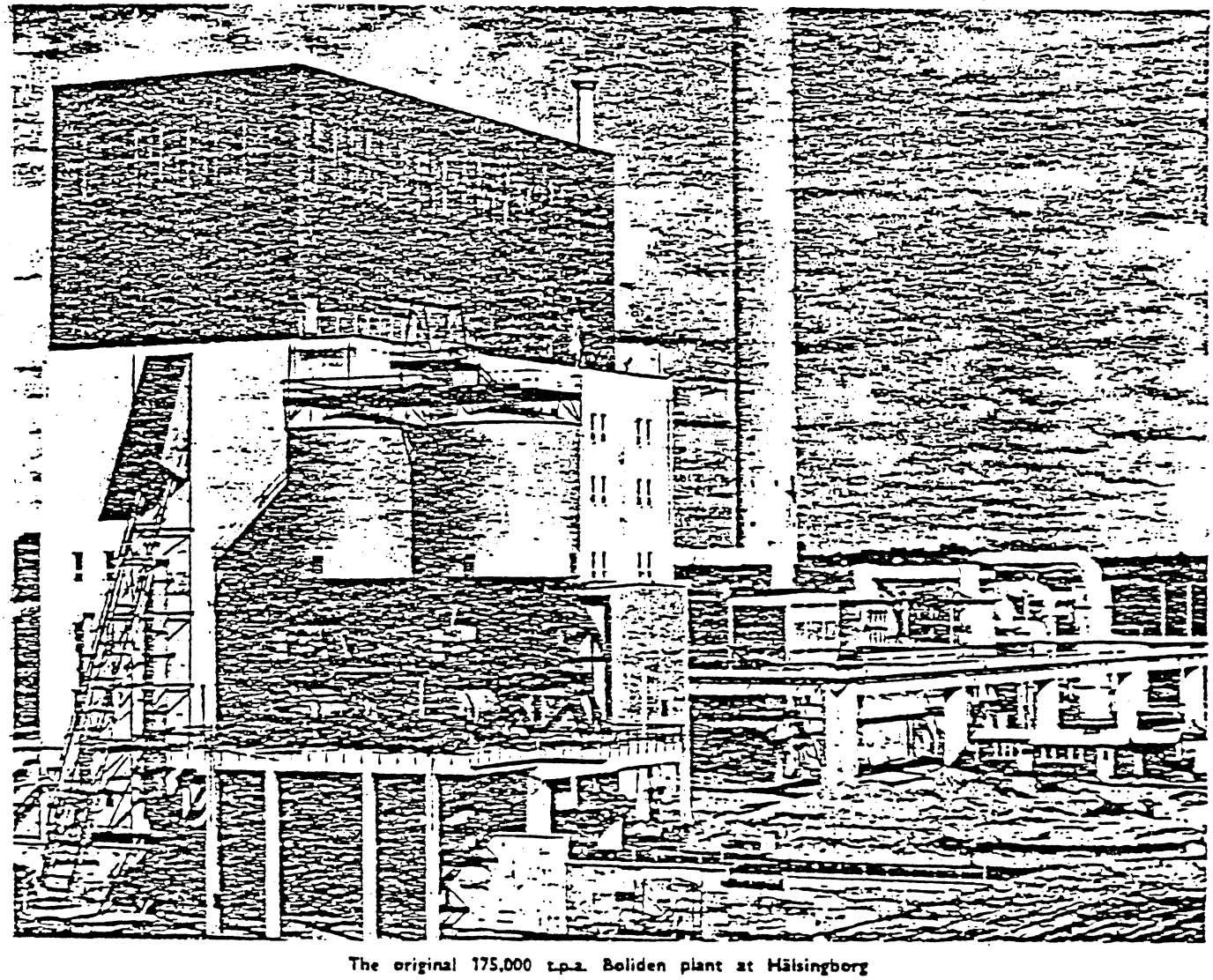
where n is the number of S_2 molecules which is dependant on the partial pressure of oxygen in the range of magnetite between curve *c* in Fig. 1 and curve *d*.

The difference between the Boliden input and the sum of the BASF inputs, i.e. 320 Nm^3/hr represents the oxygen deficiency needed to limit the oxidation of the iron to magnetite. These figures do, of course, relate to a pyrite of specific analysis, but serve to illustrate the difference between the two processes, and also between the conventional fluidized bed roasting process where the air input is of a similar order of magnitude as the sum of the inputs in the BASF two-stage process.

The Boliden process can be used for all types of feed since fluidized bed conditions are a function of the roaster and the roasting material. In the BASF-type roaster at Hälsingborg, the roaster temperature is of the order of 850°C, i.e. slightly lower than the first stage of the BASF process and slightly higher than the second. The hot cinders leaving the bed of the roaster are cooled in a small fluidized bed cooler where heat recovery also takes place in the form of steam generation.

Gas purification

The gases leave the roaster at about 900°C, and pass to a hot gas cyclone where over 90% of the dust load in the gas stream is removed. At the temperatures involved, this is almost entirely cinders, other impurities still being in the gas phase. The gases leave the cyclone at 900°C and enter a post-combustion chamber where air is added to complete the oxidation



The original 175,000 t.p.a. Boliden plant at Hälsingborg

—continued on page 37

overall sulphur removal. As would be expected, the lower the sulphur content in the final product, the greater the cost. In view of this, the choice of which process to use will be partially dictated by the product sulphur level requirements.

The processes can also be compared on the basis of a fixed product sulphur level with feedrate being a variable. Using this approach, all processes are adapted for the production of a specific product containing a fixed amount of sulphur. Figs. 5 and 6 show comparisons of the processes concerned on this basis. Fig. 5 gives a comparison between residuum and VGO hydrodesulphurization with the total atmospheric residuum feedrate being maintained at 50,000 b.p.s.d. However, the feed to the residuum HDS units is reduced from 50,000 to 18,900 b.p.s.d. with the same desulphurization level of 75%. The remaining 31,150 b.p.s.d. is by-passed around the hydrodesulphurization unit and blended with the 1.1% S product to give the same total product sulphur level of 3.1% as in the VGO process. In this way the total cost of residuum HDS is reduced from 70 to 30¢/barrel fuel oil. The VGO-HDS costs are the same as before, about 26¢/barrel fuel oil. Investment for the residuum desulphurization is cut by half from $14.8 million to roughly $7.4 million and the corresponding reduction in the investment based charges is about 17¢/barrel fuel oil. Other operating costs are reduced in direct proportion to the reduction in residuum plant feedrate, i.e. 18,900/50,000. Based on these estimates, it is evident that the VGO system may often be a first logical step in a desulphurization programme provided that the fuel sulphur content of 3.1% is within the limits required.

Fig. 6 shows a similar comparison between residuum and VGO/DAO desulphurization. In this case, product sulphur is kept at 2.4 wt. % corresponding to the nominal VGO/DAO level. Thus the residuum hydrodesulphurization unit capacity is reduced from 50,000 to 29,700 b.p.s.d. In this situation residuum desulphurization is slightly less expensive than VGO/DAO, i.e. 45¢/barrel compared to 50¢/barrel for VGO/DAO. The investment for residuum HDS is reduced from $14.8 million to $10.2 million compared to $12.1 million for the VGO/DAO process. Although the total cost of residuum HDS is slightly less than VGO/DAO, the VGO/DAO combination could be attractive in situations where the investment is to be staged over a period of years.

BOLIDEN PROCESS FOR ROASTING ARSENICAL PYRITES—continued from page 32

of the arsenic, sulphur and other impurities. The flow of secondary air amounts to about 7% of the primary air flow.

The sulphur dioxide concentration, initially of the order of 16% is diluted in the post combustion chamber by the additional air, and falls to 15%. The gas is then cooled in a waste heat boiler from about 850°C to about 350°C. Some of the impurities solidify at this temperature and are removed from the base of the exchanger, the remainder by a conventional system of gas purification prior to the entry of the gas into the contact plant. An additional post-combustion chamber is also used after the heat exchanger.

Apart from the nature of the atmosphere inside the roaster, a major difference between the Boliden process as used at Hälsingborg and a conventional fluidized bed roasting process is the position of the waste heat boiler. In a conventional process it is sited immediately down stream of the roaster, in the Boliden process it comes after the cyclone for cinders removal.

Cinders quality

The cinders produced are mainly in the form of magnetite (Fe_3O_4) and are reasonably pure since the feed used at Hälsingborg is flotation concentrate. The arsenic content is well below the limit stipulated by the steel industries in the United Kingdom and West Germany where most of the output is sold for use in blast furnaces. In this particular case, there is no requirement to extract copper, zinc, cobalt and other valuable metals often present in pyrites cinders. However, for other locations where pure concentrate is not available or the preferred feed, the valorization of the residues could present a problem. Although the lead and arsenic content would meet the requirements of DKH, it is questionable whether the nature of the iron, i.e. magnetite rather than haematite would. The process employed by DKH involves roasting the cinders together with sodium chloride to convert most of the metals present into the chloride form which can be readily extracted and separated. The processing sequence is geared to treat haematite, and the introduction of magnetite could pose problems, since amongst other things, the heat of reaction is said to be different. Undoubtedly, it is technically feasible to process magnetite, but not in the conventional type of plant used for haematite. When steel production is contemplated, this is obviously no problem, but with valuable residues, the economic utilization of the cinders may present difficulties.

Boliden has pointed out that in the magnetite form, the cinders are more suitable for the production of iron than conventional cinders, i.e. haematite. It is only in the case of chloridizing roasting in multiple hearth furnaces, as practised by DKH, that haematite cinders are preferable. Conversion of cinders from a Boliden process plant into haematite is, of course, possible by further oxidation in a turbulent layer cooling system after the roaster.

Although the emphasis here has been on arsenic separation, it should be noted that the process also gives a very good separation of lead, antimony and bismuth. Also, apart from producing high grade cinders, a further advantage to be gained with the Boliden process concerns the contact unit. No acid is formed in the acid tower which not only gives rise to higher sulphur conversions but also eliminates emission problems.

BASF Double Stage Process for Turbulent Layer Roasting of Arsenical Pyrites*

NEXT to elemental sulphur, pyrites is the most important raw material for sulphuric acid manufacture, particularly in Europe. Neither pyrites or iron pyrites is pure FeS_2, as both contain gangue as well as various additional metals such as copper, zinc, lead, cobalt, arsenic, and antimony and also trace amounts of gold and silver according to their origin. These are predominantly present as sulphides and are converted to oxides during roasting.

Effect of Arsenic and Other Impurities on Pyrites Roasting and Cinders Treatment

The residue and cinders formed by the roasting process, which is typified by the equation,

$$2FeS_2 + 11/2\ O_2 \longrightarrow Fe_2O_3 + 4\ SO_2 : \Delta H - 405\ \text{kcal} \quad (1)$$

are an economically worthwhile raw material for the production of iron because of their 40-60% iron content. In order to render these cinders suitable for smelting, they must initially be freed from their accompanying metals. These include: 0.1-4% copper, 0.5-15% zinc, 0.02-1.2% lead as well as 0.04-0.4% arsenic and 0.01-0.04% antimony and further small quantities of other elements. These elements are removed not only because of their value but also because they would otherwise have an unfavourable effect on the quality of the iron subsequently produced. This applies particularly to lead, arsenic and antimony. The presence of these metals increases the possibility of pig iron conversion during solidification, which in turn leads to the formation of cavities and cracks and thus to considerable wastage. This phenomenon arises from a carbide stabilizing effect which suppresses secondary graphite formation and causes a volume decrease during solidification.

The customary method for up-grading cinders is by chloridizing and sulphatizing roasting followed by leaching during which copper, zinc and other accompanying elements dissolve while lead, arsenic and antimony remain unchanged.

When employing the traditional multiple hearth roasting process this problem does not occur as the lead, antimony and arsenic are volatilized with the roast gases. Only with the development of turbulent layer roasting, which is economically far superior to the older process, has the problem arisen, since, these metals are retained in the cinders produced by this process. The following table gives an example of this:

	S	As	Pb	Sb
Pyrites	48.0%	0.35%	1.0%	0.04%
Cinders	2.0	0.4	1.0	0.04
Minima required for subsequent cinders treatment	2.5	0.04	0.6	0.02

* By Dr. Ing. Herbert Wolf and Dr. Wilhelm Gösele, Anorg. Abt., Badische Anilin- & Soda-Fabrik AG.

The use of the turbulent layer process has not to be limited, therefore, to the roasting of pyrites which do not contain these elements. However, in north-west Europe, non-arsenical pyrites are not available in sufficient quantities for commercial needs, whereas there is a large reserve of Iberian pyrites, containing both arsenic and lead, which would serve as a source of supply for many years to come.

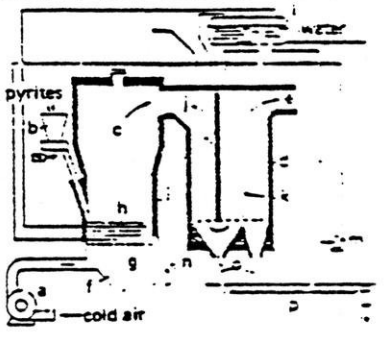
Volatilization of Impurities

Ever since the introduction of the turbulent layer roasting process, the question of the non-volatilization of certain of the accompanying elements has been raised frequently[1].

Employing the turbulent layer roaster shown in Fig. 1, the pyrites is deposited on an incandescent Fe_2O_3-containing bed by means of a delivery bunker and measuring device. The larger particles remain in the bed whilst the finer ones are carried along in the gas stream and are burnt in the empty space at the top of the furnace. The heat content of the roaster gases is used for steam generation in a waste-heat boiler. Characteristics of this process are that the pyrites is roasted relatively quickly to Fe_2O_3 at a temperature of approximately 800°C and that all the intermediate products of the roasting of FeS_2 to Fe_2O_3 are simultaneously present in the furnace.

On the other hand, when using a multiple hearth roaster (Fig. 2), the material is slowly moved from the individual hearths by means of rake-like arms. The first hearth serves as a drying stage. The material is roasted in the subsequent hearths and the degree of roasting is greatest in the upper hearths as one can see from Fig. 3 on account of the sulphur values present. On the second hearth, the maximum temperature in the

FIG. 1. DIAGRAM OF BASF TURBULENT LAYER ROASTER



(a) blower for roast air
(b) solid feeder
(c) cylindrical roasting chamber
(d) waste heat boiler
(e) roaster gas to electrostatic precipitator
(f) wind box
(g) grate
(h) turbulent layer
(i) ceramic lining
(j) steam superheater
(k) evaporator
(l) steam drum
(m) circulation pump
(n) (o) cinders outlet
(p) conveyor belt

FIG 2. MULTIPLE HEARTH ROASTER

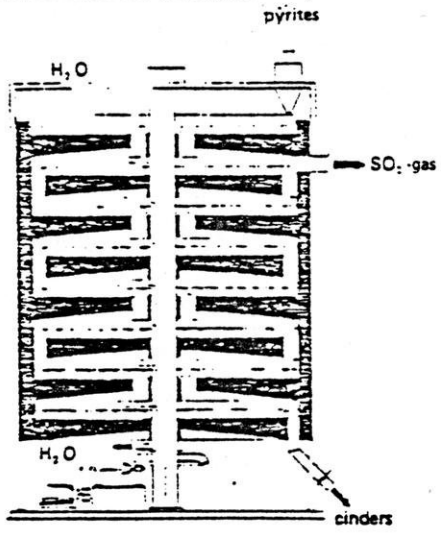
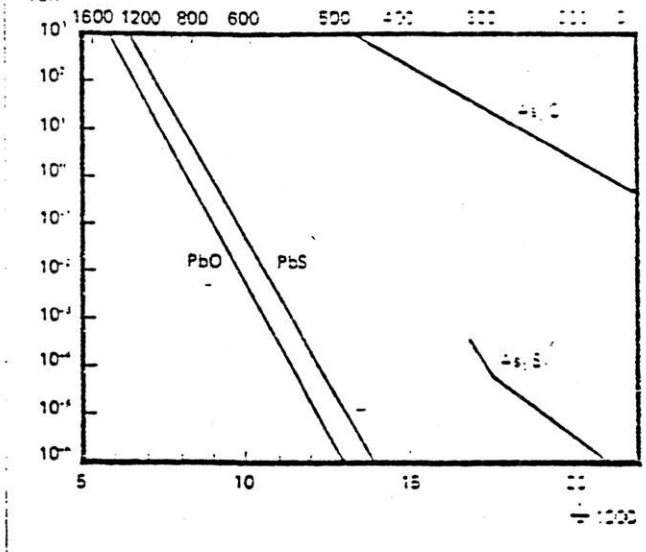


FIG 4. VAPOUR PRESSURE OF ARSENIC AND LEAD OXIDES OR SULPHIDES



kiln is reached, approximately 850°C, and this then decreases in the following hearths until the material from the last hearth exits at a dark red heat. In contrast to the turbulent layer process with a maximum retention time of approximately 45 minutes, the time in the multiple hearth kiln is 5-8 hours. Thus, over-roasting to Fe_2O_3 takes place on the lower hearths whilst at the beginning the polysulphide sulphur is decomposed and then the FeS is further roasted to Fe_3O_4 on the middle hearths.

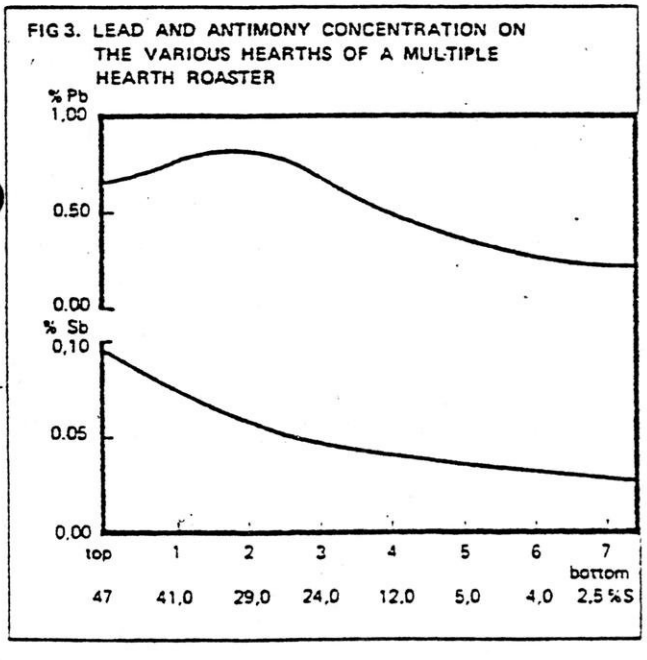
Volatilization in Multiple Hearth Roasters

An investigation of the composition of the material in the individual hearths of a multiple hearth roaster is of interest and Fig. 3 shows that the lead content increases relatively little on the first two hearths. This is due, on the one hand, to the fact that at the beginning of the roasting process only the labile polysulphide sulphur is burnt while, on the other hand, lead oxide or lead sulphate possess a relatively low vapour pressure (see Fig. 4).

These compounds are volatilized from the first hearth and become condensed as the roaster gases flow countercurrently to the cooler roasted material from the first or even second hearth; this phenomenon will be discussed later. The lead content as a function of the retention time is shown in Fig. 3.

With the turbulent layer process, therefore, the volatilization of lead ought to be less due to the lower temperatures and also because of the shorter retention time of the material in the furnace. These conditions also apply to antimony where a progressive decrease in concentration can be observed as the retention time increases.

FIG 3. LEAD AND ANTIMONY CONCENTRATION ON THE VARIOUS HEARTHS OF A MULTIPLE HEARTH ROASTER



Arsenic

Of particular interest is the arsenic curve shown in Fig. 5. As might be expected, due to the relatively high vapour pressure, the arsenic is already volatilized on the second hearth and the arsenic content varies only very slightly on the subsequent hearths. In contrast to this, no volatilization whatever takes place during turbulent layer roasting. In addition to the short retention time, the principal difference between the two systems is that the reaction product of the multiple hearth kiln still contains approximately 30 % sulphur on the second hearth where arsenic evolution is practically finished, i.e. it has a composition which more or less corresponds to FeS, whereas with the turbulent layer roasters, the bed mainly consists of Fe_2O_3. It can be assumed, therefore, that in the turbulent layer the As_2O_3 and oxygen (a roaster gas with 12 % SO_2 also contains approximately 5 % O_2) react according to the equation:

$$As_2O_3 + O_2 + Fe_2O_3 \longrightarrow 2\,FeAsO_4 \qquad (2)$$

to form a stable iron arsenate at the reaction temperature prevailing, and this hinders the volatilization of the arsenic. This supposition is further supported by the fact that arsenic from the cinders of a turbulent layer furnace can be removed by the reduction of the

material and the formation of Fe_3O_4 according to the equation:

$$6\,FeAsO_4 + 7H_2 \xrightarrow{H_2O} 2\,Fe_3O_4 + 3\,As_2O_3 + 7\,H_2O \quad (3)$$

The nature of the reducing agent is not important; what is important is that the Fe_2O_3 is converted to Fe_3O_4.

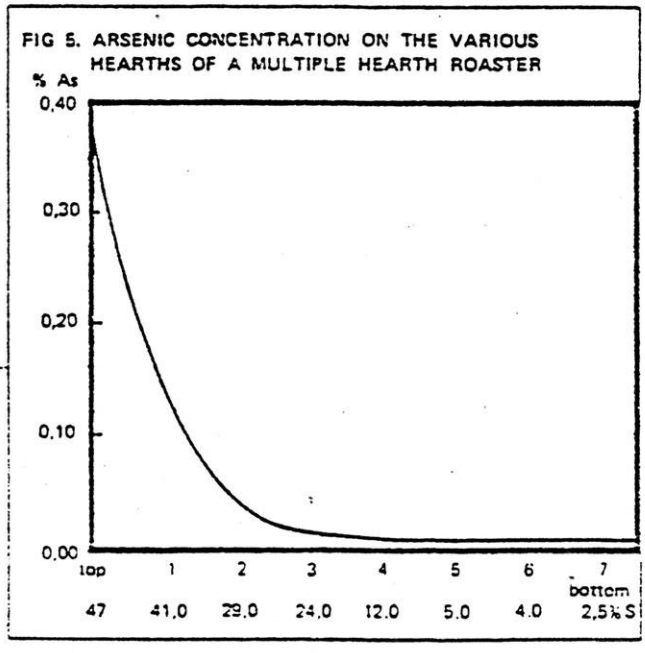
In order to support the suppositions experimentally, laboratory tests were undertaken[2]. The aim of these tests was to prove the formation of the iron arsenate with test substances under similar reaction conditions. Firstly, a sample product was produced by the precipitation of arsenic acid with iron ammonia alum in a buffer solution. The filtered and washed product was first carefully dried at 120 and 350°C and analysis showed an arsenic content of 37.4% (theoretically 38.4%). It was then heated for five hours at 850°C.

Depending on the reaction conditions in the turbulent layer roaster an air/arsenic mixture was directed, at a temperature of 800°C, into a small quartz rotary tube via finely-ground iron oxide to form a product with 42.4% arsenic. The Avdebye-Scherrer diagram of this material contained the lines of the precipitated and tempered iron arsenate; in addition, further lines appeared which are probably due to an acidic iron arsenate which is formed as a result of an arsenic surplus. Such a product is known in the form of a hydrate $2\,Fe_2O_3 \cdot 3\,As_2O_5 \cdot 22.5\,H_2O$[3].

If the same tests are carried out at a temperature of 950°C, a pure iron arsenate with 38.4% As is obtained whose laboratory analysis corresponds with the precipitated product. In this way, the formation of the iron arsenate by means of compact reaction under turbulent layer furnace conditions was proved. Obviously the acid arsenate is no longer stable at higher temperatures. Surprisingly enough, such an arsenate formation is not possible with Fe_3O_4 and if ferric oxide is replaced by Fe_3O_4 in the same experimental set-up and one uses oxygen-free nitrogen as the carrier gas, a reaction product with a maximum content of 0.1% As is obtained despite a considerable surplus of As_2O_3. Thus, the volatilization of the arsenic from the cinders with reduction to Fe_3O_4 is possible due to the fact that this oxide obviously forms no arsenic compound by a solid phase reaction.

It is clear, then, that volatilization of arsenic can take place in most of the upper hearths of a multiple hearth kiln, where no Fe_2O_3 is present.

FIG 5. ARSENIC CONCENTRATION ON THE VARIOUS HEARTHS OF A MULTIPLE HEARTH ROASTER



Roasting of Auriferous Pyrites

Roasting of auriferous arsenical pyrites in a turbulent layer process produces a cinder suitable for lixivation with cyanides to recover gold, provided that the roasting is carried out in a single turbulent layer and in such a way that the iron contained in the arsenical pyrites is only oxidized to ferrosoferric oxide (Fe_3O_4). A complete removal of the arsenic is not possible with this method and indeed it is not necessary for the purpose desired.

Also, auriferous arsenical pyrites can be roasted in two stages during the turbulent layer process so that the roaster gases in the second roasting stage can be used for the roasting of the arsenical pyrites in the first stage. In this connection, a cyclone has been built between the second and first stages on the gas side to remove the dust emitted from the second roast stage. The gas ducting required, however, has created some technical difficulties.

Furthermore, a cinder from auriferous arsenical pyrites suitable for cyanide leaching can be obtained by roasting in a turbulent layer roaster divided into two sections with separate introduction of oxygen-containing gases in each section as well as separate removal of the reaction gases[4]. In this way, roasting up to the magnetite stage can take place in the first section, while complete roasting to haematite can take place in the second section. The transfer of the preliminary roasted material from the first stage to the second should be effected through an opening in the separating wall between both sections. Because of the ever present pressure fluctuations in the turbulent layers with this method, it is not possible to avoid the arsenic-containing roaster gases in the second stage and the arsenic, by formation of arsenate, is bound to the haematite and thus remains in the cinder.

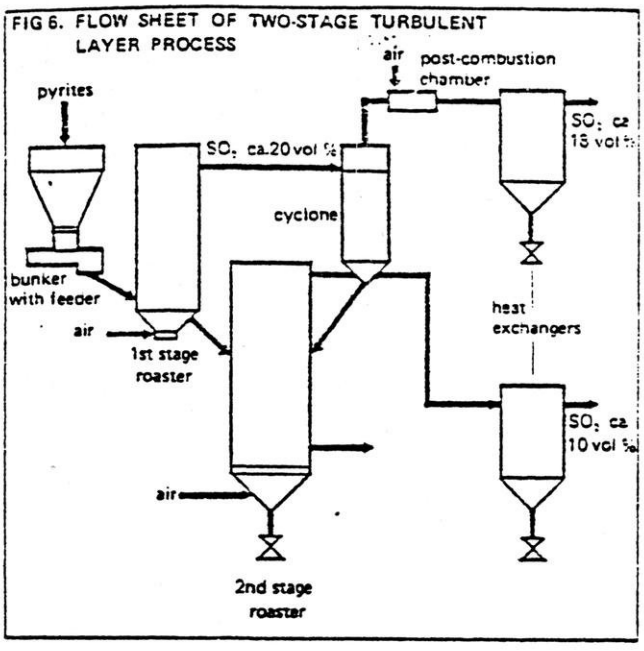
BASF Two Stage Process

In contrast to the method described above, a process has been developed by Badische Anilin- & Soda-Fabrik AG (BASF) in which particular attention has been paid to preventing contamination of the solid materials and roaster gases from the first stage with those of the second stage and vice-versa[5]. In order to remove as much arsenic as possible, it appeared particularly advisable to leave a certain amount of sulphur in the material in the first stage so that oxidation to Fe_2O_3 can be readily avoided even with fluctuations in the feed.

Especially suitable for this purpose is a material with the same sulphur content as that of material produced in the second hearth of a multiple hearth kiln, i.e. a roasted material with approximately 28-30% S. If, on the other hand, a pyrite with approximately 48% S is used, a material would have to be produced in the first turbulent layer whose sulphur content, by order of magnitude, would be FeS, so that only the labile polysulphide sulphur would be roasted as shown in the equation below:

$$FeS_2 + O_2 \longrightarrow FeS + SO_2 \quad \Delta H = 54.9\ kcal \quad (4)$$

FIG 6. FLOW SHEET OF TWO-STAGE TURBULENT LAYER PROCESS



Pyrites in the size range of 0 to 6 mm, for example, travels via the pyrites bunker and a suitable measuring device to the first stage roaster. It is roasted at a temperature of approximately 900°C according to equation (4), and arsenic, antimony and lead are volatilized, in their sulphide and also partly in their oxide forms with the roaster gases. The coarser parts of the iron sulphide form the turbulent bed, which is maintained at a height of about 1.000 mm, the bed height being determined by the sum of the dynamic resistance of the turbulent bed and the grate with slits approximately 1.22 mm in size.

While the bed material is introduced directly into the subsequent roasting stage, the finer particles of the roasted material—maximum 50%—are carried along by the roaster gases, which have a SO_2 concentration of approximately 20%, and are separated in the cyclone and led into the subsequent roasting stage.

From our observations it has been determined that As_2O_3 is bound by Fe_2O_3 according to equation (2). Due to the fact that the roaster gases of the first stage contain all the volatilized arsenic, a gas exchange between the first and second stage must be stopped otherwise the arsenic content of the Fe_2O_3 of the second stage will increase. On the other hand, the roaster gases of the second stage will contain free oxygen, which reacts immediately with the hot cyclone dust and could lead to fusion.

In the second furnace, the complete roasting to Fe_2O_3 takes place, according to the following equation:

$$4\,FeS + 7O_2 \longrightarrow 2\,Fe_2O_3 + 4\,SO_2;\ \Delta H - 590.4\ kcal \qquad (5)$$

at a temperature of approximately 800°C and a bed height of around 700 mm. A roaster gas with approximately 10% SO_2 is produced.

On the subject of roasting temperatures, it should be mentioned that according to tests carried out by Duisburger Kupferhütte, the roasting temperature of the first stage is insignificant for the subsequent copper and zinc removal whereas the temperature of the second stage should be as low as possible, otherwise ferrite formation will spoil the yield, particularly for zinc. For this reason, as well as others which will be mentioned later, 900°C has been chosen as the roast temperature of the first stage while 800°C is used for subsequent roasting due to the fact that the residual sulphur content of the cinder increases with lower temperatures.

After leaving the cyclone, the roaster gases from the first stage still contain small amounts of very fine dust as well as some sublimate sulphur which, it is believed, was formed through the thermal decomposition of pyrites dust in the gas chamber above the bed where oxygen is no longer present, according to the following equation:

$$FeS_2 \longrightarrow FeS + S;\ \Delta H + 16\ kcal \qquad (6)$$

As the sublimate sulphur can only be separated with some difficulty and since it can be drawn with the gases into the subsequent parts of the plant, it is burnt by injection of the air. At the beginning of BASF's experiments the post-combustion air, which amounts to approximately 30% of the primary roast air was heated with the hot roaster gases to approximately 250°C by means of heat exchange. However, it has since been ascertained that post-combustion is also possible with cold air. By the addition of air, both the sulphide content of the dust that is still in the roaster gas and the sublimate sulphur are burnt [6]. As these dusts contain some Fe_2O_3, the arsenic is again partly fixed; these quantities, which make up less than 10% of the total material and contain up to 5% arsenic, must subsequently be processed separately. However, it is possible to reduce the post-combustion air (approximately 15% of the primary roast air) in such a way that essentially only the sublimate sulphur is burnt; in this way, the material from the post-combustion chamber has a sulphur content of around 15-20%, and an arsenic content of only 0.1-0.2%.

Steam Generation

The heat content of the roaster gases from both stages, the temperature of which is more than 900°C, is utilized in a waste-heat boiler for the recovery of steam. Whereas no difficulties are to be expected with the waste-heat boiler of the second stage, with conditions corresponding to a single-stage turbulent layer plant, problems can occur with the cooling of the arsenic-containing roaster gases. Thus, for example, it is known from DAS 1, 117, 551 that during the cooling of the gases which originate from the roasting of arsenic-containing sulphur ores, deposits with 15-25% arsenic form on the cooling surfaces of the exchanger and these are difficult to remove and tend to scale. A possible remedy is to choose the steam pressure in such a way that the heat exchange surfaces are at a temperature in excess of 260°C, preferably 270-310°C. As the exchangers of the double-stage process are operated using the La Mont system of 40 atm pressure, the feed-water temperature is only 250°C. However, after an operational period of over 12 months, no problems have arisen so far during the operation of the exchanger. The reason for this would seem to

be that large quantities of Fe_3O_4, in addition to small amounts of Fe_2O_3 that are formed by post-combustion, do not combine with any arsenic under the prevailing reaction conditions. The highest arsenic contents found in the exchanger were, with a maximum of 6%, considerably lower than the values already mentioned.

The combination of both roaster gas streams takes place in a cooling and wash tower and the arsenic can be recovered in the conventional manner from acid recycle. It is possible to simplify the process described which operates using separate roaster gas outlets for first and second stage roasting if the outlet gases from the second stage are cleaned by a hot gas cyclone as shown in Fig. 7.

Using this method more than 90% of the fine particles of cinder that are carried in the gases from the second roaster are precipitated. At the same time, the roaster gases freed from the dust of the first and second stages, are combined and are introduced jointly into only one waste-heat boiler and one gas purification plant.

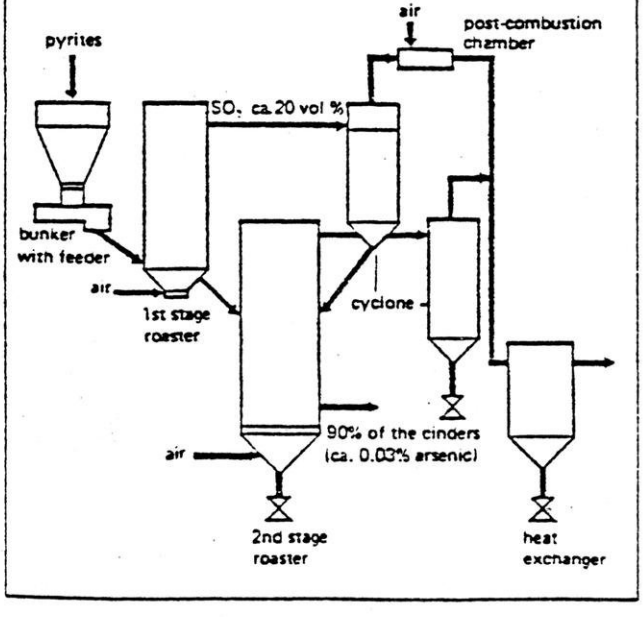
The yield of arsenic-containing material can be somewhat larger than that described in the previous process (Fig. 6), depending on the efficiency of the cyclone but with cyclones operating satisfactorily, this is not more than 10% of the total cinder amount.

Air Inputs

The air input of a single stage layer roaster normally amounts to 2.000 $m^3/m^2/h$, corresponding to a pyrites throughput capacity of 20 t.p.d. pyrites/m^2; on the other hand, with pre-roast (first stage) furnace the input amounts to 4.400 $m^3/m^2/h$.

Due to the fact that, according to equation (6), only one sulphur atom is oxidized, this corresponds to a pyrites throughput capacity of 125 t.p.d./m^2. If the two stages are taken as a whole, with a joint air input of 3.000 $m^3/m^2/h$, there is a pyrites throughput capacity of 30 t.p.d./m^2, which means that the reaction volume of the two stage plant only amounts to 67% of a single stage plant of the same capacity. The cooling surfaces of the turbulent bed of both stages do not correspond to the heat theoretically liberated according to equations (4) and (5), the ratio being approximately 1:5 and 1:2.7 respectively since during the first stage a considerable proportion of the reaction heat is used to heat the cold pyrites to reaction temperature.

FIG 7. TWO-STAGE TURBULENT LAYER PROCESS



Start-up

Because the plant installed by BASF at Ludwigshafen operates in collaboration with other turbulent layer roasters, ignition temperature is obtained by the introduction of hot, over-roasted cinders from a neighbouring furnace. Where this is not possible, the plant is started by heating a bed of inert material with an oil burner—the first stage is then started up with the necessary amount of pyrites for roasting to FeS being added from the moment operation starts. If a conversion from Fe_2O_3 to FeS is attempted by slowly increasing the pyrites feed rate, unacceptable temperature rises would occur due to higher reaction heats (equation (1)) which would lead to fusion. Approximately five minutes after the start-up of the first stage, the second roaster is started up in the same way. Both furnaces can be shut down simultaneously.

Plant Control

In order to facilitate the operation of the plant, an automatic control is envisaged that would not only control the transfer of the material from the first stage to the second stage — as already described—but would also keep the quantity of roast air constant because, for example, the discharge of the bed material would change the resistance of the bed and thus influence the air supply. This is particularly undesirable during the first roasting stage. Whereas with one-stage roasting, atmospheric oxygen is always in excess and a limited change in the pyrites air mixture—in favour of the amount of air—results in a small temperature decrease, in the first stage of the two-stage roasting process, a severe temperature increase would occur which would rapidly assume critical values. This means, therefore, that the additional atmospheric oxygen in the bed no longer finds FeS_2 with which it can react according to equation (4).

$$FeS_2 + O_2 \longrightarrow FeS + SO_2;\ \Delta H = -54.9\ kcal$$

but it contains a vast amount of FeS which can be converted according to equation 5

$$4\ FeS + 7\ O_2 \longrightarrow 2\ Fe_2O_3 + 4\ SO_2;\ \Delta H = -590.4\ kcal$$

Not only is the polysulphide sulphur burnt, but an iron oxidation takes place that can almost treble the reaction heat. Thus, very careful attention is required to ensure that the pyrites feed occurs as proportionately as possible because disturbances in this have the same effect. For this reason, the pyrites addition is based on the bed temperature of the first stage. Furthermore, it is possible to couple the first stage with the second so that the air feed to the pre-roast furnace is dependent on the temperature of the subsequent roasting; thus it is the second stage which determines the throughput of the plant.

If the temperature of subsequent second stage

roasting is too low, then the process is controlled by increasing the amount of air to the first stage which results in an increase in the temperature: on the other hand, this temperature increase causes an increase in the pyrites feed rate, so that the total throughput of the plant is somewhat increased: more material is then needed for the second stage roaster whose temperature will also rise.

Bed Temperature

At the beginning of BASF's investigations, the bed temperature of the first stage was kept relatively low; temperatures of 700°C were used initially and arsenic values of the order 0.05% were obtained while the lead content of the bed material remained virtually unchanged. Subsequently, the bed temperature was increased to 950°C and the arsenic values only changed insignificantly; they decreased to 0.02 to 0.03% in the bed material whereas with lead and antimony, a clear dependence on the temperature was established as can be seen in Figs. 8 and 9. Interestingly enough, there were certain clear differences during tests with lead at the higher temperatures in the bed and in the cyclones, and this went so far that at 900°C in the bed, only 0.2% Pb was found while in the cyclone tests the lead content rose to 2%. This state of affairs can only be accounted for by the fact that the lead was volatilized from the bed material, but in the cyclone which was only slightly isolated and where the temperature was only 700°C, it was condensed again. With suitable temperature control, satisfactory results were also obtained in these sections.

Cinders

The cinders from the second stage are removed from three outlets and classified by size. With Rio Tinto pyrites of 0 to 6 mm size, the bed product contains the coarser particles up to 6 mm which amount to approximately 30% of the total yield; the heat exchanger yield comprises material up to 300µ—this accounts for almost 50% and the electrostatic precipitator yields the very fine components under 100µ which amount to approximately 20%.

The products from the bed and the heat exchangers are identical with regard to the accompanying metals; they contain about 0.2-0.025% arsenic and 0.3 to 0.45% lead, whereas the very fine particles of the electrostatic precipitator contain 0.04 to 0.05% As and 0.7 to 0.8% Pb. In addition, approximately 5-10% of the total amount of very fine material is obtained from the post-combustion cyclone and the first-stage exchanger. This fraction, however, contains larger amounts of arsenic and lead and must be processed separately.

The average analysis of the cinder mixture showed excellent results with regard to arsenic, antimony and lead removal which are below the tolerances required for further processing (last line of the table).

	S	As	Pb	Sb
Pyrites	48.0%	0.3-0.35%	0.85%	0.03-0.04%
Cinder	3.0	0.03	0.55	0.02
Required value	2.5	0.04	0.6	0.02

Following chlorinated roasting and leaching, a purple ore is obtained from these cinders which is equal in the residual contents of Cu and Zn to multiple hearth furnace cinders.

The plant at Ludwigshafen has been operating since July 1967 without interruption and more than 60,000 tonnes pyrites have been roasted in the two-stage furnaces.

References

(1) Chem. Ing. Tech. 1952, 24, 104.
Chem. Ing. Tech. 1957, 9, 563.
(2) Unpublished Work of Dr. Helmut Zahn.
(3) H. Metzke, Z. Anorg. Ch., 1899, 19, 457.
(4) British Patent No. 677,050.
(5) West German Patents Nos. 1,024,493 & 1,034,830
(6) West German Patent No. 1,043,295.

FIG 8. DECREASE IN THE LEAD CONTENT OF THE BED MATERIAL OF THE FIRST STAGE AS A FUNCTION OF TEMPERATURE

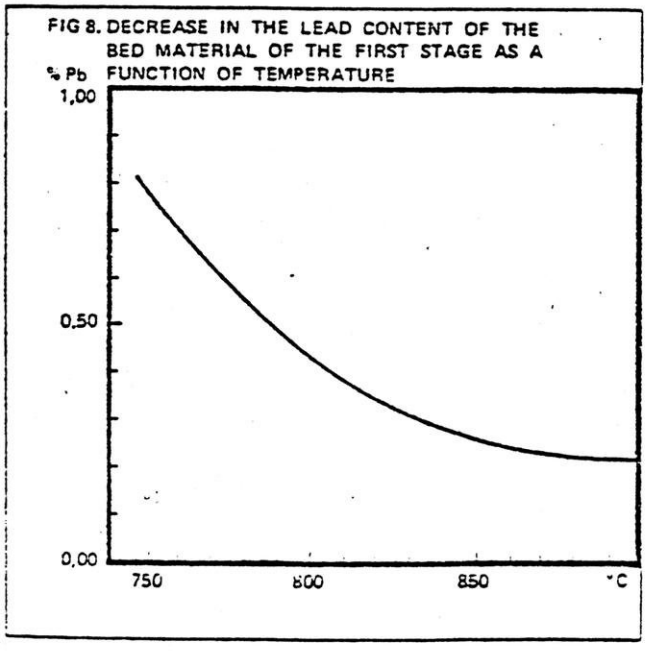
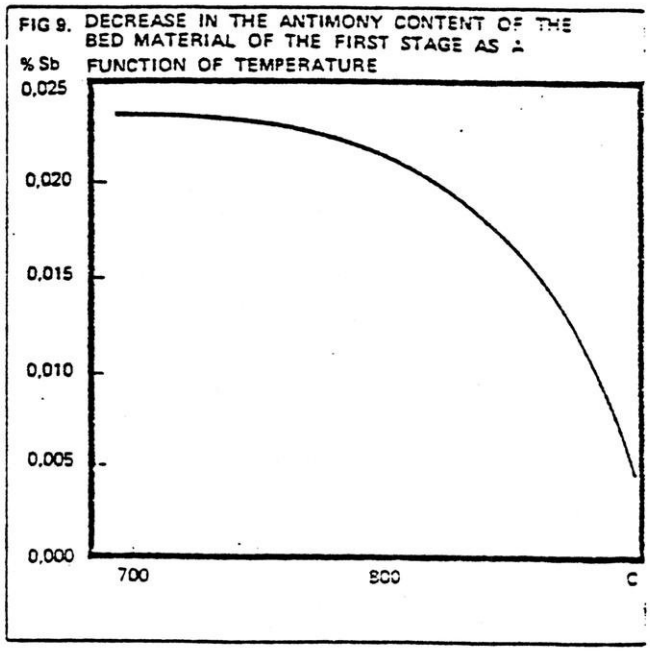


FIG 9. DECREASE IN THE ANTIMONY CONTENT OF THE BED MATERIAL OF THE FIRST STAGE AS A FUNCTION OF TEMPERATURE



AN EVALUATION OF THE LEACHING CHARACTERISTICS OF A PYRITE CALCINE RESIDUE ~~SAMPLE~~ FOR

~~HELLE~~NIC CHEMICAL AND FERTILIZERS CO. LTD.

ATHENS GREECE

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S.F.

C O N T E N T S

		Page No.
	SUMMARY	
1.	INTRODUCTION	1
2.	SAMPLE ANALYSIS	2
3.	MINERALOGY	4
	3.1 Head Sample	4
	3.2.1. Leach sample (1)	4
	3.2.2. Leach sample (2)	5
	3.3 General	5
4.	LEACHING TESTS	6
	4.1 Grinding	6
	4.2 Leaching Tests	8
5.	DISCUSSION OF RESULTS	10
	5.1 Grinding	10
	5.2 Leaching Tests	10
6.	CONCLUSIONS	13

SUMMARY

A sample of pyrite calcine residue has been examined to assess the feasibility of recovering the copper content of the residue via a leach - solvent extraction - electrowinning process.

The testwork has shown that leaching conditions required to achieve acceptable copper recoveries from the pyrite calcine residue result in leach liquors which are not directly compatible with solvent extraction processes.

Changes in the operation of the roaster could lead to a leach liquor compatible with solvent extraction processes and improved copper recovery.

1 INTRODUCTION

A 10 kg sample of a pyrite calcine residue was received from Hellenic Chemicals and Fertilizers Co. Ltd., Athens for the evaluation of leaching and leach residue settling characteristics. The testwork was orientated towards the derivation of plant design parameters for the recovery of copper from the residue via a leach - solvent extraction - electrowinning process.

The terms of reference for the project were latterly modified after examination of the preliminary mineralogical and leach test data. The majority of the subsequent testwork was carried out to determine the optimum copper extraction under various leaching conditions, with a view to evaluating a suitable process route.

2 SAMPLE ANALYSIS

The chemical analysis carried out on the "as received" sample is shown in Table 1 and the semi-quantitative spectrographic analysis in Table 2.

Table 1 - Chemical Analysis

(Loss on drying at 105°C = 6% w/w)

	Assay % (Dry Basis)
Tot. Cu	4.2
Acid-soluble Cu	1.8
Tot. Fe	45.8
Fe^{+++}	39.0
CaO	1.8
MgO	1.2
SiO_2	12.7
Al_2O_3	2.5
Tot. S	2.75
Sulphide S	2.60
Au	0.15 ppm
Ag	15 ppm

Table 2 - Semi-Quantitative Spectrographic Analysis

Si	M	M = > 5%	= major
Fe	M	m = 0.5-5%	= minor
Ca	m	t = 0.05-0.5%	= trace
Al	m	s = 0.005-0.05%	= slight
Mg	m	v = < 0.005%	= very slight
Cu	m		
Zn	t (m)		
Co	t		
Na	t		
Mn	t		
V	s		
Mo	s		
Ti	s		
Cr	s		
Sn	s		
Ni	v (s)		
Ga	v		
Pb	v		
Ag	v		

In addition to the analysis reported above the -10 mesh BS material was dry-screened, and an assay screen analysis for total and acid soluble copper was carried out. The results are shown in Table 3.

Table 3 - Assay Screen Analysis

Mesh BS		Wt%	Assay % T.Cu	Assay % AS.Cu	R	Distribution % T.Cu	Distribution % AS.Cu
-	+16	40.89	5.30	1.70	32.1	53.5	45.6
-16	+30	18.76	4.40	1.82	41.3	20.4	22.4
-30	+60	8.50	3.35	1.44	42.8	7.0	8.0
-60	+85	3.81	3.00	1.38	46.5	2.8	3.5
-85	+120	2.54	2.89	1.27	43.8	1.8	2.1
-120	+170	2.63	2.74	1.17	43.1	1.8	2.0
-170	+240	2.10	2.57	1.06	40.7	1.3	1.4
-240	+350	1.62	2.16	0.92	42.9	0.9	1.0
-350	-	19.15	2.22	1.11	50.1	10.5	14.0
Calc. Head		100.0	4.05	1.52	37.5	100.0	100.0
Assay Head		-	4.20	1.80	-	-	-

AS = Acid-soluble

R = % of total copper reporting as acid-soluble

3 MINERALOGY

3.1 Head Sample

The dried 30 mesh BS head sample was made into a polished mount and examined in incident light. It was immediately apparent that the bulk of the sample was an ultra-fine grained residue of iron-oxides, probably a mixture of hematite, geothite, and lepidocrocite. Remnant sulphide minerals made up some 5-10% of the material, and comprised chalcopyrite, delafossite, and some pyrite. A point-count of this material gave the following derived composition on a weight-percent basis :

Iron oxides		92.4%
Chalcopyrite		4.9%
Delafossite		1.9%
Pyrite		<1%
Copper oxides	(CuO	<1%
	(Cu_2O	<0.1%

It is considered that the delafossite is an oxidation product of the chalcopyrite, although no textural evidence could be seen to support this. Chemical considerations however, make it appear likely that such a transformation would occur i.e.

$$\underset{\text{chalcopyrite}}{CuFeS_2} + 2O_2 \rightarrow \underset{\text{delafossite}}{CuFeO_2} + SO_2$$

This presumably then breaks down to its constituent oxides i.e.

$$CuFeO_2 \rightarrow CuO + FeO$$

3.2.1 Leach Sample (1)

Leach conditions were :

400 gpl H_2SO_4 : 5 hours @ 65°C

20% Cu remaining in leach residue

This sample was extremely fine-grained, which made a quantitative analysis impossible. However, it was obvious that not all of the chalcopyrite and delafossite had been leached, although grains of the latter were very rare. Approximate contents of these two minerals were :

Chalcopyrite	~1%	w/w
Delafossite	~0.1%	w/w

3.2.2 Leach Sample (2)

Leach conditions were :

200 gpl H_2SO_4 : 5 hours @ 65%
SO_2 gas addition throughout
40% Cu remaining in leach residue

As before, quantitative analysis was impossible, due to the fine grained nature of the leach residue. The content of chalcopyrite was higher than leach sample (1), although the delafossite level was approximately the same. The contents of these minerals were :

Chalcopyrite	~2%	w/w
Delafossite	~0.1%	w/w

3.3 General

It is obvious that failure to attack all of the chalcopyrite is the main cause of low copper recoveries - the delafossite appears to respond readily to acid attack. This is not a function of liberation, since all grains of these minerals in the residues were fully liberated. The copper oxides were absent from the residues, and were thus presumably completely dissolved.

4 LEACHING TESTS

With the exception of the preliminary tests a standard procedure was adopted for the evaluation of the copper extraction under various leaching conditions.

4.1 Grinding

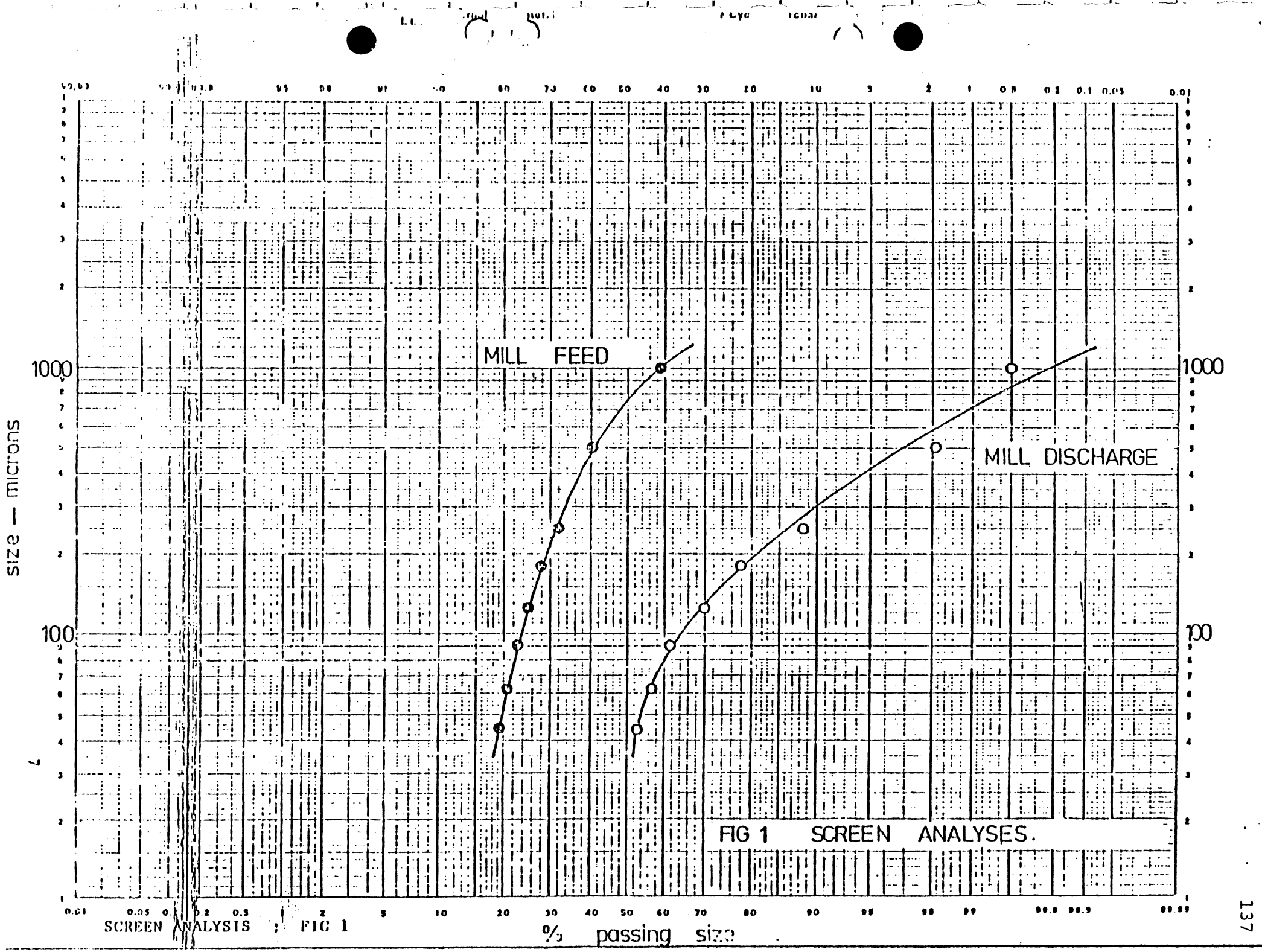
The sample 'as received' was dried at 110°C for 24 hours to remove the residual moisture (the original sample contained 6% H_2O), crushed to pass 10 mesh BS and split into 1 kg samples. Each 1 kg sample was dry ground in a laboratory ball mill (6" dia x 12" long) for 20 minutes, the mill product being sub-sampled by riffling to give 200 gm samples for the leach tests.

Screen analysis of sub-samples of mill feed and mill discharge were carried out and the results are shown in Table 4 below and graphically in Figure 1.

Table 4 - Screen Analysis Results

	MILL FEED		MILL DISCHARGE	
Mesh BS	Wt%	Cum Wt% Passing	Wt%	Cum Wt% Passing
16	40.9	59.1	0.5	99.5
30	18.8	40.3	1.4	98.1
60	8.5	31.8	9.5	88.6
85	3.8	28.0	10.5	78.1
120	2.5	25.5	8.1	70.0
170	2.6	22.9	8.5	61.5
240	2.1	20.8	4.6	56.9
350	1.6	19.2	3.2	53.7
-350	19.2	-	53.7	-
TOTAL	100.0		100.0	

Cum = cumulative



SCREEN ANALYSIS : FIG 1

The graph showing the cumulative percent passing versus particle size indicates that the work index of the pyrite calcine residue will be relatively low, as the 80% passing size had been reduced from 1450 μm to 200 μm by milling for 20 minutes. The corresponding reduction in the 50% passing size was from 730 μm to 15 μm (by extrapolation).

The 20 minute dry grinding cycle prior to leaching was retained for subsequent testwork for the sake of continuity and correlation of results.

4.2 Leaching Tests

The main leaching tests were all carried out at 50% solids in a thermostatically controlled bath; laboratory variable speed stirrers were used to provide the required agitation. After leaching, the slurries were filtered and the filter cake washed with an excess of slightly acidified water (pH5). The resultant filtrate was made up to a standard volume (3 litres) with water and analysed for total copper content. The leach residue solids were dried, weighed and analysed for total copper.

The first series of leaching tests was designed to show the effects of varying sulphuric acid concentration, ferric sulphate concentration, retention time and temperature. When other factors were varying, the standard conditions were :

200 g/l H_2SO_4, 25 g/l $Fe_2(SO_4)_3$, 50°C, 5 hours retention time

A second series of tests was carried out, based on the results from the first series, to evaluate the optimum sulphuric acid concentration at a higher temperature.

In addition, two single tests were carried out to assess the effects of gaseous sulphur dioxide and a sulphur solvent (carbon disulphide was used, being readily available) on the extraction of copper.

The results of the leaching tests, together with the conditions, are shown in Table 5 and graphically in Figures 2 to 5.

Table 5 - Leaching Balance for Test No 2

Legend	Lixiviant	Leach Residue	Leach Solution	Calculated Head
Weight (gm)	-	156.3	-	200
Volume (ml)	200	-	200	-
Assay: %T Cu	-	0.29	-	4.18
g/l T Cu	-	-	39.5*	-
$\%Fe^{++}$	-	1.01	-	7.65
g/l Fe^{++}	3.6	-	72.3*	-
$\%Fe^{+++}$	-	47.64	-	39.14
g/l Fe^{+++}	36.7	-	55.7*	-
g/l H_2SO_4	395.8	-	355.5*	-
Distribution % :				
T Cu	NA	5.4	94.6	100.00
Fe^{++}	NA	10.3	89.7	100.00
Fe^{+++}	NA	95.1	4.9	100.00
Acid Consumption :				
Total (lb/ton)				403.
By Copper (lb/ton)				122
By Gangue (lb/ton)				281

* Leach solution assays calculated from actual filtrate assays and the dilution factor

5 DISCUSSION OF RESULTS

5.1 Grinding

The original terms of reference and proposed flowsheet for evaluation did not include any grinding testwork, as it was assumed that the pyrite calcine arising would be quench leached. The grinding testwork carried out as an integral part of the project was only designed to provide a sample of material for leaching in which the minerals were completely liberated. Thus, by grinding the material for 20 minutes in the laboratory ball mill a product of 80% passing 200 μm was achieved. The milling time of 20 minutes was retained throughout the test series as it was considered that the leach test results would then not be unduly affected by particle size and liberation variations.

However, it should be pointed out that the particle size of the material leached will influence the settling characteristics of the leach residue. Therefore, whilst in general terms, the finer the grind, the more efficient the leach, the final selection of the optimum grind is inevitably a compromise between the leaching and settling characteristics. The 20 minutes grind used for the testwork was not optimised with respect to the settling characteristics of the leach residue and was considered excessive in terms of -10 μm material produced (over 50%). In general it is difficult to settle material of less than 10 μm and usually involves high thickener area requirements and increased flocculant consumption.

5.2 Leaching Tests

The adverse mineralogy of the sample received, together with the preliminary leach test result, showed that leaching conditions compatible with subsequent solvent extraction could not be expected to achieve acceptable copper recoveries. A modified approach was [illegible] based on the consideration that [illegible] in the copper leach efficiency could be achieved using aggressive leaching conditions, the resulting leach liquor could be treated by neutralisation to conform with the requirements of the solvent extraction process.

The preferred alternative to incorporating the additional neutralisation stage in the process flowsheet was to adjust the pyrite roasting conditions so that the oxidation of the copper minerals was carried through to completion. Hence the leaching conditions required could be adjusted to produce solutions directly compatible with solvent extraction without the requirement of a neutralisation step.

As ferric sulphate was known to be effective in leaching most copper sulphide minerals, with the exception of chalcopyrite which only reacts very slowly, the effects of various levels of ferric sulphate in the lixiviant were investigated. Initially it was considered that by maintaining oxidising conditions in the second stage leach using air and/or live steam, sufficient ferric sulphate for leaching would be generated in situ. However, as it was recognised that it would be difficult to assess the amount of ferric sulphate available an excess was added to the lixiviant to ensure that sufficient was present. The results showed that at low temperatures the additional ferric sulphate in the lixiviant had no effect on the copper leaching efficiency. Hence, in the latter series of tests at 65°C no additional ferric sulphate was included in the lixiviant.

Furthermore, ferric sulphate decomposes to ferrous sulphate in solution with increasing temperature and the decomposition is virtually complete at about 50°C. However, consideration of the leaching balance for test 2 in Table 5 shows that a significant amount of ferric iron reported into the final leach solution despite a 5 hour leach at 95°C. This particular test was essentially a preliminary test, but gave the best results. It was uncertain whether the excess of ferric sulphate had any direct bearing on the results achieved, as extrapolation of the temperature and sulphuric acid concentration into this range from the other tests would have approached this level of leaching.

Although true optimum leaching conditions were not self evident from the results of the testwork, practical considerations limit the desirability of increasing temperature, retention time and

acid concentration beyond the range investigated. The possible gains in leaching efficiency that could be achieved would tend to be offset by significant increases in costs.

Comparison of the results of the test 24, utilising a sulphurous acid/sulphuric acid leach, with test no. 5 (the nearest equivalent test) shows that the sulphurous acid present made no difference to the leaching efficiency.

The result of test 25, which utilised a sulphur solvent (carbon disulphide) was also compared with test no. 5 and an improvement of 6% in the leaching efficiency was noted. It was considered that this approach would be impractical and costly for a relatively low increase in copper recovery.

6 CONCLUSIONS

The mineralogy of the sample and the results of the leaching tests show that very aggressive leaching conditions are required to achieve acceptable copper leaching efficiencies. The leaching conditions required did not result in a leach liquor directly compatible with the proposed solvent extraction process; a neutralisation stage would be required in the flowsheet to reduce the terminal acid concentration to acceptable levels prior to solvent extraction.

Minor changes in the operation of the roaster could lead to a calcine that would, on leaching, produce a leach liquor compatible with solvent extraction processes and improved copper recoveries.

TABLE 6 : LEACH TEST RESULTS

Test	Conditions: Retention Time Hrs	Temp oC	Lixiviant g/l H_2SO_4	Lixiviant g/l $Fe_2(SO_4)$	Leach Residue Solids: Weight %	Assay % T Cu	Dist % T Cu	Leach** Solution Assay g/l Cu	T Cu Leach Efficiency %	Calcula Head Assay %T Cu
1*	3	35	150	NIL	94.5	2.6	64.4	12.6	35.6	3.82
2*	5	95	396	150	78.2	0.29	5.4	39.5	94.6	4.18
3	5	50	100	25	91.5	2.15	48.3	21.1	51.7	4.08
4	5	50	150	25	92.6	1.95	41.4	25.6	58.6	4.3
5	5	50	200	25	85.5	1.66	33.5	28.1	66.5	4.2
6	5	50	250	25	84.9	1.54	31.9	29.3	69.1	4.2
7	5	50	300	25	84.3	1.50	29.7	30.0	70.3	4.2
8	5	50	200	10	86.7	1.78	37.1	26.3	62.9	4.1
9	5	50	200	30	86.7	1.62	34.9	26.3	65.1	4.0
10	5	50	200	40	86.5	1.73	36.3	26.3	63.7	4.1
11	5	50	200	50	86.9	1.69	35.9	26.3	64.1	4.0
12	3	50	200	25	88.1	2.15	44.4	23.7	55.6	4.2
13	4	50	200	25	86.7	1.80	39.2	24.5	60.8	4.0
14	4	50	200	25	87.0	1.45	32.4	26.3	67.6	3.8
15	5	50	200	25	85.8	1.44	30.6	28.0	69.4	4.0
16	5	40	200	25	89.1	1.85	41.3	23.4	58.7	3.9
17	5	60	200	25	85.8	1.22	26.4	29.1	73.6	3.9
18	5	70	200	25	85.5	1.11	24.0	30.0	76.0	3.9
19	5	80	200	25	86.0	1.08	25.1	30.9	74.9	4.0

Test	Conditions: Retention Time Hrs	Temp oC	Lixiviant: g/l H_2SO_4	Lixiviant: g/l $Fe_2(SO_4)$	Leach Residue Solids: Weight %	Assay % T Cu	Dist % T Cu	Leach ** Solution Assay g/l Cu	T Cu Leach Efficiency %	Calculated Head Assay %T Cu
20	5	65	250	NIL	84.4	1.17	23.0	33.0	77.0	4.29
21	5	65	300	NIL	79.2	1.12	20.8	33.7	79.2	4.26
22	5	65	350	NIL	80.4	1.09	20.6	33.7	79.4	4.25
23	5	65	400	NIL	75.3	1.09	19.5	33.7	80.5	4.19
24	5	65	200 (SO_2 gas)	25	82.9	2.00	39.2	25.7	60.8	4.22
25	5	65	200 (10ml CS_2 added at 1ml/½hr)	25	85.9	1.34	27.3	30.6	72.7	4.21

** The leach solution assay was calculated from the actual assay of the filtrate and the dilution factor on filtration

* Preliminary test.

TABLE 6 - LEACH TEST RESULTS

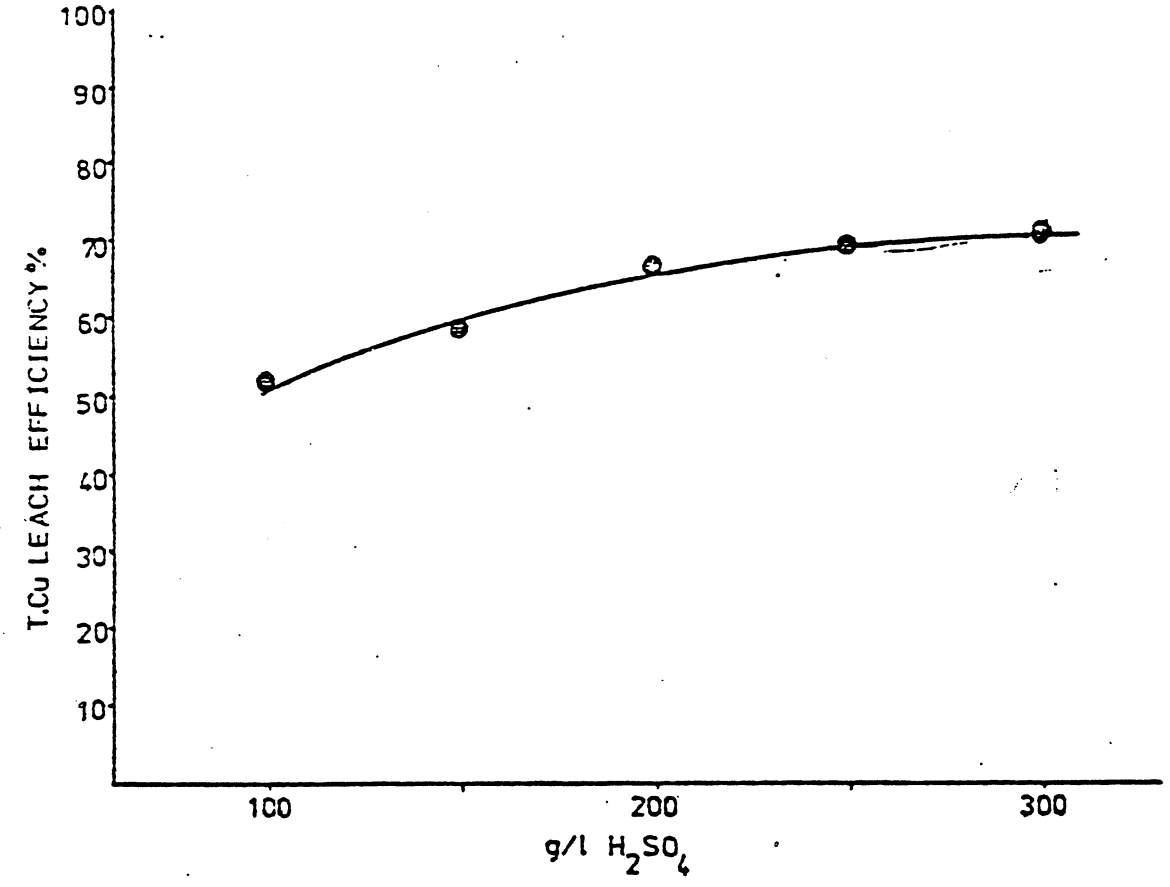


FIGURE 2

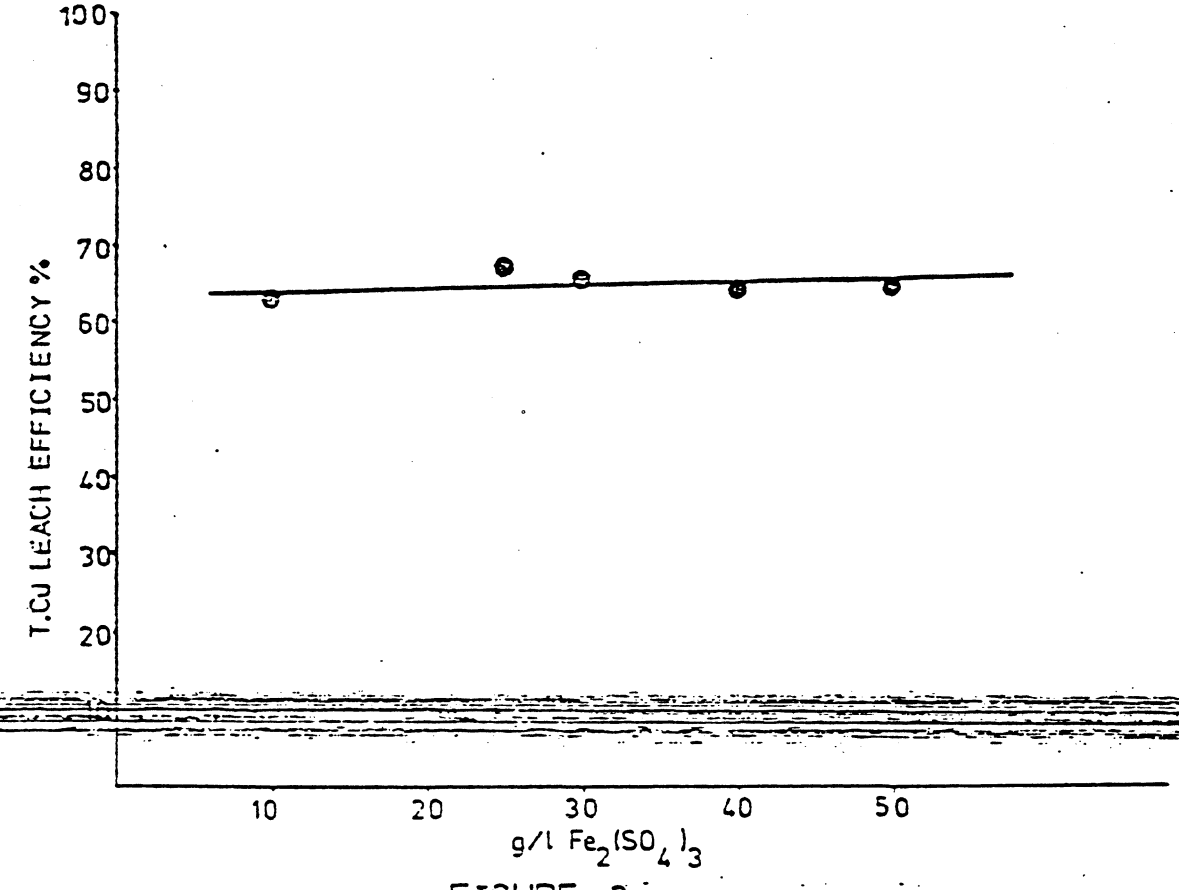


FIGURE 3

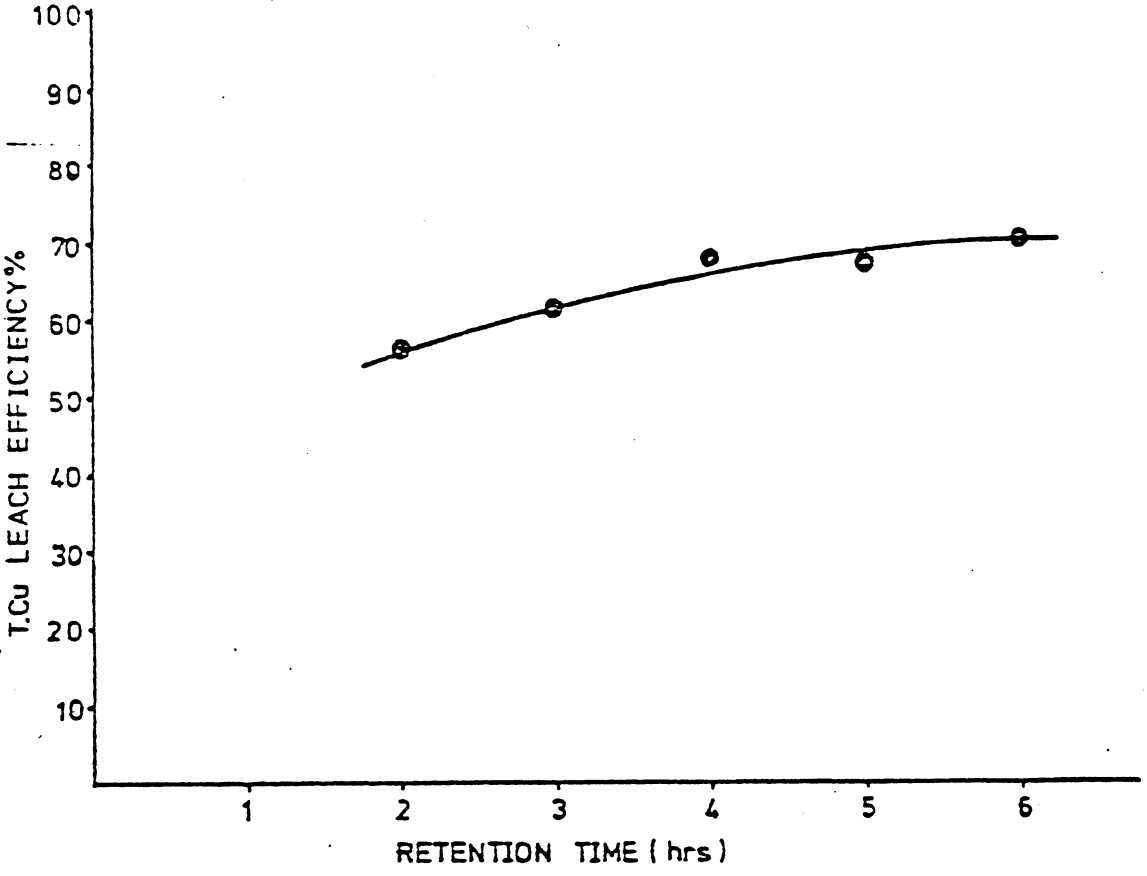


FIGURE 4

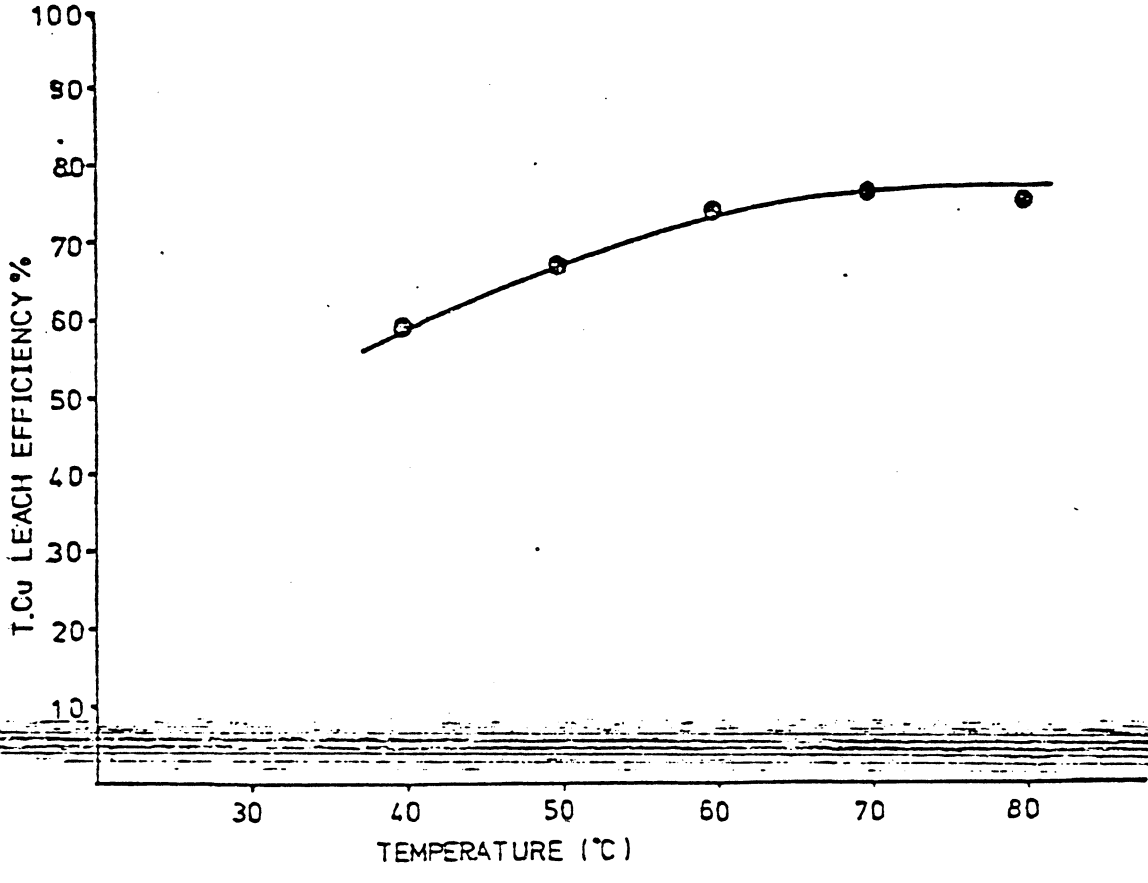


FIGURE 5

HELLENIC CHEMICAL PRODUCTS
& FERTILIZER CO. LTD.

1700 TPA COPPER RECOVERY PLANT

TECHNICAL INTRODUCTION SECTION 2

2.1 INTRODUCTION

The following Sections comprise the Technical Proposal prepared by PGL and include the Process Description, the Basis of the Plant Design, and the Expected Performance together with an equipment list with an outline specification of each item, a flow sheet and suggested arrangement of the plant.

The plant design parameters have been developed from laboratory work on raw material supplied by Hellenic Chemical Products and Fertilizer Co. Ltd. (Hellenic). The following discusses the steps in the flowsheet, PGL Drawing No. 9010/2793/2000/A1.

2.2 LEACHING

The leaching of the cinder is carried out using an agitated sulphuric acid leach. Aggressive leaching conditions are used to achieve about 90% recovery of the copper from the cinder, viz: 95°C and 400 gpl sulphuric acid. Materials of construction have been selected for these conditions and indirect steam heating is used to maintain the leaching temperature whilst maintaining the water balance of the process. Furthermore it is necessary to reduce the particle size of the incoming cinder to 40% w/w passing 350 mesh (53 micron) to obtain efficient leaching and a closed circuit ball mill has been included for this purpose.

2.3 NEUTRALISATION AND SOLIDS REMOVAL

Neutralisation of the excess acid from leaching prior to solvent extraction will be carried out using ground marble. PGL have used ground limestone for our test work and we would expect to achieve similar results with ground marble. However, to be certain on this point PGL would ultimately require to test a sample of ground marble.

The neutralisation and solids removal process are conventional using thickening and pressure leaf filtration. A flocculating agent is required to ensure good settling in the thickeners and test work has established the best reagents for this case and the quantities required.

2.4 SOLVENT EXTRACTION AND ELECTROWINNING

The use of solvent extraction techniques for the recovery of metals stems from the development of technology for the atomic energy projects of the USAEC and the UKAEA during the decade 1945-55.

Since then, the techniques have been applied to the separation and recovery of many of the rarer metals.

Recently, intensive research has been directed towards developing solvents for the recovery of the commoner metals. General Mills Inc. and Ashland Chemicals Inc. of the USA have now produced solvents which are specific for the extraction of copper from solutions with pH as low as 0.5.

PGL have considerable experience in the solvent extraction process and PGL mixer/settler units are proposed. The raffinate from solvent extraction is recycled to neutralisation so that its copper content is largely recovered and the solvent extraction plant has the minimum number of stages for a given overall copper recovery.

In the electrowinning design we have assumed that starting sheets will be purchased rather than making starting sheets on a plant of this capacity. This will make the plant design and operation simpler. However, if starting sheets cannot be obtained then the plant could be designed to allow for starting sheet production. Additional tanks and equipment would be required however.

2.5 FINAL NEUTRALISATION AND WASTE REMOVAL

The test work on this section of the plant showed that it was difficult to produce a ferric hydroxide/waste precipitate that was amenable to filtration. However, on further investigation it was found that it was possible to neutralise with a moderate excess of limestone and produce a waste that solidified during neutralisation. PGL therefore propose to perform this step in a pug mill which will discharge a solid. This solid material can then be handled by front-end loader into trucks for removal or taken directly to the spoil heap.

HELLENIC CHEMICAL PRODUCTS
& FERTILIZER CO. LTD.

1700 TPA COPPER RECOVERY PLANT

PROCESS DESCRIPTION SECTION 3

(See Flow Diagram 9010/2793/3000/A1).

The process includes Grinding, Leaching Liquid Neutralisation and Dilution, Liquid/Solid Separation and Washing, Solvent Extraction and Electrowinning.

3.1 GRINDING

Quenched calcine is taken from the Calcine Storage Bin and fed at a controlled rate to a Ball Mill to reduce the particle size.

3.2 LEACHING

The fine calcine falls directly into the first of five cascade Leach Vessels, and is leached for a period of five hours as the calcine passes through the Leach Vessels. Tank house bleed liquor and 97% sulphuric acid are added to give an acidity of 400 grams per litre and a slurry density of 56% solids. The leaching temperature is maintained at 95°C by indirect steam heating and the Leach Vessels are equipped with Agitators.

3.3 NEUTRALISATION AND DILUTION

The slurry is discharged from the leaching system to an Agitated Tank, and ground marble is added to reduce the acidity to 1.0 g/l H_2SO_4. The copper content is also adjusted to 6.45 g/l Cu by the controlled addition of solvent extraction raffinate that has been used in one stage of washing in No. 2 Thickener.

3.4 LIQUID/SOLID SEPARATION AND WASHING

The slurry leaves the Neutralising Vessel and passes to No. 1 Thickener. The overflow from the Thickener is pregnant solution containing a small amount of fine solids that are removed by filtering in a Pressure Precoat Filter to render the solution

acceptable for solvent extraction. The underflow from the Thickener, at 50% solids, is mixed with solvent extraction raffinate to reduce the copper content to 1.077 g/l and is pumped to No. 2 Thickener. Thickening rates are improved by the use of a suitable flocculant.

The overflow from No. 2 Thickener is used to dilute the discharge from the leaching system. The underflow is waste, but is first treated with ground marble in a pug mill to precipitate iron etc. to give a solid high iron product which can be handled with front end loaders.

3.5 SOLVENT EXTRACTION

The extraction of copper from aqueous solution by the application of organic solvents such as LIX64N or Kelex 100 proceed chemically according to the following equation:

$$(2RH)_{\text{organic}} + CuSO_{4\ \text{aqueous}} = (R_2Cu)_{\text{organic}} + H_2SO_{4\ \text{aqueous}}$$

It will be seen that the extraction of copper into the organic phase is accompanied by an increase in the acid level of the aequous phase.

The selectivity of reagents such as LIX64N for copper is very high in comparison with that for other metals with which it is commonly associated. The only metal ion picked up to a measurable extent is ferric ion. Even so, the ratio of copper to ferric ion extracted is of the order of several hundreds to one and the iron concentration is controlled by a small bleed.

During leaching, iron is taken into solution in addition to copper, thus making the solution unsuitable for the direct recovery of copper by electrowinning.

Solvent extraction is adopted to produce purified copper sulphate solution containing a small quantity of iron from which copper cathodes can be obtained by electrowinning. The cathodes produced are high quality copper suitable for direct sale to copper wire cable, tube etc. manufacturers.

An organic solvent, LIX64N in kerosene is employed to transfer the copper from the pregnant feed solution to the organic phase. The transfer is effected in two Extraction Mixer/Settler units working in series.

The organic solution, loaded with copper, leaves the second Extraction Mixer Settler and is pumped to the stripping section of the plant. The organic solution is stripped of copper by spent electrolyte from the tank house in two Stripping Mixer/Settler units working in series.

The stripped organic solution is returned to the extraction stage and the raffinate is returned to the thickener circuit.

A small quantity of organic is entrained in the aqueous phase and a small quantity of aqueous is entrained in the organic phase. The entrained material is recovered in flotation units.

3.6 ELECTROWINNING

The copper sulphate solution from the solvent extraction section is pumped to the electrowinning tank house where copper metal is won by electrolytis in 12 electrolytic cells containing lead anodes and copper cathodes. The cells will be constructed from concrete and lined with flexible PVC "Paraliners". The passage of an electric current through the cells causes part of the copper from the solution to be deposited on the cathodes. Power will be fed to the cells through busbars supplied with DC current from the transformer rectifier station.

Initially the cathodes are installed as thin copper "starting sheets", which because of the scale of the project are best purchased rather than made in the plant. After 6 days of operation the fully grown cathodes are removed from the cells, washed, and dispatched for sale.

The spent electrolyte (solution depleted in copper by electrowinning) is returned to the solvent extraction section for stripping the organic solvent of copper, and so becomes again the loaded electrolyte fed to the tank house.

To promote the formation of good cathodes, certain reagents are added to the electrolyte. Also, to prevent the build-up of iron in the electrolyte because of small unavoidable pick-up during solvent extraction, a small quantity of electrolyte is bled to the leaching stage to control the iron content in the tank house at 2 grams per litre.

3.7 MARBLE STORAGE

Finely ground marble is stored in two Hoppers from which it is conveyed pneumatically as required to two small Feed Hoppers equipped with variable speed Feeders.

These are automatically controlled to give the desired acidity in the slurry passing to No. 1 Thickener and in the underflow from No. 2 Thickener which is mixed with marble powder in a pug mill before discharge.

HELLENIC CHEMICAL PRODUCTS
& FERTILIZER CO. LTD.

1700 TPA COPPER RECOVERY PLANT

DESIGN BASIS SECTION 4

4.1 The plant has been designed to treat 45,000 metric tons per year of Calcine and to produce a nominal 1700 metric tons per year of Electrowon Cathode Copper.

The plant has been assumed to operate 340 days/year.

The plant has been designed on the availability of Raw Materials and Utilities as summarised below.

4.2 RAW MATERIALS

Pyrite Calcine - 45,000 mtpa as a dry free flowing powder essentially free of lumps and unburnt pyrites.

Dry Analysis	
Cu	4.35 %
Fe	48.25 %
S	2.08 %
Al	1.94 %
Ca	1.43 %
Mg	0.73 %
Mn	0.17 %
Zn	0.42 %
As	0.026%
SiO_2	12.33 %
Co	0.09 %

Screen Analysis	
+16	40.89 %
-16 +30	18.76 %
-30 +60	8.5 %
-60 +85	3.81 %
-85 +120	2.54 %
-120 +170	2.63 %
-170 +240	2.10 %
-240 +350	1.62 %
-350	19.15 %

Sulphuric Acid

Analysis

97% H_2SO_4
3% H_2O

Temperature - Ambient

Pressure - Sufficient to deliver Acid into Storage Tank 1222

Marble Powder

Dry and free running powder

Dry Analysis

CaO	55.2%
MgO	9.67%
SiO_2	0.24%
Al_2O_3	0.10%
Fe_2O_3	0.05%

Screen Analysis (ASTM)

On Screen No. 10	Zero
On Screen No. 20	10%
On Screen No. 50	30%
On Screen No.100	50%
On Screen No.200	70%
Passing through No. 200	30%

4.3 UTILITIES

Steam

Dry saturated steam at a minimum pressure of 4.25 Kg/cm^2g

Electricity

440 volts, 3 phase, 50 cycle

Process Water

Clean, non-corrosive, non-scaling, chloride free at a pressure of 4.25 Kg/cm^2g and 28°C max.

Instrument Air

Dry and oil free at 7 Kg/cm^2g with a dew point of $-5^{\circ}C$.

Plant Air

Oil free 7 Kg/cm^2g

McKee

Flue Gas Desulfurization and Fertilizer Manufacturing **Pircon-Peck Process**

Presented by

R.B Boyda

Arthur G. McKee & Company/Engineers & Constructors/10 S. Riverside Plaza/Chicago, Il. 60606/USA

FOREWARD

Information presented in this paper is intended to introduce the Pircon-Peck flue gas desulfurization process and highlight some of its attractive features. Because process developments are still generating patent applications, in addition to those already issued or still pending and allowed, many key details are not included. We invite anyone desiring additional information to contact Mr. Gene Barber in McKee's Chicago office at telephone number (312) 454-3899.

TABLE OF CONTENTS

	Page No.
INTRODUCTION	1
PROCESS DESCRIPTION	1
PROCESS HISTORY	7
PROCESS EVALUATION	9
CONCLUSIONS	14
APPENDIX I	15
HETEROGENEOUS REACTOR	

INTRODUCTION

The Pircon-Peck flue gas desulfurization (FGD) process presented in this paper was developed by Mr. Ladd Pircon and Dr. Ralph Peck. The process utilizes patented heterogeneous reactor technology developed by Mr. Pircon as cooling and absorber towers in conjunction with chemistry developed and demonstrated by Mr. Pircon and Dr. Peck at the Illinois Institute of Technology. The process is unique in that in addition to providing a means of controlling SO_2 emissions, it provides the owner with an opportunity to earn a profit on the invested capital.

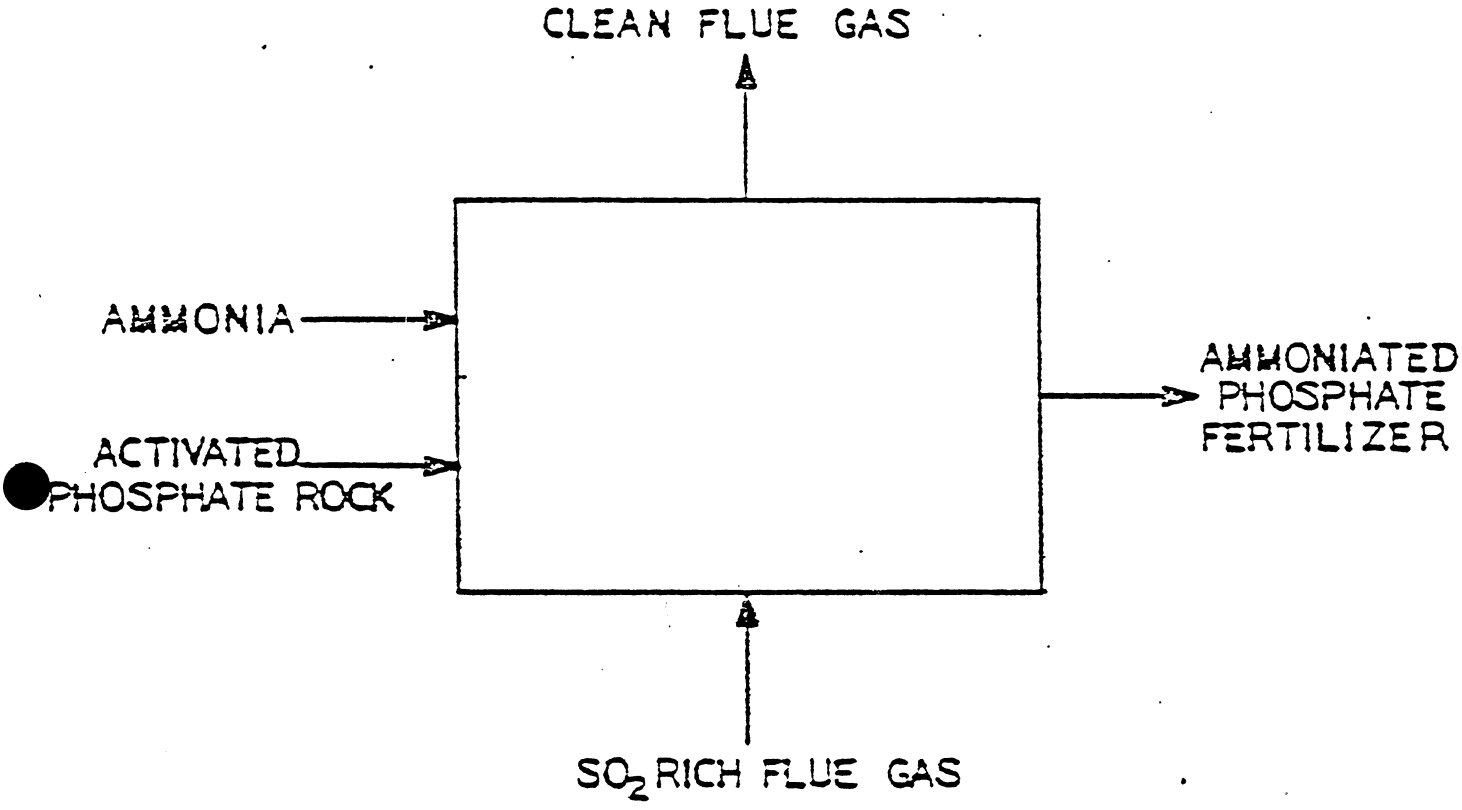
PROCESS DESCRIPTION

The Pircon-Peck FGD process, as shown in Figure I, utilizes "activated" phosphate rock, ammonia, and flue gas as raw materials to produce ammoniated phosphate fertilizers. Laboratory and pilot plant testing indicate that in the process of producing fertilizer, sufficient SO_2 can be removed from the flue gas to provide compliance with all EPA regulations, both existing and proposed.

The chemistry utilized to produce the product material can be summarized by three chemical reactions. These are:

(1)	Sulfur Dioxide	+	Diammonium Phosphate	⟶	Ammonium Bisulfite	+	Monoammonium Phosphate
	SO_2		$(NH_4)_2HPO_4$		NH_4HSO_3		$NH_4H_2PO_4$

FIGURE - I



(2)

Phosphate Rock		Ammonium Bisulfite		Calcium Sulfite		Diammonium Phosphate
	+		⟶		+	
$Ca_3(PO_4)_2$		$3NH_4HSO_3$		$3CaSO_3$		$(NH_4)_2HPO_4$
					+	Monoammonium Phosphate
						$NH_4H_2PO_4$

(3)

Monoammonium Phosphate		Ammonia		Diammonium Phosphate
	+		⟶	
$NH_4H_2PO_4$		NH_3		$(NH_4)_2HPO_4$

An important feature of this chemistry is the pretreatment of the phosphate rock which facilitates the reaction of the rock with the weak sulfurous acid produced in the scrubber. Standard phosphate fertilizer chemistry requires concentrated sulfuric acid to acidulate the rock and liberate the desired phosphate molecule.

In many ways, the Pircon-Peck process is similar to standard double alkali technology. In each system, a soluble alkali is utilized in the scrubber portion of the process and in each system this alkali is regenerated by a calcium source. In the Pircon-Peck process, the soluble alkali is diammonium phosphate and the calcium source is phosphate rock. However, where alkali regeneration with lime produces water as a by-product, diammonium phosphate regeneration with phosphate rock produces additional phosphate. Neutralization of this by-product with ammonia produces the final diammonium phosphate product.

In addition to producing diammonium phosphate, the regeneration reaction also produces calcium sulfite and sulfate. This material can be included in the fertilizer product or separated for disposal. If included in the fertilizer product, the material would be similar to superphosphate fertilizers presently produced by the fertilizer industry.

These fertilizers contain the calcium sulfate solids produced by the acidulation of phosphate rock with sulfuric acid. While the final product form will be dictated by the local market conditions, the advantage of including the calcium sulfite/sulfate solids in the product is obvious.

Figure II provides a view of the scrubber portion of the process. Flue gas enters the system and is first passed through a high efficiency particulate control device. The use of a particulate removal system minimizes the possibility of product contamination from fly ash. After fly ash removal, the gas is sent to a cooling tower where it is quenched and saturated to its adiabatic saturation temperature. The cooled and saturated flue gas is next processed through the heterogeneous reactor tower (see Appendix I) where the flue gas is contacted with a saturated solution of diammonium phosphate and the SO_2 is removed. After passing through a demister, the SO_2 free flue gas is sent to the stack. If necessary, reheat can be added to aid in plume dispersion.

The SO_2 rich absorption liquor is taken from the heterogeneous reactor system and sent to an agitated attack tank where it is contacted with ammonia and phosphate rock. The slurry generated in the attack tank is next sent to a product separator (clarifier) where solid diammonium phosphate and calcium sulfite/sulfate crystals are withdrawn as a slurry. The product slurry is sent to a fertilizer plant where the product is converted to its final form. The overflow from the product separator is a saturated solution of diammonium phosphate and is sent back to the heterogeneous reactor tower for further reaction with SO_2.

PIRCON-PECK
FGD PROCESS

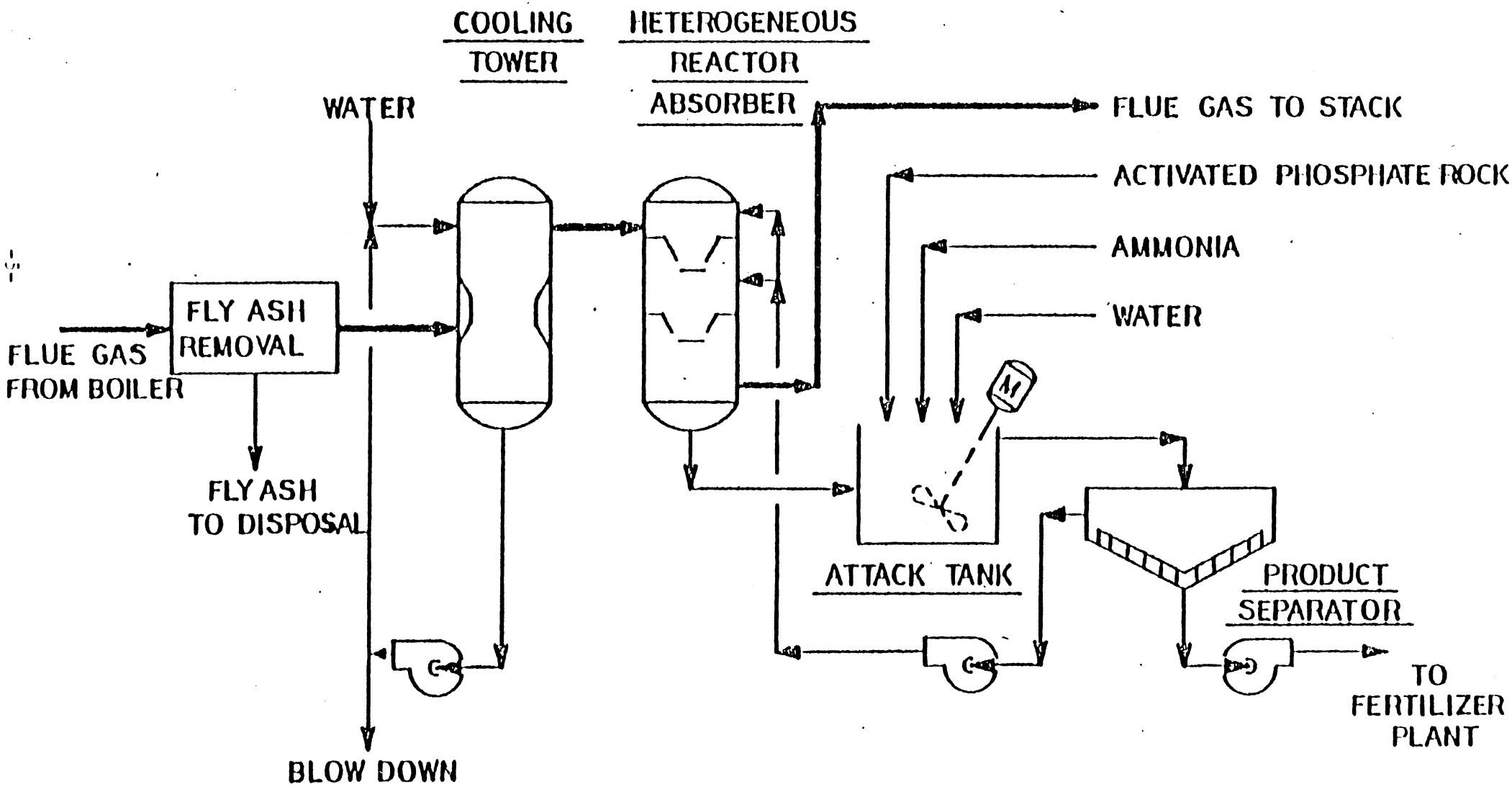


FIGURE-II

The material from the product separator, on a dry basis, has an approximate analysis of 7-20-0 (N, P_2O_5, K_2O). This analysis can be adjusted as desired by the addition of ammonia, phosphoric acid, or other N-P-K materials. The product form chosen by McKee for evaluation is a granular material with an analysis of 9-30-0. This analysis was chosen because posted prices are available to facilitate an economic evaluation of the process. Since fertilizer granulation plants are standard technology, no details are included.

As indicated, it is possible to produce product in various forms. Some alternates to granules with N and P_2O_5 values are:

1. Pure diammonium phosphate
2. Granules with N, P, and potassium values
3. Suspensions
4. Flakes

PROCESS HISTORY

The Pircon-Peck process evolved from Mr. Pircon's knowledge of phosphate chemistry, which he developed during his employment in the fertilizer industry, and his invention of the heterogeneous reactor technology. Mr. Pircon invented the heterogeneous reactor technology in the early 1970's and commercialized it as a low cost, high efficiency particulate control device. This technology was marketed commercially and over a dozen installations are presently in operation.

The major event in the development of the technology occurred when funding was obtained from the Illinois Institute for Environmental Quality for the design, construction and operation of an 800 acfm pilot plant. This pilot plant was installed at the Illinois Institute of Technology (IIT) and operated by graduate students for more than two years. This work was supervised by Dr. Ralph Peck. Work performed by students resulted in IIT granting two doctorate and six masters degrees in chemical engineering.

The operation of this pilot plant provided confirmation of the process principles and information for design of a commercial sized demonstration plant. In addition, sufficient fertilizer product was produced so that test work could be performed by Argonne National Laboratories. This test work was also funded by the Illinois Institute for Environmental Quality.

At the conclusion of the pilot plant work, the following items were demonstrated:

1. More than 95% of the sulfur oxides present in flue gases generated by a 6.2% sulfur coal, could be removed by the pilot plant scrubbing system.

2. Particulates generated by the underfeed stoker fired boiler were removed so that no particulates were visible in the stack plume.

3. The process produced a satisfactory fertilizer product.

4. The required liquid/gas ratios for the system were considerably less than those for conventional scrubbers.

5. The overall pressure drop across the pilot plant system, including the boiler, cooling tower and scrubber, was about two inches of water.

PROCESS EVALUATION

McKee's evaluation of the Pircon-Peck process was performed by reviewing laboratory data, pilot plant records and pilot plant operating experience. In addition, extensive discussions were held with the process inventors to develop additional background information. This investigation has shown that:

1. The process can be carried out in a plant of very simple design.
2. Few moving parts are involved in the equipment.
3. There is considerable flexibility in the process.
4. The process can be run with clear liquids or slurries in the heterogeneous reactor tower.
5. The product fertilizer analysis can be adjusted to fit the needs of the local market.
6. Scaling in the absorber is not a problem due to the process chemistry.
7. For the same removal rates, equipment is simpler and smaller than for other scrubbing processes.

The economics of the process were evaluated by preparing a mechanical design and a heat and material balance for the 100 mw sized facility. Once this was complete, capital and operating cost estimates were made and an economic analysis performed. The design basis used for this work was:

Fuel: 3.5% Illinois High Volatile C Coal @ 11,500 Btu/lb.

Heat Rate: 11,500 Btu/kwh

Flue Gas: 2.12 scfm/kw @ 75° F

SO_x Removal: 95%

Phosphate Rock Conversion: 95%

Service Factor: 85% (7450 Hr./Yr.)

On this basis, it was estimated that the plant, including the scrubber and fertilizer granulation plant, would cost approximately $10.7 million and produce 128,600 tons per year of a 9-30-0 analysis granular fertilizer product. It was estimated that the margin between the fertilizer manufacturing cost and selling price would be $50.00 per ton.

Using these economic parameters, a project feasibility analysis was performed. This analysis was based on:

- Discounted Cash Flow Techniques
- Twenty Year Project Life
- Income Tax @ 50%
- Sum of the Years Digits Depreciation
- Working Capital of 13% of Sales

This study indicated that the project would have an Investors Rate of Return (ROI) of 22% over the life of the project.

Because of the preliminary nature of the estimate and the inherent uncertainty of prices in the fertilizer industry, McKee believes that the significance of the indicated ROI is not its absolute value, but the fact that it is significantly positive for even a small sized facility.

The economic viability of the process was further confirmed by studies of the sensitivity of ROI to changes in key economic parameters. Parameters studied included capital cost, production volume, variable costs and margin. As an example of this work, Figure III shows the sensitivity of ROI to variations in the margin between selling price and manufacturing cost. These analyses show that this margin is the most sensitive parameter. A summary of the projected operating costs is given in Figure IV.

McKee has also looked at the market for the process product. At the present time the market for fertilizer, on a P_2O_5 basis, exceeds 10 million tons per year and is expanding at a rate of approximately 6% per year. On the design basis presented in this paper, a 500 mw plant would produce 190,000 tons per year of P_2O_5 equivalent product which would fit easily into the growing fertilizer market. This is particularly true in the midwest and farm belt regions.

FIGURE - III

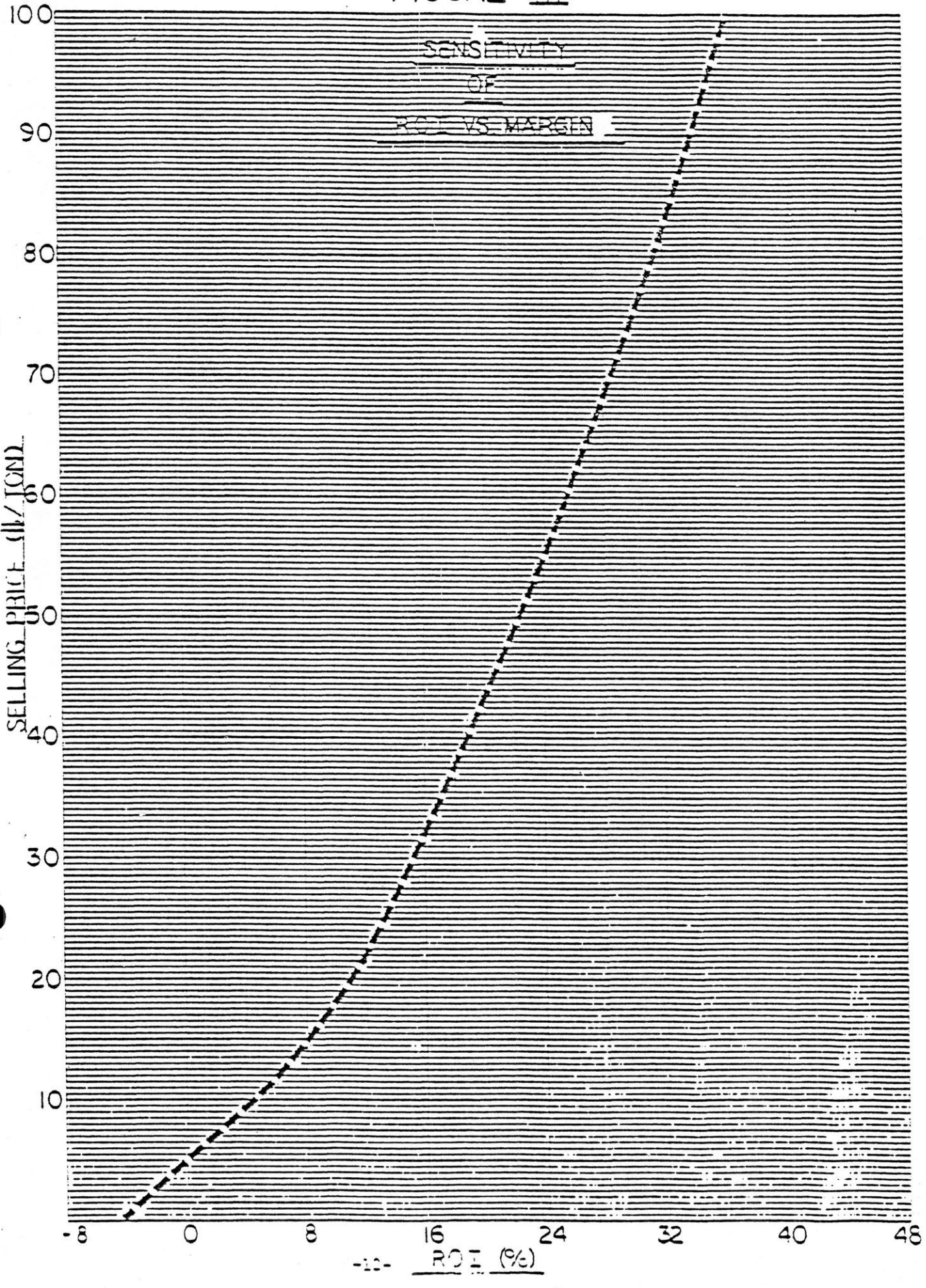

SENSITIVITY
OF
ROI VS MARGIN
SELLING PRICE ($/TON)
100
90
80
70
60
50
40
30
20
10
-8
0
8
16
24
32
40
48
ROI (%)

FIGURE IV

CAPITAL & OPERATING COST SUMMARY

INVESTMENT	$ 10,726,000
PRODUCTION VOLUME	128,635 Tons/Yr.
SALES MARGIN	$ 50 Ton

SEMI VARIABLE COSTS	
MAINTENANCE	$ 845,000
LABORATORY	96,000
INSURANCE & PROPERTY TAX	370,000
PLANT OVERHEADS	534,000
ADMINISTRATION & MARKETING	294,000
	$ 2,139,000

VARIABLE COSTS	
RAW MATERIAL	$ 8,225,000
LABOR & SERVICES	1,009,000
UTILITIES & FUEL	924,000
	$ 10,158,000

TOTAL OPERATING COSTS	$ 12,297,000

CONCLUSION

As a result of our process studies McKee believes that the Pircon-Peck process offers significant advantages over existing commercial processes. Not only does the process provide an opportunity to make pollution control profitable, it actually provides an economic incentive to utilize high sulfur coals. This incentive results from the fact that the quantity of fertilizer product producted is directly proportional to the quantity of sulfur captured. As a result, the plant operator will want to operate the system at SO_2 capture rates in excess of EPA standards.

McKee has recently entered into an agreement with the process owner, Mr. Ladd Pircon, to commercialize the technology. It is our present co-objective to accomplish this by the design, construction, and operation of a commercial sized demonstration plant with a minimum rating of 100 mw. At the present time we are working to put together the four items necessary to achieve our objective. These four items are; funding, a site for the project, an operator with fertilizer production experience and a commitment from a fertilizer company to market the fertilizer product. Significant progress has been made in this effort at two separate locations.

APPENDIX I

HETEROGENEOUS REACTOR TOWER

The heterogeneous reactor tower included in this design utilizes differential velocities between liquid, gas, and solid particles to obtain high mass transfer coefficients. The tower internals (see Figure V) consist of a series of two conical restrictions preceded by spray nozzles and followed by impinger plates. Each plate is washed by a dedicated spray nozzle.

The differential velocities are achieved at a low absolute velocity as the gas enters the conical restrictions. Because the gas phase is compressible it accelerates more rapidly in the cones than the solid or liquid particles which are accelerated by drag forces from the gas. When the gas exits the conical restriction and impinges on the plate, the streamlines of the gas cross those of the droplets and the solid particles and again produce a high contact efficiency.

As indicated in the process history section this technology has been commercialized as a low cost high efficiency control device. This success with large scale units, plus field tests of the process chemistry, provides strong indications that the demonstrated success of the pilot plant scrubber can be duplicated in commercial units.

HETEROGENEOUS REACTOR

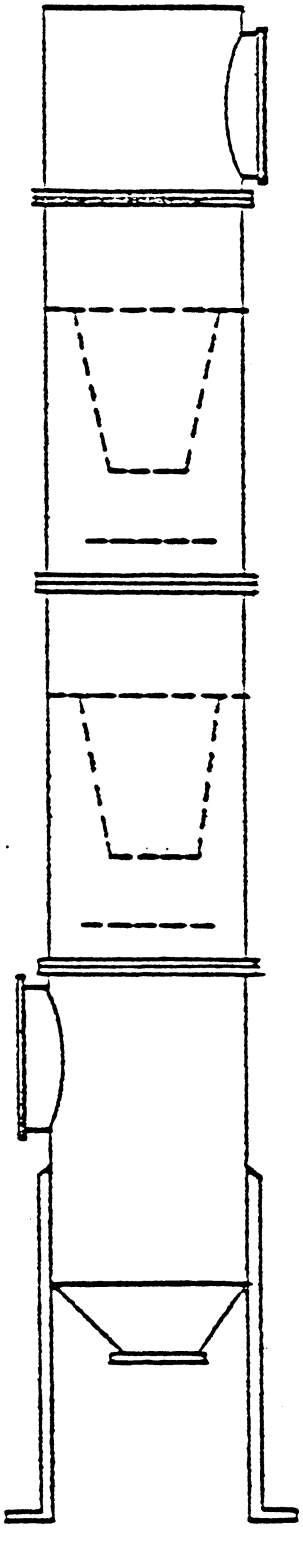


FIGURE-V

Davy McKee

ENGINEERS AND CONSTRUCTORS

INTER OFFICE COMMUNICATION

RECEIVED

NOV - 5 1979

TO: Art Raub

FROM: G. Munson

REFERENCE: Exxon PN 2489

COPY: A.V. Richardson

SUBJECT: PERCENTAGE BREAKDOWN

November 5, 1979

At your request, the percentage range breakdown of our Capital Cost Estimates for general catagories is:

Major Process Equip.	30 - 40%
Bulk Materials	25 - 35%
Construction	20 - 30%
Home Office & Fees	10 - 15%

GM:ecs

Davy McKee
ENGINEERS AND CONSTRUCTORS

INTER OFFICE COMMUNICATION

RECEIVED
SEP 21 1979

TO: A. V. Richardson DATE: September 20, 1979

FROM: L. J. Friedman/E. A. Gize COPIES: A. L. Raub

REF: PN 2489

SUBJECT: Exxon Minerals Co. USA
Pyrite Processing Study

Please revise the memo dated September 19, 1979, and use the following to obtain O.O.M. cost for the following pyrite plant only:

A. Double Absorption H_2SO_4 Plant

Basis for purification section - ASARCO, El Paso, PN 4121
Basis for converter section - ASARCO, El Paso II, 2348/0

1. Gas cleanup starts at the open scrubber
2. Comparison rates scfm

Purification Section	ASARCO 4121 59,000 scfm	Exxon Minerals Co. 1 train @ 63,000 scfm
Converter Section	ASARCO 2348/0 90,000 scfm	Exxon Minerals Co. 1 train @ 80,000 scfm
Acid Produced as 100% H_2SO_4	Double Absorption	Exxon Minerals Co. 1 train @ 1,375 STPD

E. A. Gize

/dp

Davy McKee
ENGINEERS AND CONSTRUCTORS

INTER OFFICE COMMUNICATION

E-9

RECEIVED
OCT 11 1979

TO: [redacted]
FROM: G. Munson
REFERENCE: Exxon PN 2489

COPY: A. V. Richardson
October 10, 1979

SUBJECT: ESTIMATE

Our Order-of-Magnitude Estimate for the following battery limit plants and associated offsites is...

$80,000,000

- Wet Rock Grinding	120 STPH
- P_2O_5 Attack/Filtration	800 STPD
- P_2O_5 Evaporation (28% to 54%) Including Fluorine Recovery	400 STPD
- Clarification	400 STPD
- DAP	77 STPH
- Offsites	

Qualifications to the estimate are the same as indicated in my memo to you dated October 8, 1979.

It should not be misconstrued that the cost of the B/L H_2SO_4 plant and associated offsites, is the delta between the $100 MM "complex" estimate of October 8, 1979, and the above $80 MM estimate.

The adjusted value of the B/L H_2SO_4 plant within the $100 MM is $18 MM.

Later, when the San Mateo estimate is received by you, Estimating will estimate the B/L H_2SO_4 plant and required offsites in association with the Roaster, Pyrite Cinders and Pellet Plants.

GEM/ehm

Davy McKee
ENGINEERS AND CONSTRUCTORS

INTER OFFICE COMMUNICATION

To: A. V. Richardson Date: September 21, 1979

From: A. L. Raub

Subject: Exxon Minerals Co. USA
Pyrite Processing Study
Davy McKee No. 2489

This memorandum relates to the estimating work that you are doing on the Pyrite Processing Study, Davy McKee 2489, for Exxon Minerals Company USA. At this time you should have received process information on the sulfuric acid plant, phosphoric acid plant and the DAP plant. Later on, we may ask you to estimate the cost of a plant to produce elemental sulfur, either from SO_2 gas or by a direct reduction method.

As things shape up now, it is planned to include roasting, sulfuric acid, cinder processing as a complex. If the economics so warrant, phosphoric acid and DAP will be added.

Davy McKee San Mateo is doing the material receiving, roasting plant, and cinder processing including balling and Kowa Seiko.

Lakeland will do as indicated above.

In the sulfuric acid plant you are to include storage for 40,000 metric tons of acid, including acid load-out, both to barges and railroad cars.

In the DAP plant you are to include 50,000 metric tons of storage.

In the phos acid plant you will include the gyp pond costs.

The offsites that you will provide will be as follows:

1. Administration building with laboratory.
2. Parking lot for 300 cars.
3. Change house, fire station and first aid.
4. Guard house and truck scale.
5. Maintenance shop and warehouse as an integrated unit.
6. Effluent treatment plant.
7. Sewage treatment plant.
8. Incoming power source - transformer by power company.
9. Plant road system.
10. Perimeter fencing.

San Mateo will furnish costs for:

1. Material receiving including covered storage.
2. Railroad dumper.
3. Railroad scale.

The costs generated will be order of magnitude and will be used to generate operating costs and R.O.I.

If you have any questions, please contact the writer.

A. L. Raub

ALR:cb

cc: G. L. Stevenson/C. B. Earl
R. H. Curtis
J. V. Beall
G. Munson
J. C. Taylor, Jr.
F. G. Prado

Davy McKee
ENGINEERS AND CONSTRUCTORS

INTER OFFICE COMMUNICATION

To: J. H. Marten Date: August 30, 1979

From: A. L. Raub

Subject: Exxon Minerals Company, U.S.A.
Pyrite Processing Study
Davy McKee 2489

For the Exxon Pyrite Processing Study, we will need the aid of the Process Department relative to the sulfuric acid plant.

The pyrite roasters will operate as follows:

Pyrite Roasting	-	318 days/year
Roaster Capacity	-	840 M.T.P.D.
Sulfur in Pyrite	-	49.12%
Sulfuric Acid Strength	-	100%
Sulfur in Calcine	-	0.5%
Dust Loading to Acid Plant	-	2 grains/cubic foot

Please provide all the statistics for the acid plant of this size, complete with estimated gas volumes, strengths, horsepower requirements, imports and exports, etc., and estimated costs.

Also to be provided is the operating personnel required for normal operation and the order of magnitude cost estimate for the plant.

The same information is to be provided for a phosphoric acid plant to utilize the acid produced in this plant (probably 1250-1300 MTPD) plus the sulfuric acid from the zinc plant, 800 tons per day. Further, from the statistics of the phosphoric acid plant, so sized, we will need the same information on the DAP plant.

We believe that all the information required to do this exercise can come from existing files and information, sizing and costs can be factored to come up with the O.O.M. quantities.

All this information should be in our hands by September 28, 1979.

If you have any questions concerning this matter, please contact Faustino Prado or the writer.

A. L. Raub

ALR:cb

Distribution: R. A. Harang
R. E. Curtis
G. L. Stevenson/C. B. Earl
J. V. Beall
L. Friedman
J. Enriquez
J. Scruggs
J. Geniesse
A. V. Richardson
F. G. Prado

Davy

ENGINEERING COMPUTATION SHEET
Davy Powergas Inc.
LAKELAND, FLORIDA

FORM NO. 624

SUBJECT: DESIGN BASIS SHEET: OF

CLIENT: DATE:

COMPUTED BY: CHKD. BY: JOB: CONTRACT NO.:

FINE PYRITE CONCENTRATE = 764 MTPD

350 days/year operation:

764 × 350 = = 267,400 MTPY

ROASTERS

~~34 MTPH × 24~~ = ~~816 MTPD~~

~~3277 days/year operation (90%)~~

35 MTPH × 24 = 840 MTPD

318.3 days/year (87%)

S in Pyrite = 49.12% = 412.6 MTPD (S)

100% ACID = 1263.6 MTPD (H_2SO_4)

GAS TO ACID PLANT

35 MTPH SO_2

By Volume - SO_2 = ±%, O_2 = 0.1%; N_2 = 84% Dry Basis

SO_3 = traces

Temperature - 50°C - saturated with H_2O

TOTAL GAS = 76560 m^3/H (NPT) ≈ 36140 SCFM

PROCESS TRANSMITTAL

DELIVER TO: A Raub — DATE: 9-20-79

STATION: — COPIES TO: L Friedman

SENT BY: E. A. Gizi

PROJECT NAME: EXXON MINERALS COMPANY USA

PN: 2489

ITEM: Attached Please find
Brief Process Description
a Raw Materials & Utilities Imported
c Product + Utilities Exported
For the Pyrite Roasting Sulfuric Acid
Plant for 1375 STPD

REMARKS:

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: _____ SHEET: 1 OF 2
CLIENT: _____ DATE: 9-20-79
COMPUTED BY: _____ CHKD. BY: _____ JOB: 2489 CONTRACT NO.: _____

2489
Sept 1979
Exxon Minerals Company U.S.A.

PYRITE ROASTING SULFURIC ACID PLANT
DOUBLE ABSORPTION

B. RAW MATERIALS & UTILITIES IMPORTED

1. Pyrite Roaster Gas

a. Rate, scfm (@32°F + 760 mm Hg) Dry Basis		50,150
b. Temperature, °F		660
c. Pressure, inches W.G. at top of scrubber		-1
d. Composition	Vol % Dry Basis	
SO_2	13.6	
O_2	7.0	
N_2	83.4	
H_2O	—	
	100.0	

2. Process Water

a. Rate, gpm	15
b. Temperature, °F	Ambient
c. Pressure, psig	20

3. Electric Power

a. Operating load, hp	6500

c. Includes purification section and acid section, recycle fan cooling water pumps & fans

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: _____ SHEET: 2 OF 2
CLIENT: _____ DATE: 9-20-79
COMPUTED BY: _____ CHKD. BY: _____ JOB: _____ CONTRACT NO.: _____

4	Cooling Water	
	a Rate, gpm	12500
	b. Temperature, °F	80
	c. Pressure, psig	50
5	Instrument Air	
	a Rate, scfm	200
	b. Pressure, psig	60
	c Dew point	-40
6.	Makeup Water To Scrubber	
	a Rate, gpm	705
	b Temperature, °F	Ambient
	c Pressure, psig	20
7	Cooling Tower Makeup Water	
	a Rate, gpm	935
	b. Temperature, °F	Ambient
	c Pressure, psig	20
8	Boiler Feed Water	
	a Rate, gpm	745
	b Temperature, °F	110
	c Pressure, psig	50

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: _____ SHEET: 1 OF 2
CLIENT: _____ DATE: _____
COMPUTED BY: _____ CHKD. BY: _____ JOB: _____ CONTRACT NO.: _____

2429
Sept 79
EXXON MINERALS COMPANY USA

PYRITE ROASTING SULFURIC ACID PLANT
DOUBLE ABSORPTION

C. PRODUCTS & UTILITIES EXPORTED

1. 93% Sulfuric Acid (100% H_2SO_4 Basis)	
a Rate, STPD	1375
b Temperature, °F	110
c Pressure, psig	55
2. Weak Acid Purge	
a Rate, gpm	220
b Temperature, °F	140
c Pressure, psig	30
d Acid, wt%	1-5
3 Absorption Tower Stack Gas	
a Rate, scfm (@ 32°F & 760 mm Hg)	69,300
b Temperature, °F	170
c SO_2 content, ppmv	600
4 High Pressure Steam (See Note)	
a Rate, lb/hr	115,000
b Temperature, °F	700
c Pressure, psig	650

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: _____ SHEET: 2 OF 2
CLIENT: _____ DATE: 9-12-79
COMPUTED BY: _____ CHKD. BY: _____ JOB: 2489 CONTRACT NO.: _____

5. Cooling Water

a. Rate, gpm	13500
b. Temperature, °F	118
c. Pressure, psig	20

NOTE STEAM EXPORTED IS NOT PRODUCED IN THE SULFURIC ACID PLANT. IT IS PRODUCED IN THE PYRITE WASTE HEAT STEAM GENERATORS AND CAN BE USED TO PRODUCE POWER THROUGH A TURBOGENERATOR FOR THE ELECTRICAL REQUIREMENTS OF THE SULFURIC ACID PLANT.

C. Boiler Blowdown

a. Rate, gpm	10
b. Temperature, °F	212
c. Pressure, psig	atmos

Davy McKee
ENGINEERS AND CONSTRUCTORS

INTER OFFICE COMMUNICATION

RECEIVED
SEP 17 1979

TO: A. L. Raub

FROM: J. M. Enriquez

REF: PN 2489

SUBJECT: Exxon Minerals Company, U.S.A.
Pyrite Processing Study

DATE: September 13, 1979

COPIES: R. A. Harang
R. H. Curtis
J. H. Marten
A. V. Richardson
F. G. Prado

Find attached the information that you requested in your memo to Mr. Marten dated August 30, 1979.

If you have any questions on the information submitted, please contact me.

Julio M. Enriquez
J. M. Enriquez

/dp

Attachments

WET ROCK GRINDING - CAPACITY 120 STPH

Raw Materials & Utilities Imported

1. Receipt of Unground Phosphate Rock

a. Mill design rate, dry basis	120 STPH
w/12% moisture	134 STPH

2. Receipt of Process Water

a. Average rate	168 gpm

3. Receipt of Plant Air (Intermittent)

a. Average rate	30 SCFM

4. Receipt of Instrument Air

a. Average rate	25 SCFM

5. Receipt of Electrical Power (closed circuit)*

a. Connected load @ 480 V	360
b. Connected load @ 4160 V	1800 hp

*Depends on type of rock

Product & Waste Exported

1. Discharge of Ground Rock Slurry

a. Average rate, dry basis	120 STPH
wet basis	400 gpm

PHOSPHORIC ACID PLANT - CAPACITY 800 STPD P_2O_5 (ATTACK & FILTRATION)

Imports, Raw Materials & Utilities

1.	Receipt of Ground Phosphate Rock	
	a. Average rate (dry basis), 66 BPL	2800 STPD
2.	Receipt of 100% H_2SO_4	
	a. Average rate	2240 STPD
3.	Receipt of Defoamer	
	a. Average rate	2400 PPD
4.	Receipt of L.P. Steam	
	a. Intermittent for clean out	10,000 PPH
5.	Receipt of Cooling Tower Water	
	a. Average rate	440 gpm
6.	Receipt of Pond Water	
	a. Average rate	5000 gpm
7.	Receipt of Potable Water (Intermittent)	
	a. Average rate	20 gpm
8.	Receipt of Plant Air (Intermittent)	
	a. Average rate	400 SCFM
9.	Receipt of Instrument Air	
	a. Average rate	100 SCFM
10.	Receipt of Electrical Power	
	a. Connected load @ 480 V	960 hp
	b. Connected load @ 4160 V	1700 hp

Products & Waste Exported

1.	Discharge of Product Acid	
	a. Average rate, P_2O_5	800 STPD
2.	Discharge of Gypsum Slurry	
	a. Average rate, 20% solids	21600 STPD
3.	Discharge of Pond Water	
	a. Average rate	1450 gpm
4.	Discharge of Cooling Tower Water	
	a. Average rate	450 gpm
5.	Discharge of Effluent Gas	
	a. Average rate	30000 SCFM

PHOSPHORIC ACID EVAPORATION

CAPACITY - 400 STPD P_2O_5 from 28 to 54%
No fluorine recovery
2 x 14' Ø evaporators

Raw Materials & Utilities Imports

1.	Receipt of 28% P_2O_5 Acid	
	a. Average rate, P_2O_5	400 STPD
2.	Receipt of Medium Pressure Steam	
	a. Average rate	1250 PPH
3.	Receipt of Low Pressure Steam	
	a. Average rate	71700 PPH
4.	Receipt of Pond Water	
	a. Average rate	5300 gpm
5.	Receipt of Process Water	
	a. Average rate	10 gpm
6.	Receipt of Instrument Air	
	a. Average rate	50 SCFM
7.	Receipt of Electrical Power	
	a. Connected load, 480 V	600 hp

DAP PLANT - CAPACITY 70 STPH

Raw Materials & Utilities Imported

1.	Receipt of 28% P_2O_5 Acid	
	a. Average rate, P_2O_5	395 STPD
2.	Receipt of 54% P_2O_5 Acid	
	a. Average rate, P_2O_5	395 STPD
3.	Receipt of Anhydrous Ammonia - 99.5%	
	a. Average rate	315 STPD
4.	Receipt of 100% Sulfuric Acid	
	a. Average rate	12 STPD
5.	Receipt of Low Pressure Steam (Intermittent)	
	a. Average rate	500 PPH
6.	Receipt of Defoamer	
	a. Average rate	1000 PPD
7.	Receipt of No. 6 Fuel Oil	
	a. Average rate	2600 GPD
8.	Receipt of Pond Water	
	a. Average rate	5000 gpm
9.	Receipt of Potable Water (Intermittent)	
	a. Average rate	50 gpm
10.	Receipt of Instrument Air (Intermittent)	
	a. Average rate	100 SCFM
11.	Receipt of Plant Air (Intermittent)	
	a. Average rate	200 SCFM
12.	Receipt of Electrical Power	
	a. Connected load @ 480 V	1680 hp
	b. Connected load @ 4160 V	2030 hp

Product & Waste Exported

1.	Discharge of Product (18-46-0)	
	a. Average rate	70 STPH
2.	Discharge of Pond Water	
	a. Average rate	5100 gpm
3.	Discharge of Effluent Gas	116,000 SCFM

OPERATING PERSONNEL

	Area Superintendent Per Day	Plant Supervisor Per Shift	Operator Per Shift	Assistant Operator Per Shift	Laborer Per Shift
Rock Grinding			1	1	
Attack	1	1	1	1	2
Filtration			1	1	
Evaporation and Acid Storage			1	1	1
DAP	1	1	2	2	1

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: MANPOWER - DAP SHEET: ____ OF ____
CLIENT: EXXON DATE: ____
COMPUTED BY: FP CHKD. BY: ____ JOB: 2489 CONTRACT NO.: ____

Rock Reception, Phos Acid, DAP & Gyp disposal

3 Shifts/Day - 4 Shifts total

BASE CASE

Phos Acid

1 Foreman/shift		= 4 Foremen
4 Operator/shift	+ 2 day shift	= 18 Operators
7 Laborer/shift	+ 2 day shift	= 30 Laborers
	total	= 52 men

DAP

1 Foreman/shift		= 4 Foremen
2 Operator/shift	+ 1 day shift	= 9 Operators
3 Laborer/shift	+ 1 day shift	= 13 Laborers
	Total	26 men
	TOTAL	= 78 men

ALTERNATE CASE

Acid	2 Foremen/shift		= 8 For.
DAP	1 Foreman/shift		= 4 For.
Handling	1 Foreman/day		= 1 For.
Acid	5 Operator/Shift	+ 3 day shift	= 23 Op.
DAP	2 Operator/shift	+ 2 " "	= 10 Op.
Acid	10 Laborer/shift	+ 3 " "	= 43 Lab.
DAP	4 Laborer/shift	+ 2 " "	= 18 Lab.

TOTAL = 107 men

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: MANPOWER - IRON & Non Ferrous SHEET: ____ OF ____
CLIENT: EXXON DATE: ____
COMPUTED BY: FP CHKD. BY: ____ JOB: 2489 CONTRACT NO.: ____

BASE CASE

1 Foreman/shift		= 4 Foremen
3 Operator/shift	+ 1 day shift	= 13 Operators
6 Laborer/shift	+ 4 day shift	= 28 Laborers

TOTAL = 45 men

ALTERNATE CASE

2 Foremen/shift	+ 1 day shift	= 9 Foremen
6 Operator/shift	+ 2 day shift	= 26 Operators
12 Laborer/shift	+ 4 day shift	= 52 Laborers

TOTAL = 87 men

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: Manpower - Sulfuric Acid SHEET: ____ OF ____
CLIENT: EXXON DATE: ____
COMPUTED BY: E.P. CHKD. BY: ____ JOB: 2489 CONTRACT NO.: ____

Base Case

Includes Pyrite handling & Roasting

3 Shifts / Day - 4 Shifts Total

1 Foreman / shift		= 4 Foremen
2 Operator / shift	+ 1 day shift	= 9 Operators
2 Laborer / shift	+ 2 day shift	= 10 Laborers
	Total	= 23 men

Alternate Case

2 Foreman / shift		= 8 Foremen
6 Operator / shift	+ 2 x 2 day shift	= 28 Operators
6 Laborer / shift	+ 4 x 2 day shift	= 32 Laborers
	Total	= 68 men

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: LABOR RATES SHEET: ____ OF ____
CLIENT: EXXON DATE: ____
COMPUTED BY: FP CHKD. BY: ____ JOB: 2489 CONTRACT NO.: ____

FOREMAN = $16.00/hour

OPERATOR = $12.00/hour

LABORER = $8.00/hour

All benefits included

2080 hours/year-man

Davy McKee

2489/0
November 1979

EXXON MINERALS CO. USA
PYRITE PROCESSING STUDY

NONFERROUS METALS & PRECIOUS METALS

GREEN BAY & EVANSVILLE

(ALTERNATE)

Pyrite - fine 764 MTPD

Pyrite - sand 2364 MTPD

3128 MTPD

Fe - (764 x 43.6 + 2364 x 42.1)/3128 = 42.47

S - (764 x 49.12 + 2364 x 51.34)/3128 = 50.80

Analysis provided by Exxon, June 18, 1979 is average for 3128 MTPD (-20 and +20 micron)

Fe - 42.47%
S - 50.80%
Cu - 0.19%
Pb - 0.12%
Zn - 0.38%
Au - 0.96 gm/mt
Ag - 20.58 gm/mt

				Recov.	Year
Cu =	3128 x 350 x	0.19/100 =	2080 MT x	0.90 =	1870 MT
Pb =	3128 x 350 x	0.12/100 =	1314 MT x	0.80 =	1050 MT
Zn =	3128 x 350 x	0.38/100 =	4160 MT x	0.90 =	3740 MT
Au =	3128 x 350 x	0.96/1000 =	1050 Kg x	0.80 =	840 Kg
Ag =	3128 x 350 x	20.58/1000 =	22,530 Kg x	0.80 =	18,024 Kg

Davy

ENGINEERING COMPUTATION SHEET
Davy Powergas Inc.
LAKELAND, FLORIDA

FORM NO. 624

SUBJECT: _____ SHEET: ____ OF ____
CLIENT: _____ DATE: _____
COMPUTED BY: _____ CHKD. BY: _____ JOB: _____ CONTRACT NO.: _____

ASSUME Gypsum 85#/CF (WET)

THEN ONE TON WOULD REQUIRE = 2000 #/T ÷ 85 #/CF = 23.52 CF

ONE ACRE = 43560 Sq ft

ONE ACRE FOOT WOULD HOLD = 43560 CF ÷ 23.52 CF/T =
1852 TONS

2160 Acre Ft Gyp
vs
700 Acre Ft Pyrite

at 70#/cu ft (wet)

2000 #/T ÷ 70 = #/cu ft = 28.6 Cu ft.

43560 cu ft ÷ 28.6 = 1523 tons / Acre

$\frac{4,000,000}{1523}$ = 2626 acres feet

vs

$\frac{2000}{150}$ = 13 cu ft

43560 ÷ 13 = 335 tons / acre

$\frac{267,400}{335}$ = 803

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT FACTOR) + IND. COST

Estimate No. 2301 A

Sheet _____ of _____

Made by DWO Date 10-12-71

ESTIMATE FOR: PYRITE PROCESS STUDY FOR EXXON MINERALS CO

F.S.-No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total DC + IND Cost
A	RECIEVING STOCKPILE + RECLAIMING	1	Lot.						4000000
B	ROASTING	1	Lot						21500000
C	IRON RECOVER	1	LOT						11400000
D.	NON FERROUS METAL	1	LOT						1500000
	TOTAL DIRECT + INDIRECT COST W.O. ESCALATION, CONTINGENCY OR FEE.						Lot		38500000
							0		-4000000

Rec'd 9-21-78 PS

Job No SC 2301A

PH Code 286 2591

Receiving, Stockpiling & Reclaiming

A 1 ~~Receiver~~ HOPPER

9'W x 30'L x 10'H : Top - to 30"W at bottom

A. 2 Apron Feeder (Belt dr) X

36"W - @ 30 FPM - 25 HP - 36' Long

A 3 Stockpiling Conveyor X

420 MTPH (463 stph) - 125 M³PH -

~~24~~"W @ 225 FPM - 50 H.P. -

150 mts (492 ft) - elevation 15 mt (49 ft) in 60 mt (197 ft)

A 4 Storage - Covered STOCKPILE

90 m± L x 30 m± W x 15 m± H - Roof

Angle of Repose - 35°

A. 5 ~~Reclaimer~~ Two Front End loader, 5 cu. yd each X

A 6 ~~Hopper~~ (Belt feeder) 10' x 10' x 10' : Top to 12" at bottom X

~~A-7~~ Reclaim Conveyor X

80 MTPH (88 stph) - 25 M³ PH

18"W @ 125 FPM - 15 HP

200 mt (656 ft) - elevation 20 mt (66 ft) in 86 mt (282 ft)

? ~~A-7~~ ~~Distributor~~ Reversible Conveyor X

= 20% of A-6

Davy McKee

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT)

Estimate No. S.C. 2301A

Sheet _____ of _____

Made by DMP Date 9-28-79

ESTIMATE FOR: AREA A - RECEIVING STOCKPILING + RECLAIMING

F.S. No.	Item	Unit	Quantity	Manhours	Process * Equipment	Material	Labor	Subcontract	Total
A-1	RECIEVING HOPPER 9'X30' x 10' H. CTR + 30° W BOTTOM	1	EA.		40000				
A-2	APRON FEEDER 36"X36'-25H	1	EA.		70000				
A-3	STOCKPILING CONVEYOR 30"X449' 50HP	1	EA		90000				
DELETE A-4	~~ALLOWANCE FOR TRANSFER BOW ONLY STOCKPILE CONVEYOR - COVERED 90M X 30M X 15M HIGH.~~	1	LOT		~~30000~~	Deleted			
DELETE A-5	~~FRONT END LOADERS 5 C.Y.~~	2	EA		~~300000~~				
ADD A-4-5	STORAGE BLDG W/RECLAIMER	1	LOT			Add.			2400000
A-6	HOPPER 10'X10'X10' TOR	1	EA.		20000				
A7	RECLAIM CONVEYOR 18"X282'-15HP	1	EA.		40000				
A8	REVERSIBLE CONVEYOR	1	EA.		10000				
									2400000
	FACTOR EQUIP X 3 =				270000	(3)	=		810000
	TOTAL D.C.								3210000
	ADD FOR IND. 25%								810000
	SUB TOTAL								4020000
	TOTAL AREA 7								4020000

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. SC. 2301 A

Sheet _____ of _____

Made by ~~TRP~~ _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: RECIEVING HOPPER - 9'×30'×10'H

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R BINS	20	TON	1300					26000			
3200	GATES	1	ea					4000				
3745	AIR. LINERS	10	TON	1000					10000			
								4000	36000			

40,000

S EST-9 REV. 6/78

MAIN ITEM NO. A1

207

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by RMB Date 9-28-79

QUANTITY: (1)

ESTIMATE FOR: APRON FEEDER 36" X 36' LONG - 25 HP

Acct	Item	Quantity	U/M	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
51000	APRON FEEDER	1	Ea.					70000				
	Job 2129. FS #1-603.											
	48" x 27' long Apron = 108 HP											
	Escal. 1.50 x 41,405											
	= 62,537											
	2500 motor HP											
	65,000											
								70,000				

S EST-9 REV. 6/78

MAIN ITEM NO. A-2

McK WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

QUANTITY: (1)

Made by [illegible] Date 9-29-79

ESTIMATE FOR: STOCPILING CONVEYOR 30"x492' - 50HP

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BELT CONVEYOR	1 lot						90000				
								90000				

S EST-9 REV. 6/78

MAIN ITEM NO. A-3

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. SC 2301A

Sheet _____ of _____

Made by DWP Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: STORAGE BUILDING WITH RECLAIMER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	STORAGE BUILDING WITH RECLAIMER	1 LOT									2400000	2400000
											2400000	2400000

S EST-9 REV. 6/78

MAIN ITEM NO. A-4-5

McK WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. SC. 2301 A-

Sheet _____ of _____

Made by DMR Date 9-28-79

QUANTITY: (1) LOT

ESTIMATE FOR: STORAGE STOCKPILE 90M x 30M. x 15M High

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	Not Equip	1										
	allow for Blow or Tripper.							30000				
								30000				

S EST-9 REV. 6/78

MAIN ITEM NO. A-4

211

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. SC 2301A

Sheet _____ of _____

Made by DEP Date 9-28-79

QUANTITY: (2)

ESTIMATE FOR: FRONT END LOADERS - 5 Cu yds.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	FRONT END LOADERS	2	ea	150000				300000				
								300000				

See A-4-5

MAIN ITEM NO. A-5

S EST-9 REV. 6/78

McKee Wkg

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by LHO Date 9-28-79

QUANTITY: (1)

ESTIMATE FOR: HOPPER 10'X10' + 10' to 12° @ BOTTOM

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	HOPPER	10	TON	1300					13000			
6000	GATE CONTROLS	1	Lot					2000				
								2000	13000			

$15,000.

S EST-9 REV. 6/78

MAIN ITEM NO. A-6

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by DJP Date 9-28-79

QUANTITY: (1)

ESTIMATE FOR: RECLAIM CONVEYOR 18" x 282' — 15 HP

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYOR	1	EA					40000				
								40000				

S EST-9 REV. 6/78

MAIN ITEM NO. A 7

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by DRF Date 9-28-79

QUANTITY: (1)

ESTIMATE FOR: REVERSABLE CONVEYOR 20% of $ Cost of A-7

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	REVERSIBLE CONVEYOR							10000				
								10000				

5 EST-9 REV. 6/78

MAIN ITEM NO. A-8

ROASTING

B-1 ✱ Surge Bin (TWO)
50 M³ each (150 MT each) X

B-2 ✱ Weigh Belt Feeder (TWO) X
20 MTPH - each

B-3 ✱ Roaster (TWO) and auxiliaries - D.O. Description

B-4 ✱ Waste Heat Boiler (TWO) Each unit: 272845CFM at 925°C (1700°F), 542 lb/min dust ~ 139 grains/SCF, 31.5 grains/ACF IN-LET: 62,976 ACFM 343°C (650°F), 165 lbs/min dust ~ 18.4 grains/ACF % SO_2, 10.48; SO_3, 0.22; O_2, 0.68; N_2, 67.03; H_2O, 21.59

B-5 ✱ Cyclones - TWO LINES - Included in D.O. item 10

B-6 ✱ Electrostatic Precipitator (TWO)
Each 62,976 ACFM 343°C (650°F) Wagner
66 lb/min dust ~ 7.3 grains/ACF Wet Gas Analysis 10.48% SO_2, —

B-7 ✱ Hot Cinder Conveying System
? Dorr Oliver ?

B-8 Rotary Cooler (TWO)

6' ϕ x 30', steel construction with brick and castable lining. (M. FRIORD 717-8222161 - VULCAN) 9/19/79

B-9 Cooled Cinder Conveyor

100MTPH(110STPH) - 30M³PH

18" W @ 125FPM - 10HP

100mt(328ft) - elevation 14mt(46ft) in 61m(200ft)

Davy McKee

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT)

Estimate No. 2301A

Sheet 1 of 1

Made by [illegible] Date 10-1-79

ESTIMATE FOR: AREA B - ROASTING

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
B-1	SURGE BINS-150 MT EA	EA	2		162000				
B-2	WEIGH BELT FEEDER	EA	2		60000				
B-3	ROASTERS W/AUXILLARIES PRICE ENCL/DORR OLIVER PACKAGE	EA	2					17000000	17000000
B-4	WASTE HEAT BOILER	EA	2	INCLD W/B3	-0-				
B-5	CYCLONE LINES	EA	2	INCLD W/B3	-0-				
B-6	ELECTROSTATIC PRECIPITATORS	EA	2	-	900000				
B-7	HOT CINDER CONVEYING SYS	EA	2	INCLD W/B3	-0-				
B-8	ROTARY COOLER-6'X30' REFRACT LINED	EA	2	-	300000				
B-9	CONICO CINDER CONVEYER W/TRIPPER	EA	1		80000				
	TOTAL							17000000	17000000
	FACTOR EQUIP. X 3				1500000				4500000
									21,500,000

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A-

Sheet _____ of _____

QUANTITY: (2)

Made by [illegible] Date 10-1-79

ESTIMATE FOR: SURGE BINS 50 M³ EA (150 MT EA) SAY 6M Φ × 6M.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R BINS	80	TONS	1300					104000			
3745	STEEL A R LINER	40	TON	1000					40000			
5100	CASE FEED	2	EA	8000				16000				
								16000	144000			

160,000

MAIN ITEM NO. B-1

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by BJP Date _____

QUANTITY (2)

ESTIMATE FOR: WEIGH BELT FEEDERS.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BELT FEEDERS.	2	EA.	30000				60000				
								60000				

5 EST-9 REV. 6/78

MAIN ITEM NO. B-2

220

McKee Wheelabrator wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DRR Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: ROASTERS INCLUDING AUXILARIES (PART OF DORR OLIVER PACKAGE)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	EQUIPMENT	1	Lot					10,000,000			1000000	
	DORR OLIVER QUOTE											
	COMPLETE PACKAGE -											
	INCLUDING 2 each of											
	B-3 - ROASTERS.											
	B-4 - WASTE HEAT BOILER											
	B-5 - CYCLONES											
	B-7 - HOT CINDER CONVEYORS.											
	$10,000,000 MATERIAL FOB											
	JOBSITE											
								10000000			7000000	17000000

S EST-9 REV. 6/78

MAIN ITEM NO. B-3

22

McKEE WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 - A.

Sheet _____ of _____

Made by BDO Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: WASTE HEAT BOILER COMPLETE

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	INCL. W/DOOR DELIVERY PACKAGE							-0-				

S EST-9 REV. 6/78

MAIN ITEM NO. B-4

McKee Wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DJD Date 10-1-79

QUANTITY: (2) LINES

ESTIMATE FOR: CYCLONES.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	ENCLUDED W/ DOMEQUIP PACKAGE											
								-0-				

S EST-9 REV. 6/78

MAIN ITEM NO. B-5

223

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by BMP Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: ELECTROSTATIC PRECIPITATORS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	ELECTROSTATIC PRECIPITATOR	2	EA	450,000				900,000				
	ENVIROTECH QUOTE 450,000											
								900,000				

S EST-9 REV. 6/78

MAIN ITEM NO. 8-6

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DMD Date Oct 1, 1977

QUANTITY: (1) LOT

ESTIMATE FOR: HOT CINDER CONVEYING SYSTEM.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	PART OF DORR-OLIVER QUOTATION							-0-				

S EST-9 REV. 6/78

MAIN ITEM NO. B-7

McKee wka

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by [illegible] Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: CONVEYOR 18"x330' - 10HP - W/TRIPPER.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3100	Conveyor & Tripper	1						80000				
	see Calc											
								80000				

S EST-9 REV. 6/78

MAIN ITEM NO. B-9

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2501-A

Sheet _____ of _____

Made by [illegible] Date _____

QUANTITY: (2)

ESTIMATE FOR: ROTARY COOLERS: 6'X30' - STEEL W/REFRACTORY LINING.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	ROTARY COOLERS	2	EA	150,00				300000				
	QUOTE VULCAN 150,000 EACH											
								300000				

5 EST-9 REV. 6/78

MAIN ITEM NO. B-8

IRON RECOVERY

C-1 Blending Conveyor
= 75% of B-9 X

C-2 Blending Bin - FOUR X
3.6m D (12 ft) x 9.0m H (30 ft) conical bottom - EACH
Steel Construction - 50mm (2") Wood lining

C-3 Ball Mill Conveyor Feeder (TWO) X
- 15% C-1

C-4 Ball Mill (TWO)
2.5m D (8 ft) x 4.5m L (15 ft)
20 RPM - Balls: 100mm (4")
Rubber Lined

C-5 Pug Mill Conveyor Feeder (TWO) X
50% C-3

C-6 Pug Mill (TWO)
1.00m W (3'4") x 3.50m L (12') x 0.60m H (24").
Double Paddle.
Manganese Steel Lining - Stellite Tips

C-7 Balling Disc Conveyor Feeder (TWO) X
Same as C-5 - Vide Supra

C-8 Balling Disc (TWO)
3.65 m Diam. (12'); 0.80m depth (32")
45° Slope - 10 RPM
2 x 120,000 = 240,000

C-9 Green Balls Conveying System X
$ = 50% B-9

C-10 CONVEYOR DRYER Proctor Schwartz 9/18/79 called
25 DMTPH, 12% H_2O, 250°C discharge temperature
1 @ 2 14'-7" x 145'
$ 457,000 letter
Proctor Schwartz 9/19/79

C-11 DRY PELLETS CONVEYOR X
$ = 50% C-9

C-12 ROTARY KILN Vulcan 9/17/79
TWO SECTIONS 3.0m I D x 20m L followed by 3.5m ID x 80m L
TWO burners, 1250°C, 0.6 to 1.0 RPM. High temperature zone alumina brick, firebrick refractory bricks, other zones

C-13 SHAFT COOLER
DESIGN - 25 MTPH x 3 ÷ 3 = 25 M³

C-14 IRON PELLETS CONVEYING SYSTEM X
$ = 39

C-15 PELLETS BINS (4) X 4 BINS
Concrete, 4.6 m ϕ (15 ft) x 12 m H (40 ft) each

C-16 DUST CHAMBER
10 only 20,000 PER LARSEN

C-17 GAS COOLING TOWER Two Cylindrical Sections. Inlet Section 1.6 m ϕ (5.25) x 6.0 m (19.7) mild steel rubber & acid proof brick lined. Outlet Section 3.4 ϕ (11'6") x 7 m (23'). rubber & silicon carbide brick lined. Connection Ti Pd alloy line + Ti nozzles $25,000 allowance 75000 V.

C-18 GAS WASH TOWER
TCA Scrubber FRP Construction 9.2 m ϕ (7.22') x 9 m H (29.53') with 2 stages each 0.25 m H (0.82') packed with 1½" ϕ hollow spolypropylene Spheres (416-675 5544) Dominic Chung 1@55000

C-19 MIST COTTRELL (TWO)
each 14,000 NM³/hr, 40°C

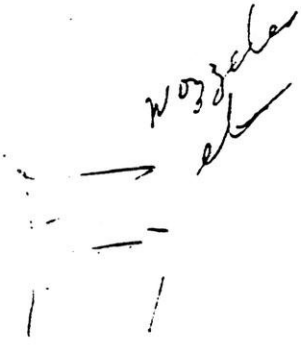
C-20 STACK BLOWER - Rubber lined
28,000 NM³/hr 18" H₂O suction
20,000 ACFM.

C-21 STACK 150' High 3'6" to 2'6" C.S. Steel
NO LINER

C-22 SOLUTION COOLER (2)
TCA Scrubber FRP Construction 2.7m ϕ by 9.0m H with 2 stages, each 0.25m High packed with 1½" ϕ hollow propylene spheres (416-6755544) D Chemg. (2-70p70)

C-23 GAS COOLING TOWER RECYCLING PUMP
3000 GPM 150 feet head 150HP R.V.

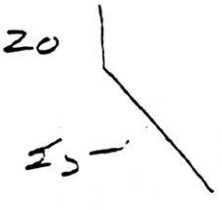
C-24 WASH TOWER EFFLUENT PUMP
Same ~ C-23



C-25 WASH TOWER RECYCLING PUMP
Same ~ C-23 X

C-26 SOLUTION COOLER AIR BLOWER
2 ea. @ 40,000 ACFM
or 1 @ 80,000 ACFM.

C-27 RECYCLE SETTLER R.L. Stahl.
15'ϕ - 20' wall.



Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT)

Estimate No. 2301 A
Sheet 1 of 3
Made by DVR Date 10-2-79

ESTIMATE FOR: AREA C - IRON RECOVERY

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
C-1	BLENDING CONVEYOR	EA	1		40000				
C-2	BLENDING BINS	EA	4		160000				
C-3	CONVEYORS FOR BALL MILL FEED	EA	2		30000				
C-4	BALL MILLS	EA	2		500000				
C-5	FEEDERS TO PUG MILLS	EA	2		20000				
C-6	PUG MILLS	EA	2		100000				
C-7	FEEDER TO BALLING DISCS	EA	2		20000				
C-8	BALLING DISCS	EA	2		240000				
C-9	CONVEYING SYS. FOR GREEN BALL	EA	1		40000				
C-10	DRYER - CONVEYOR	EA	1		460000				
C-11	CONVEYOR FOR DRY PELLETS	EA	1		40000				
C12	ROTARY KILN	EA	1		350000				
C-13	SHAFT COOLER	EA	1		140000				
	PAGE 1 TOTAL				2110000				

S EST 10 REV 6/79

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301A
Sheet 2 of
Made by DAP Date 10-2-79

ESTIMATE FOR: AREA C - IRON RECOVERY

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
C14	CONVEYING SYSTEM FOR PELLETS	EA	1		80000				
C-15	PELLET BINS	EA	4		140000				
C16	DUST CHAMBER	EA	1		20000				
C-17	GAS COOLING TOWERS	EA	1		90000				
C-18	GAS WASH TOWER	EA	1		40000				
C-19	MIST COTTRELL	EA	2		280000				
C-20	STACK BLOWER	EA	1		20000				
C21	STACK	EA	1		30000				
C22	SOLUTION COOLERS	EA	2		100000				
C23	PUMP FOR RECYCLING COOL TOWER	EA	1		10000				
C-24	PUMP - FOR WASH TOWER EFFLUENT	EA	1		10000				
C25	PUMP - FOR WASH TOWER RECYCLE	EA	1		10000				
C26	AIR BLOWERS FOR SOLUTION COOLER	EA	2		80000				
C-27	RECYCLE SETTLER	EA	1		30000				
					940000				

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301-A
Sheet 3 of 3
Made by [illegible] Date 10-12-79

ESTIMATE FOR: AREAC - IRON RECOVERY

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
	PAGE - 1				2110000				
	PAGE - 2				740000				
	TOTAL AREAC FACTOR (3)	D.C			3050000	x(3) =			9150000
	ADD FOR IND COST	25%							2290000
	TOTAL DC + IND COST								11440000
								50%	11,440,000

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A-

Sheet _____ of _____

Made by DMP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: BLENDING CONVEYOR 75% of B-9

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYOR 75% of B-9 (Spare for Conveyor)	1	Ea					40000				
								40000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-1

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DJP Date 10-1-79

QUANTITY: (4)

ESTIMATE FOR: BLENDING BINS 12'ϕ x 30' W/CONICAL BOTTOM - STEEL CONSTR. W/2" WOOD LINING

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R SIA: SHOPFAB	60	TON	1300					78000			
3639	TIMBER LINING	10	MBF	600					6000			
5100	GATES & FEEDING	4	EA	4000				16000				
								16000	84000			
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-2

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DDD Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: CONVEYORS FOR BALL MILL FEED- 15'x4 C-1

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYORS	2	ea	15000				20000				
								30000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-3

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A-

Sheet _____ of _____

Made by DDP Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: BALL MILLS 8'8" 15' RUBBER LINED

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BALL MILLS	2	ea	250000				500000				
	See Proposal											
								500000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-4

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by KWB Date 10-1-79

QUANTITY (2)

ESTIMATE FOR: FEEDERS - TO PUG MILLS 5100 W/ C-3

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	Feeders	2	@	X,XXX				20000				
								20000				

MAIN ITEM NO. C-5

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by BWK Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: PUG MILLS - 3'-4" x 12' x 2' HIGH W/ MANGANESE STEEL LINERS + STELLITE TIPS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	PUG MILLS	2	EA	EQUIP				100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-6

McK WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by ADP Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: FEEDERS TO GRILLING DISCS. SAME AS C-5

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	FEEDERS	2	EA	10000				20000				
								20000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-7

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-C

Sheet _____ of _____

Made by [illegible] Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: BALLING DISCS 12'ϕ X 32" dgth.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BALLING DISCS 12'ϕ X 32" dgth	2	EA.	120,000				240,000				
	PHONE QUOTE OF											
	CHARLIE SYSKO CLEVELAND											
								240,000				

5 EST-9 REV. 6/78

MAIN ITEM NO. C-8

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

QUANTITY: (1)

Made by DJD Date 10-1-77

ESTIMATE FOR: CONVEYING SYS. FOR GREEN BALLS (50% of C-9.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	EQUIP 50% of	1	Ea.					40000				
								40000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-9 N A W

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

QUANTITY: (1)

Made by DNO Date 10-1-79

ESTIMATE FOR: CONVEYOR DRYER - 14'-7"X 145' - 25d MTPH, @ 12% H2O - 250°C DISCHARGE TEMP

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	DRYER	1 ea						460000				
	Set											
								460000				

EST-9 REV. 6/78

MAIN ITEM NO. C-10

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DMD Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: CONVEYOR FOR DRY PELLETS (50% of C-9)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYOR	1	Ea					$40000				
	(50% of C-9)											
								$40000				

5 EST-9 REV. 6/78

MAIN ITEM NO. C-11

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

QUANTITY: (1)

Made by DDD Date 10-1-79

ESTIMATE FOR: ROTARY KILN - 2 SECTIONS - 1 SL. 3.4M x 20M - 2 nd 3.5M ϕ x 16 M L.
2 BURNERS 1250°C - REFRACTORY LINED

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	ROTARY KILN	1	EA					380000				
	QUOTE VALCOME											
	10-12-79											
								380000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-12

McKee wka

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DM Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: SHAFT COOLER - 25 MTPH. — 25 m³

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	SHAFT COOLER	1	ea					140000				
								140000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-13 247

McKee Wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by ~~DAD~~ Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: CONVEYING SYSTEM FOR TRAM PULLEYS (SAME AS 8-7)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYING SYS.	1	Ea.					80000				
								80000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-14

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301

Sheet _____ of _____

Made by [illegible] Date 10-1-79

QUANTITY: (4)

ESTIMATE FOR: PELLET BINS 15'ϕ x 40' - CONCRETE

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
2400	Conc Frcs.	140	cy.								20000	
2600	Conc Walls	400	cy	300							120000	
											140000	

140,000

MAIN ITEM NO. C-15

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: DUST CHAMBER -

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	DUST CHAMBER							20000				
								20000				

MAIN ITEM NO. C-16

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by BMP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: GAS COOLING TOWERS - 2-CYLINDRICAL SECTIONS - 1.6 M Ø x 6.5 M. - MILD STEEL R.L. RUBBER LINED
OUTLET SECTION 3.2 M Ø x 7 M. - R.L. & SILICON CARBIDE ACID BRICK LINED

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL TANKS	20	Ea	1300					26000			
3254	RUBBER LINING	1500	ft²	10					15000			
3700	ACID BRICK	1500	ft²	15.00					23000			
5100	MISC NOZZLES ETC PLEASE SEE 2500 FOR	1	Lot					25000				
	ph ch @ 80,000 base on.											
								90000				

MAIN ITEM NO. C-17

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by RRP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: GAS WASH TOWER - FRP CONSTRUCTION 22 MD x 8 ft dia - PACKED WITH 1½" 8 lb Low Density POLYPROPYLENE SPHERES

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3755	FRP TANK	1	EA.					3000				
5100	VALVES, SAMPLE COCK	1 LOT						1000				
	Rex to 55000							60000				
								64000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-18

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 - A

Sheet _____ of _____

Made by BDD Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: MIST COLLECTOR 14,000 Nm³/HR 40°C.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	MIST COLLECTOR	2	ea	140000				280000				
								280000				

9 EST-9 REV. 6/78

MAIN ITEM NO. C-19

253

McKee wka

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

QUANTITY: (1) = 20,000 ACFM

Made by [illegible] Date 10-2-79

ESTIMATE FOR: STACK BLOWER 28,000 NM³/HR 18" H₂O SUCTION

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	FAN	1	ea					20000				
	axflow											
								20000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-20 254

McKee wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DAP Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: STACK - 150' HIGH. 3'Ø & 2'Ø

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3705		20	Ton	1500				30000				
								30000				

MAIN ITEM NO. C-21

McKee wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DMR Date 10-1-78

QUANTITY: (2)

ESTIMATE FOR: SOLUTION COOLER - E.R.P. 23M Ø x 9.0M (29'-5") HIGH W/2 STAGES EACH 0.25M HIGH PANEL W/1½" ALLOWANCE FOR RAILS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5795	E.R.P. TANK COOLER	2	EA.	70000				140000				
								140000				

McKee wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DM Date 10-1-71

QUANTITY: (1)

ESTIMATE FOR: PUMP (FOR GAS COOLING TOWER RECYCLING) 3,000 GPM - 150' head 150 HP. K.L.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	PUMP	1	Ea					20000				
								Load				

3 EST-9 REV. 6/78

MAIN ITEM NO. C-23

McK wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by DMD Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: PUMP, (WASH TOWER EFFLUENT) SAME AS C-23

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	PUMP	1	Ea					10000				
								10000				

9 EST-9 REV. 6/78

MAIN ITEM NO. C-24

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by RMP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: PUMP (FOR WASH TOWER RECYCLING) SAME AS C-23

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	PUMP	1	Ea.					10000				
	Same as C-23											
								10000				

5 EST-9 REV. 6/78

MAIN ITEM NO. C-25

McK WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by RRP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: BLOWER FOR COOLER AIR BLOWER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5070	BLOWERS	2	EA	40,000				80000				
								80000				

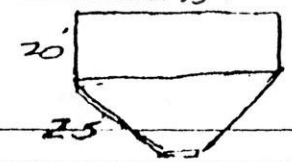
S: EST-9 REV. 6/78

MAIN ITEM NO. C-26

McKEE WKO

ESTIMATE WORKSHEET

DOMESTIC



Estimate No. 2301 A

Sheet _____ of _____

Made by RWD Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: RECYCLE SETTLER R.L. STEEL

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL OR TANK SHELL	15	TON	1,300					19500			
3254	R.L.	1700	#	5.00					8500			
									28000			

Say 39000.

S EST-9 REV. 6/78

MAIN ITEM NO. C-27

E48

NON FERROUS METALS

D-1 IRON PLANT BLEED THICKENER

D-2 CLARIFIED SOLUTION SURGE TANK 20 M^3 (706 ft^3) Volume
2.743 m dia. (9') x 3.353 m (11') high; PVC lined mild steel tank with closed top

D-3 LIMESTONE ADDITION TANK (TWO) WITH AGITATOR
Two 7.5 M^3 (264.8 ft^3) volume
2.133 m. dian. (7') x 2.133 m (7') high, PVC lined mild steel tank with closed top, four 0.2m (8") wide, 2m (6'6") long baffles. Each Tank with top mounted 0.71 M (2'4") diam. radial type turb. agitator with 50 HP motor (220rpm)

D-4 GYPSUM PRECIPITATION TANK WITH AGITATOR
one 150 M^3 (5296.5 ft^3) Volume
5.486 m dian (18') x 6.4 m (21') high, PVC lined mild steel tank closed top, four 0.54 m (1'9") wide, 6.1 m (20') long baffles. Top mount 1.829 m (6') diam. axial type turbine agitator with 50 HP motor (50 rpm)

D-5 GYPSUM THICKENER

D-6 GYPSUM FILTER

D-7 METALS SOLUTION SURGE TANK
SAME AS D-2 20M3

EL 9

9

D-8 KENNECOTT/CONE

D-9 CEMENT COPPER FILTER (TWO)

✓ D-10 LEAD PRECIPITATION TANK W. AGITATOR (ONE) X
ONE 4.0M³ (141.2 ft³)
1.676 m (5.5') diam. x 1.829 m (6') high rubber lined mild steel tank with closed top, four 0.152m (6") wide, 1.676m (5.5') long baffles
Top mounted 0.559 m (1'10") diam axial type turbine agitator with 1 HP m.

D-11 LEAD SULFIDE THICKENER

D-12 LEAD SULFIDE TAILINGS FILTER (TWO)

✓ D-13 IRON PRECIPITATION TANK (THREE) W. AGITATOR X
8.0M³ (282.5 ft³)
2.133 m diam (7') x 2.286m (7.5') high rubber lined mild steel tanks with closed top, four 0.2m (8") wide, 2.1 m (6'11") long baffles.
Each tank with top mounted 0.71 m. (2'4") diam axial type turbine agitator with 1 HP motor

D-14 IRON THICKENER

10

D-15 IRON FILTER (TWO)

D-16 ZINC PRECIPITATION TANK W. AGITATOR
8 m^3 (282.5 ft^3)
Same as D-13

D-17 ZINC THICKENER

D-18 ZINC FILTER

D-19 CALCIUM CHLORIDE SOLUTION SURGE TANK
20 M^3 (706 ft^3)
Same as D-2

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301 A
Sheet 1 of 2
Made by [illegible] Date 10-12-79

ESTIMATE FOR: AREA D - NON FERROUS METALS

F.S. No.	Item	Unit	Quantity	Manhours	* Process Equipment	Material	Labor	Subcontract	Total
D-1	THICKENER-FOR IRON PRECIP SOLN	EA	1		100000				
D-2	TANK-FOR CLARIFIED SOLUTION SURGE	EA	1		10000				
D-3	TANKS W/AGGIT. FOR LIMESTONE ADDITION	EA	2		20000				
D-4	TANK W/AGGITATOR FOR GYPSUM PRECIP	EA	1		50000				
D-5	THICKENER-GYPSUM	EA.	1		100000				
D-6	FILTER FOR GYPSUM	EA	1		75000				
D-7	TANK-METALS SOLUTION SURGE	EA	1		10000				
D-8	COPPER PRECIPITATION	EA			80000				
D-9	FILTERS FOR CEMENT COPPER	EA	2		24000				
D-10	TANK W/AGGIT FOR LEAD PRECIP.	EA	1		10000				
D-11	THICKENER FOR LEAD SOLN	EA	1		100000				
D-12	LEAD FILTERS	EA	2		24000				
D13	IRON PRECIP. TANKS	EA	3		30000				
					633000				

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301 A.
Sheet 2 of 2
Made by DMD Date 10-12-79

ESTIMATE FOR: AREA D - NON FERROUS METALS

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
D-14	IRON THICKENER	EA	1	120000					
D-15	IRON FILTER	EA	2	24000					
D-16	TANK W/AGITATOR	EA	1	10000					
D-17	THICKENER	EA	1	100000					
D-18	ZINC FILTER	EA	1	75000					
D-19	TANK FOR CACL. CHLORIDE	EA	1	10000					
	TOTAL PAGE 1			319000					
	TOTAL FROM PAGE 2			633000					
	TOTAL AREA D FACTOR (3)			952000	X(3)				2856000
	TOTAL D.C.								2856000
	ADD 25% FOR IND COST								720000
	TOTAL DC + IND COST								1580000
									1,600000

McKee Wiko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DLP Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: THICKENER (FOR IRON PLANT BLEED)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	24' THICKENER. TANK QUOTE.	1	ea					100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-1

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DDP Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: TANK-(FOR CLARIFIED SOLUTION SURGE) 8'ϕ x 11' HIGH W/CLOSED TOP MILD STEEL W/FRP LINING.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL TANK	35	Ea	130					4600			
3760	PVC LINING	440	ft²	50¢							2200	
									6600		2300	

14000

MAIN ITEM NO. D-2

EST-9 REV. 6/78

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by [illegible] Date 10-2-79

QUANTITY: (2)

ESTIMATE FOR: TANKS W/AGGITATOR - 7'ϕ X 7' HIGH W/CONICO TOP - MILD STEEL W/ PVC. LINING.
4-BAFFLES - 8" X 6'-6" - AGITATOR - 2'-4"ϕ RAD. TURBINE - 50 HP.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL PR TANK	4	TON	1300					5200			
37	PVC LINING	600	SF	500							3000	
5100	AGGITATOR - 50 HP 4500 1500 MOTOR COM. 6000	2	EA	6000				12000				
								12000	5200		3000	

20,000

S EST-9 REV. 6/78

MAIN ITEM NO. D.3

269

McKee Wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A-

Sheet _____ of _____

Made by LWD Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: TANK FOR GYPSUM PRECIPITATION W/AGITATOR - 18'8" X 21' HIGH W/CLOSED TOP MILD STEEL, P.V.C. LINED, CLOSED TOP - 4 BAFFLES 1'-9" X 20' - 6'8" AGIT. TURBINE 30HP

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL TANK	18	TON	1300					23400			
3700	P.V.C. LINING	2000	SF	.05/.10							10000	
5100	AGITATOR	1	EA					15000				
								15000	23400		10000	

50,000

MAIN ITEM NO. D-4

270

5 EST-9 REV. 6/78

McKee Wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by EMC Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: THICKNESS - FOR GYPSUM.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKNESS 24'0	1	EA.					100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-5

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: GYPSUM FILTER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	GYPSUM FILTER Belt Feller 316 SS + Vac Pump.	1	ea					75000				
								75000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-6

McKEE WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by LMD Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: TANK FOR METALS SOLUTION SURGE (Same as D-2)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL TANK	3 ½	TON	1,300					4600			
3715	PVC. LINING	440	ft²	@ 5/ft²							2200	

5 EST-9 REV. 6/78

allow - 7000

MAIN ITEM NO. D-7

McKee wkg

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

QUANTITY: (1) COPPER PRECIPITATION

ESTIMATE FOR: KENECOTT (OWEN)

Made by DSP Date 10-11-79

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3000	COPPER PRECIPITATION SYSTEM	1	ea					80000				
								80000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-8 274

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by BDP Date 10-12-79

QUANTITY: (2)

ESTIMATE FOR: FILTER FOR CEMENT CONVEY

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	FILTERS CE CONVEY	2	EA	12,000				24000				
								24000				

S-EST-9 REV. 6/78

MAIN ITEM NO. D-9

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A -

Sheet _____ of _____

Made by DRR Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: TANK W/AGITATOR, FOR LEAD PRECIPITATION - 55% 6' HIGH W/CLOSED TOP (170 "P AXIAL TURBINE IMP) 4-BAFFLES 6"x 55" LONG; MILD STEEL W/RUBBER LINED.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R. TANK	1	Ea	1300					2000			
3754	R. L	200	ft	8.00							1600	
5100	AGITATOR.	1	Ea					3000				
								3000	2000		1600	
								6600				

S EST-9 REV. 6/78

MAIN ITEM NO. D-10

McKee Wkg

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by BMD Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: THICKENER - FOR LEAD SULFIDE

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKENER	1 ea						100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-11

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by [illegible] Date 10-12-79

QUANTITY: (2)

ESTIMATE FOR: FILTERS - FOR LOAD

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	FILTERS	2	Ea					24000				
								24000				

5 EST-9 REV. 6/78

MAIN ITEM NO. D-12

McKEE WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (3)

ESTIMATE FOR: TANKS W/AGITATORS - M.S. R.L.; CLOSED TOP; 7'Ø x 7.5' HIGH; AGIT 2-4" AXIAL FLOW

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R TANKS	5	Ea	1,300					6500			
3754	RUBBER LINED	650	D'	8.00							5200	
5100	AGITATORS	3	Ea	6000				18000				
								18000	6500		5200	
								29,700				
								30,000				

S. EST-9 REV. 6/78

MAIN ITEM NO. D-13

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 23014

Sheet _____ of _____

Made by DMP Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: IRON THICKENER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKENER	1	ea					100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-14

280

McKEE WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DMP Date 10-12-79

QUANTITY: (2)

ESTIMATE FOR: IRON FILTERS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours S/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	FILTERS	2	Ea	12000				24000				
								24000				

MAIN ITEM NO. D-13

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 23018-

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: TANK W/AGITATOR FOR ZINC PRECIPITATION (SAME D-13)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R. TANK	2	EA	1300					2600			
3754	RUBBER LINED	210	SF	8.00							1700	
5100	AGITATORS	1	EA	6000				6000				

10,000

MAIN ITEM NO. D-16

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by DMC Date 10-12-75

QUANTITY: (1)

ESTIMATE FOR: ZINC THICKENER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKENER	1 ea						100000				

MAIN ITEM NO. D-17

S EST-9 REV. 6/78

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A -

Sheet _____ of _____

Made by BMS Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: ZINC FILTER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	ZINC FILTER 8'x8' Rotary Drum-filter + V.D.C. Pump	1	EA					75000				
								75000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-18

McKEE WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A.

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: TANK FOR CALCIUM CHLORIDE SOLUTION SURGE TANK SAME AS D-2

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL A TANK	3	TOT	1500					4600			
3760	PVC LINING	440	#	5.50							2200	
								10000				

MAIN ITEM NO. D-19

S EST-9 REV. 6/78

Davy McKee Corporation

CALCULATION SHEET

BY EDP DATE 10-11-79 SUBJECT Costs/Lurgi Sizes SHEET NO. ____ OF ____

CHKD. ____ DATE ____ JOB NO. 2301A

EACH

each 24' Thickener, Tank & Mechanism Lined $100,000 each

9-12 Each Filter Presses ~~10,000~~ 12,000 each

2 each (one) Gypsum filter Model 2612 Eimco Extractor (hood + oil seal-filter 316 S.S. $75,000
Vacuum pump

10 each (one) Zinc filter 8' x 8' Rotary drum filter + Vac pump Plastic $75,000

B8 Rotary Coolers Each @ $150,000

C-19 Mist Collector (includes support steel) each $140,000

B-6 Electrostatic Precipitator (includes support steel) each $450,000

$10,000,000
400,000
$2 x 150 300,000
1.7
Area B

Roasting

D-8 Copper Precipitation System $80,000

C-12 Kiln 380,000

C-13 Shaft Cooler 140,000

C-4-5 Storage Building & Reclaimer Total 2,400,050 Lkd 10% each

B-3 Roaster, etc 10,000,000 x 1.65

Total 16,500,000

Rec'd 9-27-79 BMP

SCM PROCTOR & SCHWARTZ INC.
SUBSIDIARY OF SCM CORPORATION

7TH STREET & TABOR ROAD, PHILADELPHIA, PENNSYLVANIA 19120

REPLY TO:
PROCTOR & SCHWARTZ, INC.
6455 Almaden Expressway
San Jose, California 95120
Phone: (408) 997-1768

PHONE: (215) 329-6400
(TWX): 710-670-8886
CABLE: "PROCTOR"

September 19, 1979

Arthur G. McKee Co.
2700 Campus Dr.
San Mateo, CA 94403

Attn: Armondo Lonzo, Project Manager

Subject: Budget Estimate for Drying Iron Pyrite Pellets

Dear Mr. ALonzo:

Thank you for calling PROCTOR & SCHWARTZ, INC. yesterday requesting budget estimates for drying Iron Pyrite Pellets. It was good to talk with you again.

For the budget estimate you requested, I utilized the specifications you gave me by phone which are listed below. I also made two assumptions from the data: (1) The drier length and width of the unit you saw in Japan were the conveyor dimensions, and (2), the bulk density of the Iron Pyrite was given at a Bone Dry weight. The estimated prices of the units follow the specifications.

Specifications:

Japanese Drier Size:	2-1/2 meters x 30 meters (assumed conveyor dimension)
Total Capacity:	12-1/2 metric tons/hr. (on above machine) 25 metric tons/hr. total required
Bulk Density:	3.0 kilograms/liter = 187 lbs./ft.^{3}
Maximum Air Temp.:	250°
Initial Moisture Control:	12%
Final Moisture Content:	0.3 - 0.5%
Load Depth:	150 mm 6 inches

Job Lexington, N. C.
weight

September 19, 1979

C-10

Estimated Budget Prices

Description	12.5 Metric Tons/Hr.	25 Metric Tons/Hr.
Overall length, ft. (includes dryer feed and delivery end extentions	approx. 93'	approx. 145'
Overall width, ft.	approx. 12' - 7"	approx. 14' - 7"
Conveyor Belt Width	10' - 6"	12' - 6"
Total Estimated Base Price including circulating fans gas burners, exhaust fans and motors	$251,000.00	$420,000.00
Oscillating spreader conveyor at feed end, hydraulically operated	$ 13,000.00	$ 13,000.00
Power/Control Cubical	$ 18,000.00	$ 24,000.00
Quantity required for 25 metric ton/hr. capacity	2	1

The units priced above include the following features:

1. Special heavy duty construction of 3" square tubular steel with all metal 16 gauge or lighter of aluminized steel and all metal 14 gauge or heavier covered with epoxy.

2. Dryers have our "all door" construction for easy accessability to the internal body for periodical cleaning.

3. Insulation provided throughout the dryer of 4" fiberglass including the doors, subfloor, ceiling and dryer end panels.

4. Gas burners with indicating temperature controllers and burner safety controls.

5. Circulating and exhaust fans, centrifugal type, with motors.

6. Variable speed conveyor drive for mild steel constructed perforated conveyor.

7. Oscillating conveyor feeder at the feed end to distribute product evenly across the perforated conveyor bed.

8. Power/Control Cubical including recording temperature controllers, flame safety devices, motor starters, main power disconnect, all prewired internally.

Again, thank you very much for calling PROCTOR & SCHWARTZ to request our pricing for this equipment. If we can be of service to you in answering any questions, please do not hesitate to call us.

Very truly yours,

PROCTOR & SCHWARTZ, INC.

John M. Michalec
Sales Engineer

JMM:pf

Encl.: Bulletins: 563/75
492-1/74

cc: Craig Schoeller
Philadelphia

Davy McKee
ENGINEERS AND CONSTRUCTORS

October 12, 1979

Dr. Faustino Prado
Davy McKee Corporation
P.O. Box 5000
Lakeland, Florida 33803

Contract No. 2301A

Dear Dr. Prado:

Confirming our telephone conversation this afternoon, the estimated installed cost of the various sections of the pyrite treatment plant are as follows:

	Direct & Indirect Costs	
Section A	$ 4,000,000	- Pyrite Handling, etc.
Section B	$21,500,000	- Roasting
Section C	$11,400,000	- Iron Pellets
Section D	$ 1,600,000	- Non-Ferrous recovery
Total	$38,500,000	

These costs do not include escalation and contingency. I will mail to you next Monday copies of the estimate worksheets.

Yours truly,

DAVY McKEE CORPORATION

Armando Alonso

AA/kh

Total installed
Direct + indirect and Home office

Davy McKee
ENGINEERING AND CONSTRUCTION

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT FACTOR) + IND. COST

Estimate No. 2301A

Sheet _____ of _____

Made by DWD Date 10-12-77

ESTIMATE FOR: PYRITE PROCESS STUDY FOR EXXON MINERALS CO

AFFA

F.S.-No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total DC + IND Cost
A	RECIEVING STOCKPILE + RECLAIMING	1	Lot.						4000000
B	ROASTING	1	Lot						21500000
C	IRON RECOVER	1	LOT						11400000
D.	NON FERROUS METAL	1	LOT						1600000
	TOTAL DIRECT + INDIRECT COST W.O. ESCALATION, CONTINGENCY OR FEE.						Lump		38500000

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: PYRITE HANDLING - EQUIPMENT SHEET: 1 OF 1
CLIENT: EXXON DATE:
COMPUTED BY: FP CHKD. BY: AA JOB: 2489 CONTRACT NO.:

A-1 Receiver
9'W x 30'L x 10'H : Top to 30"W at bottom

A-2 Apron or Belt Feeder
36"W - @ 30 FPM - 36'Long - 25HP

A-3 Stockpiling Conveyor
420 MTPH - 125 m^3ph
24"W @ 225 fpm - 50HP
150m L - elevation 15m.

A-4 Storage - Covered stockpile
90m L x 30m W x 15m H - V Roof
Angle of Repose - 35°

A-5 Reclaimer
Rail mounted scrapper - electrical
80 MTPH

A-6 Reclaim Conveyor
80 MTPH - 25 m^3PH
18"W @ 125 fpm - 15HP
200m L - elevation 20m.

A-7 Reversible Conveyor
$ = 20% of A-6

Davy McKee

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT)

Estimate No. S.C. 2301A

Sheet _____ of _____

Made by RRP Date 9-28-79

ESTIMATE FOR: AREA A - RECEIVING STOCKPILING & RECLAIMING

F.S. No.	Item	Unit	Quantity	Manhours	Process * Equipment	Material	Labor	Subcontract	Total
A-1	RECEIVING HOPPER 9'X30'X10' H. CTER + 30° IN BOTTOM	1	EA.		40000				
A-2	APRON FEEDER 36"X36'-25HP	1	EA.		70000				
A-3	STOCKPILING CONVEYOR 30"X442' 50HP	1	EA		90000				
	ALLOWANCE FOR TRANSFER BELT ONLY								
DELETE A-4	STACKER-STERE-CONVEY 90M X 30M X 15M HIGH.	1	LOT		300000	MATERIAL			
DELETE A-5	FRONT END LOADERS 5 C.Y.	2	EA		300000				
ADD A-4-5	STORAGE BLDG W/RECLAIMER	1	LOT			1300.			2400000
A-6	HOPPER 10'X10'X10' TOP	1	EA.		20000				
A7	RECLAIM CONVEYOR 18"X282'-15HP	1	EA.		40000				
A8	REVERSIBLE CONVEYOR	1	EA.		10000				
									2400000
	FACTOR EQUIP X 3 =				270000	(3)	=		810000
	TOTAL D.C.								3210000
	ADD FOR IND. 25%								810000
	SUBTOTAL								4020000
	TOTAL AREA 7								4020000

S EST 10 REV 8/78 * TANKS, BINS, ETC.

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. SC. 2301 A

Sheet _____ of _____

Made by LWP Date _____

QUANTITY: (1)

ESTIMATE FOR: RECIEVING HOPPER - 9'x30' x 10'H

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R BINS	20	TON	1300					26000			
3200	GATES	1	ea					4000				
3715	AR. LINERS	10	TON	1000					10000			
								4000	36000			

40,000

MAIN ITEM NO. A1

3 EST-9 REV. 6/78

McK WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

QUANTITY: (1)

ESTIMATE FOR: APRON FEEDER 36"x36' LONG - 25HP

Made by RDS Date 9-28-79

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
51000	APRON FEEDER	1	Eq.					70000				
	J#02129. FS#1-603.											
	48"x27' long 1000 = 108"											
	Escal. 1.51% 4/1/80											
	= 62,537											
	2500 motor ikc											
	65,000											
								70,000				

S EST-9 REV. 6/78

MAIN ITEM NO. A-2

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by _____ Date 9-29-79

QUANTITY: (1)

ESTIMATE FOR: STOCPILING CONVEYOR 30"x492' - 50HP

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BELT CONVEYOR	1	lot					90000				
								90000				

S EST-9 REV. 6/78

MAIN ITEM NO. A-3

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 5C 2301A

Sheet _____ of _____

Made by DRP Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: STORAGE BUILDING WITH RECLAIMER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	STORAGE BUILDING WITH RECLAIMER	1 LOT									2400000	2400000
											2400000	2400000

S EST-9 REV. 6/78

MAIN ITEM NO. A-4-5

McKee Wkc

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. SC. 2301 A -

Sheet _____ of _____

Made by DWR Date 9-28-79

QUANTITY: (1) Lot

ESTIMATE FOR: STORAGE STOCKPILE 90M x 30M. x 15M High

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	Not Equip.											
	Allow for Blow on Tripper.							30000				
								80000				

S EST-9 REV. 6/78

MAIN ITEM NO. A-4

McK wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 5C 2301 A

Sheet _____ of _____

Made by DJP Date 9-28-79

QUANTITY: (2)

ESTIMATE FOR: FRONT END LOADERS - 5 Cu yds.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	FRONT END LOADERS	2	ea	150,000				300000				
								-300000				

A-5

S EST-9 REV. 6/78

MAIN ITEM NO. A-5

McKee wkg

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by GWD Date 9-28-79

QUANTITY: (1)

ESTIMATE FOR: HOPPER 10'X10' + 10' to 12° @ Sutton

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	HOPPER	10	TON	1300					13000			
6000	GATE CONTROLS	1	Lot					2000				
								2000	13000			

$15,000.
2000

MAIN ITEM NO. A-6

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by DJP Date 9-28-79

QUANTITY: (1)

ESTIMATE FOR: RECLAIM CONVEYOR 18" x 282' — 15 HP

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	Conveyor	1	EA.					40000				
								40000				

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by DSP Date 9-28-79

QUANTITY: (1)

ESTIMATE FOR: REVERSABLE CONVEYOR 20% of $ Cost of A-7

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours S/MH	Process Equipment	Material	Labor	Subcontract	Total
500U	REVERSIBLE CONVEYOR							10000				
								10000				

S EST-9 REV. 8/78

MAIN ITEM NO. A-8

SUBJECT: ROASTING - EQUIPMENT - Cap. Cost SHEET: 1 OF 2
CLIENT: EXXON DATE:
COMPUTED BY: EP CHKD. BY: AA JOB: 2985 CONTRACT NO.:

B-1 Surge Bin (TWO)
50 m^3 each (150 MT each)

B-2 Weigh Belt Feeder (TWO)
20 MTPH - each

B-3 Roaster (TWO) and auxiliaries
Dorr Oliver Package - see letter

B-4 Waste Heat Boiler (TWO) D.O. Package

B-5 Cyclones - Two Lines D.O. Package

B-6 Electrostatic Precipitator (TWO)
63,000 ACFM, 343°C each
66 lb/min dust ~ 7.3 grains/ACF
Enviro-tech Quote

B-7 Hot Cinder Conveying System
included in ~~Dorr~~ ~~Otto~~ Oliver Package
letter Aug. 3, 1979

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: ROASTING - EQUIPMENT - Cap. Cost SHEET: 2 OF 2
CLIENT: EXXON DATE:
COMPUTED BY: FP CHKD. BY: AA JOB: 2489 CONTRACT NO.:

B-8 Rotary Cooler (TWO)

6'ϕ x 30'L
Steel Construction, with brick and castable lining

Quote by Mr. Friend - Vulcan Iron Works
717-822-2161 - 9/19/79

B-9 Cooled Cinder Conveyor

100 MTPH - 30 m³ PH
18" W @ 125 fpm - 10 HP
100 mt L - elevation: 14 m.

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT)

Estimate No. 2301A
Sheet 1 of 1
Made by [illegible] Date 10-1-79

ESTIMATE FOR: AREA B - ROASTING

F.S. No.	Item	Unit	Quantity	Manhours	Process* Equipment	Material	Labor	Subcontract	Total
B-1	SURGE BINS-1 BOILER	EA	2		160000				
B-2	WEIGH BELT FEEDER	EA	2		60000				
B-3	ROASTERS W/AUXILLARIES: PRICE EACH / DORR OLIVER PACKAGE	EA	2					17000000	17000000
B-4	WASTE HEAT BOILER	EA	2	3x40/83	-0-				
B-5	CYCLONE LINES	EA	2	3x40/83	-0-				
B-6	ELECTROSTATIC PRECIPITATOR	EA	2	-	900000				
B-7	HOT CINDER CONVEYING SYS	EA	2	3x40/83	-0-				
B-8	ROTARY COOLER-6'x36' REFRACT LINED	EA	2	-	300000				
B-9	CONICO CINDER CONVEYOR W/TRIPPER	EA	1		80000				
	TOTAL							17000000	17000000
	FACTOR EQUIP. X 3				1500000				4500000
									21,500,000

S EST 10 REV. 6/78 *EQUIP. FOB PLANT FARM

McKee Wka

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A-

Sheet _____ of _____

Made by DSP Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: SURGE BINS 50 M³ EA (150 MT EA) SAY 6M ϕ x 6M.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R BINS	80	TONS	1300					104000			
3745	STEEL A.R LINER	40	TONS	1000					40000			
5100	CONE FEED	2	EA	8000				16000				
								16000	144000			

160,000

MAIN ITEM NO. B-1

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by BMG Date _____

QUANTITY (2)

ESTIMATE FOR: WEIGH BELT FEEDERS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BELT FEEDERS	2	EA.	30,000				60000				
								60000				

8 EST-9 REV. 6/78

MAIN ITEM NO. B-2 '307

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

QUANTITY: (2)

Made by RRR Date 10-1-79

ESTIMATE FOR: ROASTERS INCLUDING AUXILARIES (PARKERSBURG OLIVER PACKAGE)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	EQUIPMENT	1	Lot					10,000,000			1,000,000	
	DORR OLIVER QUOTE											
	COMPLETE PACKAGE -											
	EXCLUDING 2 ends of											
	B-3 - ROASTERS.											
	B-4 - WASTE HEAT BOILER											
	B-5 - CYCLONES											
	B-7 - HOT UNDER CONVEYOR.											
	10,000,000 LBS/HR FOUR											
	TONS/HR											
								10,000,000			1,000,000	11,000,000

5 EST-9 REV. 6/78

MAIN ITEM NO. B-3

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A.

Sheet _____ of _____

Made by [illegible] Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: WASTE HEAT BOILER COMPLETE

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
	INCL. W/ DOOR DELIVERY PACKAGE							-0-				

S EST-9 REV. 6/78

MAIN ITEM NO. B-4

308

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by _____ Date 10-1-79

QUANTITY: (2) LINES

ESTIMATE FOR: CYCLONES.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	ENCLOSED W/ DOCKSIDER PACKAGE							-0-				

S EST-9 REV. 6/78

MAIN ITEM NO. B-5

310

McKee WKC

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DDP Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: ELECTROSTATIC PRECIPITATORS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	ELECTROSTATIC PRECIPITATOR	2	EA	450,00				900,000				
	ENVIROTECH QUOTE 450,000											
								900,000				

9 EST-9 REV. 6/78

MAIN ITEM NO. B-6

3115

McK WKo

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by BNP Date Oct 4, 1977

QUANTITY: (1) LOT

ESTIMATE FOR: HOT CINDER CONVEYING SYSTEM.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
	PART OF DURR-DILLER QUOTATION							-0-				

MAIN ITEM NO. B-7

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DMR Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: CONVEYOR 18" x 330' - 10HP - W/TRIPPER.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
3100	Conveyor & Tripper	1						80000				
	See Calc											
								80000				

S EST-9 REV. 6/78

MAIN ITEM NO. B-9

81

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2501-A

Sheet _____ of _____

Made by BRP Date _____

QUANTITY: (2)

ESTIMATE FOR: ROTARY COOLERS: 6'X30' - STEEL W/REFRACTORY LINING

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	ROTARY COOLERS	2	EA	150,000				300000				
	QUOTE VULCAN 150,000 EACH											
								300000				

MAIN ITEM NO. B-8

DORR-OLIVER INCORPORATED

INTERNATIONAL HEADQUARTERS:
STAMFORD, CONNECTICUT 06904, U. S. A.
CABLE: DORROLIVER STAMFORD

August 3, 1979

Mr. Arthur Raub
Davy McKee Corporation
P.O. Drawer 5000
Lakeland, FL 33803

SUBJECT: Your Feasibility Study for Exxon-Crandon
Proposed FluoSolids FeS_2 Roasting System

Dear Mr. Raub:

We talked 16 July about the feasibility study you are conducting for Exxon-Crandon and the FeS_2 Roasting Section that would be a part of that study. This is to provide you with an order-of-magnitude price for a FluoSolids System to carry out this roasting step.

Here are the conditions on which this O/M estimate is based:

Feed Rate, dry basis, mtpd	764
Sulfur in FeS_2 Feed, percent	50
Feed Size, microns	all minus 20
Altitude	sea level
Number of Trains	two

Sketch Sk 8-2 is a flow sheet which shows the equipment included in the proposed FeS_2 roasting system. We recommend preparing a slurry of this minus 20-micron pyrite for optimum feeding to roasters. We would supply you with a method of feeding this pyrite in a non-liquid form if asked to do so. We expect, however, that feeding cake would result in less sulfur utilization, more interruptions to the flow of feed and more problems with fugitive dust at various points throughout the flow sheet.

We have indicated use of the well-known Lammont-type horizontal-flow boiler, but we would in all probability use a less-conservative selection based on our work in recent years with newer types for incinerators, fluidized bed boilers and

zinc roasters. As you know, the cost of the boiler is nearly half the cost of the pyrite roasting section.

We have shown a scrubber in Flowsheet SK 8-2 but did not include one in our O/M price. As you know, the scrubber is usually considered part of the acid plant.

We have indicated the use of a thickener with the scrubber and the possibility of recycling thickener underflow to the slurry preparation system.

Our estimate includes the following equipment on SK 8-2:

Slurry Preparation Section:	tk 203, tk 204, mx 205, tk 206
Slurry Storage Section:	tk 251 ab, P 253 abc, mx 254
Roasting Section:	re 101
Calcine Handling Section:	mx 501 and mx 502 and mx 503
Fluidizing Air Section:	bl 301
Hot Gas Handling System:	b 501, dc 701 ab
Instrumentation:	instrument and instrument panel for semi-automatic operation.

An order-of-magnitude price for the equipment listed would be: 10 million dollars, f.o.b. cars USA plant site.

Not included in the estimated price are items such as the following which are ordinarily supplied by the erection contractor:

equipment supports (except for roaster supports which are included)
access platforms
small piping, and lighting
motor starters
outside insulation

We would expect that the equipment included in our estimate could be erected and necessary erection supplies supplied for approximately 7 million dollars. Again, a big unknown in this estimate is the boiler that would be selected.

We would furnish an erection representative at the perdiem rate prevailing at that time plus expenses to assist with the use of our erection drawings. Also, of course, start-up service would be available at the rate in existence at that time.

DORR-OLIVER

None of these estimates include foundations, a building, substations, or the like.

We would like the opportunity of discussing this project with you and your client so that we could refine this estimate and make the flow sheet more closely fit with the rest of the complex. In the meantime if there are any questions which arise, please telephone.

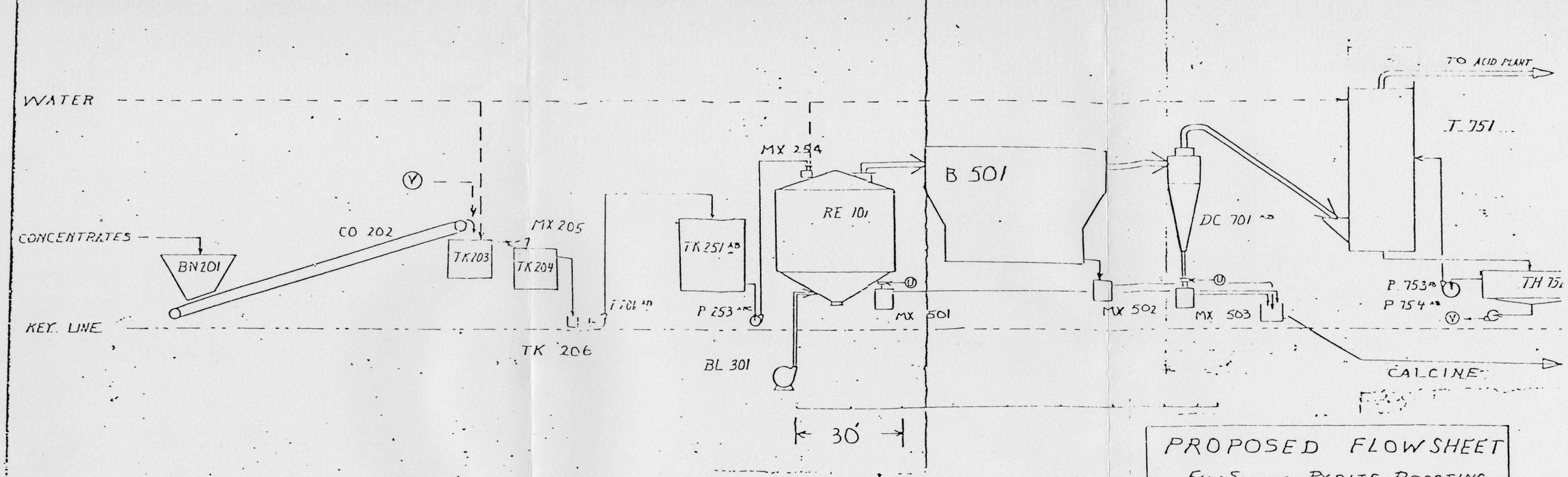
Very truly yours,

DORR-OLIVER INCORPORATED

L. V. Lee
Thermal Processing

LVL/mlm

Enclosures



PROPOSED FLOWSHEET

FLUOSOLIDS PYRITE ROASTING

6568 LVL SK8-2

DORR-OLIVER INCORPORATED

INTERNATIONAL HEADQUARTERS:
STAMFORD, CONNECTICUT 06904, U. S. A.
CABLE: DORROLIVER STAMFORD

August 22, 1979

Mr. Arthur L. Raub
Davy McKee Lakeland Inc.
P. O. Drawer 5000
Lakeland, FL. 33803

Re: FeS_2 Roasters
Exxon Minerals Co.

Dear Mr. Raub:

Thanks for the data on your minus 20-micron FeS_2 flotation concentrate. We are considering them. Here are preliminary comments.

We should run a laboratory test to see whether this pyrite may decrepitate more or not and to observe its pumpability ourselves.

We should further discuss how you will handle the Fe_2O_3 calcine. We may wish to follow the cyclones by an electrostatic precipitator instead of using so much power on the scrubber.

I will phone you when I return to Stamford in mid-September.

Yours very truly,

DORR-OLIVER INCORPORATED

L. V. Lee
Thermal Processing Division

LVL/vjl

cc: R. L. Klaer Atlanta
M. W. Brandt Ridge Manor

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: IRON RECOVERY - EQUIPMENT - COST Est. SHEET: 1 OF 5
CLIENT: EXXON DATE:
COMPUTED BY: F.P. CHKD. BY: AA JOB: 2489 CONTRACT NO.:

IRON RECOVERY

C-1 Blending Conveyor

= 75% of B-9

C-2 Blending Bin - FOUR

3.6 m D (12 ft) x 9.0 m H (30 ft) conical bottom
Steel construction - 50 mm (2") wood lining

C-3 Ball mill Conveyor Feed (TWO)

= 15% of C-1

C-4 Ball mill (TWO)

2.5 m D (8 ft) x 4.5 m L (15 ft)
20 RPM - Balls 100 mm (4")
Rubber Lined

C-5 Pug Mill Conveyor Feeder (TWO)

= 50% C-3

C-6 Pug Mill (TWO)
1.00 m W (3'4") x 3.50 m L (12') x 0.60 m H (24")
Double Paddle
Manganese Steel Lining - Stellite Tips

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: CCE - Iron Recovery - Equipment SHEET: 2 OF 5
CLIENT: Exxon DATE:
COMPUTED BY: FP CHKD. BY: AA JOB: 2489 CONTRACT NO.:

C-7 Balling Disc Conveyor Feeder (TWO)

Same as C-5

C-8 Balling Disc (TWO)

3.65m D (12'); 0.80m depth (32")
45° slope - 10 RPM

2 x $120,000 = $240.000

Charles Szako, Cleveland, by phone

C-9 Green Balls Conveying System

$ = 50% of B-9

C-10 Conveyor Dryer

25 dmtph, 12% H_2O - 250°C discharge

ONE 14'7" x 145' $

$457,000

letter Proctor & Schwartz 9/19/79

C-11 Dry pellets conveyor

$ = 50% of C-9

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: CCE-Iron Recovery - Equipment SHEET: 3 OF 5
CLIENT: Exxon DATE:
COMPUTED BY: EP CHKD. BY: AA JOB: 2489 CONTRACT NO.:

C-12 Rotary Kiln

Two sections: 3.0 m ID x 20. m L followed by 3.5m ID x 26 m L
Two burners, 1250°
0.6 to 1.0 RPM
Alumina brick High temperature zone
Fireclay Refractory Brick, other zones

Vulcan Iron Works - 9/19/79 phone # 380,000 Quote 10-12-79

C-13 Shaft Cooler

S. Mateo design: 25 M^3

C-14 Iron Pellets Conveying System

$ = B.9

C-15 Pellets Bin (4)

Concrete, 4.6 m ϕ (15ft) x 12 m H (40ft) each

C-16 Dust Chamber

Fabricated - carbon steel

$ 20,000 (local manufacturer estimate) Lakeland

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: CCE - Iron Recovery - Equipment SHEET: 4 OF 5
CLIENT: EXXON DATE:
COMPUTED BY: FP CHKD. BY: AA JOB: 2489 CONTRACT NO.:

C-17 Gas Cooling Tower
Two cylindrical sections.
Inlet section: 1.6m ϕ x 6.0m H mild steel
rubber & acid resistant brick lining
Oulet section: 3.4m ϕ x 7.0m H mild steel
rubber & silicon carbide brick lining.
Connection: Ti-Pd alloy line & Ti nozzles

C-18 Gas Wash Tower
TCA scrubber, FRP construction
2.2m ϕ x 9.0m H with two stages, each
packed with 1½" hollow polypropylene spheres

Dominic Chung - (416-675-5544)

C-19 Mist Cottrell (TWO)
Each 14,000 Nm^3/hr, 40°C

C-20 Stack Blower
28,000 Nm^3/hr - 20,000 ACFM - 18" H_2O suction
Rubber lined

C-21 Stack
150' high - 3' ϕ to 2' ϕ carbon steel
no liner

C-22 Solution Cooler (TWO)

TCA scrubber - FRP construction
2.7 m ϕ x 9.0 m H with two stages, each 0.25m high packed with 1½" hollow polypropylene spheres.

D. Chung (416-625-5548)
$ 70,000 - two

C-23 Gas Cooling Tower Recycling Pump

C-24 Wash Tower Effluent Pump

C-25 Wash Tower Recycling Pump

3,000 GPM each
150 feet head each
Rubber lined
150 HP each

C-26 Solution Cooler Air Blower (TWO)
40,000 ACFM each

C-27 Recycle Settler
15' ϕ x 20' side
Rubber Lined

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301 A
Sheet 1 of 3
Made by DWP Date 10-2-78

ESTIMATE FOR: AREA C - IRON RECOVERY

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
C-1	BLENDING CONVEYOR	EA	1		40000				
C-2	BLENDING BINS	EA	4		100000				
C-3	CONVEYORS FOR BALL MILL FEED	EA	2		30000				
C-4	BALL MILLS	EA	2		500000				
C-5	FEEDERS TO PUG MILLS	EA	2		20000				
C-6	PUG MILLS	EA	2		100000				
C-7	FEEDER TO BALLING DISCS	EA	2		20000				
C-8	BALLING DISCS	EA	2		240000				
C-9	CONVEYING SYS. FOR GREEN BALLS	EA	1		40000				
C-10	DRYER - CONVEYOR	EA	1		460000				
C-11	CONVEYOR FOR DRY PELLETS	EA	1		40000				
C12	ROTARY KILN	EA	1		330000				
C-13	SHAFT COOLER	EA	1		140000				
	PAGE 1 TOTAL				2110000				

S EST 10 REV. 6/78

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301A
Sheet 2 of
Made by DMP Date 10-2-79

ESTIMATE FOR: AREA C - IRON RECOVERY

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
C-14	CONVEYING SYSTEM FOR PELLETS	EA	1		80000				
C-15	PELLET BINS	EA	4		120000				
C-16	DUST CHAMBER	EA	1		20000				
C-17	GAS COOLING TOWERS	EA	1		70000				
C-18	GAS WASH TOWER	EA	1		40000				
C-19	MIST COTTRELL	EA	2		280000				
C-20	STACK BLOWER	EA	1		20000				
C-21	STACK	EA	1		30000				
C-22	SOLUTION COOLERS	EA	2		100000				
C-23	PUMP FOR RECYCLING COOL TOWER	EA	1		10000				
C-24	PUMP - FOR WASH TOWER EFFLUENT	EA	1		10000				
C-25	PUMP - FOR WASH TOWER RECYCLE	EA	1		10000				
C-26	AIR BLOWERS FOR SOLUTION COOLER	EA	2		80000				
C-27	RECYCLE SETTLER	EA	1		30000				
					844000				

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301-A
Sheet 3 of 3
Made by ~~DDD~~ Date 10-12-79

ESTIMATE FOR: AREAC - IRON RECOVERY

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
	PAGE - 1				2110000				
	PAGE - 2				740000				
	TOTAL AREAC FACTOR (3)	D.C			3050000	x(3) =			9150000
	ADD FOR IND COST	25%							2290000
	TOTAL DC + IND COST								11440000
								5%	11,440,000

S EST 10 REV 8/78

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A-

Sheet _____ of _____

Made by DJL Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: BLENDING CONVEYOR 75% of B-9

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours S/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYOR 75% of B-9 (Shown for Conveyor)	1	Ea					40000				
								40000				

MAIN ITEM NO. C-1

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet ____ of ____

Made by DAP Date 10-1-79

QUANTITY: (4)

ESTIMATE FOR: BLENDING BINS 12'ϕ x 30' W/CONICAL BOTTOM - STEEL CONSTR. W/2" WOOD LINING

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL FR SIDE SHORING	60	TON	1300					78000			
3639	TIMBER LINING	10	MBF	600					6000			
5100	GATES & FEEDING	4	EA	4000				16000				
								16000	84000			

100000

MAIN ITEM NO. C-2

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DDD Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: CONVEYORS FOR BALL MILL FEED. 15'W C-1

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYORS.	2	LC	15000				30000				
								30000				

MAIN ITEM NO. C-3

S EST-9 REV. 6/78

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A-

Sheet _____ of _____

Made by DWL Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: BALL MILLS 8'6" X 15' RUBBER LINED

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BALL MILLS	2	ea	250,000				500000				
	See Proposal											
								500000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-4

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2307 A

Sheet _____ of _____

Made by DWD Date 10-1-79

QUANTITY (2)

ESTIMATE FOR: FEEDERS - TAPUC MINES 5100 & C-3

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	Feeders	2	EA					20000				
								20000				

MAIN ITEM NO. C-5

McK WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by BWC Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: PUG MILLS - 3'-4" X 12' X 2' HIGH W/ MANGANESE STEEL LINING & STELLITE TIPS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	PUG MILLS	2	EA	EACH				100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-6

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by SPP Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: FEEDERS TO GRINDING DISCS. SAMPLE C-5

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	FEEDERS	2	EA	1000				20000				
								20000				

MAIN ITEM NO. C-7

S EST-9 REV. 6/78

McKee wka

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 3301-C

Sheet _____ of _____

Made by [illegible] Date 10-1-79

QUANTITY: (2)

ESTIMATE FOR: BALLING DISCS 12'ϕ X 32" d.ph.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	BALLING DISCS 12'ϕ X 32" d.ph.	2	EA.	120,000				240,000				
	PHONE QUOTE OF CHARLIE SPOKANEMAN											
								240,000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-8

335

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DDP Date 10-1-77

QUANTITY: (1),

ESTIMATE FOR: CONVEYING SYS. FOR GREEN ROLLS (50% of C-9.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	EQUIP 50% of	1	EA					40000				
								40000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-9

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by DJO Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: CONVEYOR DRYER - 14'-7" X 145' - 25 d MTPH, @ 12% H2O - 250° C DISCHARGE TEMP

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	DRYER	1 ea						$460000				
	Sel											
								$460000				

MAIN ITEM NO. C-10

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DMD Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: Conveyor for Dry Pellets (50% of C-9

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	Conveyor	1	Ea					40000				
	(50% of C-9)											
								40000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-11

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DDD Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: ROTARY KILN - 2 SECTIONS - 1st 3 M x 20 M - 2nd 3.5 ø x 16 M L.
2 BURNERS 1250°C - REFRACTORY LINED

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	ROTARY KILN	1	EA					580000				
	QUOTE VALCANO											
	10-12-79											
								380000				

McKee WKC

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DJO Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: SHAFT COOLER - 25 MTPH. — 25 M³

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5040	SHAFT COOLER	1	ea					140000				
								140000				

MAIN ITEM NO. C-13

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DAP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: CONVEYING SYSTEM FOR TRAY PALLETS (SAME AS A-7)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	CONVEYING SYS.	1	Ea.					80000				
								80000				

MAIN ITEM NO. A-14

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301

Sheet _____ of _____

Made by GMC Date 10-1-79

QUANTITY: (4)

ESTIMATE FOR: PELLET BINS 15'8" x 40' - CONCRETE

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
2400	Conc Frcs.	140	CY								200000	
2600	Conc Walls	400	CY	300							120000	
											140000	

140,000

MAIN ITEM NO. C-15

McKee wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: DUST CHAMBER -

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	DUST CHAMBER							20000				
								20000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-16

McKee WKo

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by MMP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: GAS COOLING TOWERS - 2-CYLINDRICAL SECTIONS - 1.6 M DIA x 6.5° M - MORTAR RL. BRICK
OUTLET SECTION 3.5 M DIA x 7 M - RL. + SILICON CARBIDE ACID BRICK M.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL TANKAGE	20	Ea	1300					26000			
3254	RUBBER LINING	1500	ft²	10					15000			
3700	ACID BRICK	1500	ft²	15.00					23000			
5100	MISC NOZZLES & ALLOW 2500 FOR	1 Lot						25000				
	OH CK @ 80,000 same as -											
								90,000				

MAIN ITEM NO. C-17

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by MRP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: GAS WASH TOWER, FRP CONSTRUCTION 22'0" x 8'0" dia. - PACKED WITH 1½" 8 lb. LOW DENSITY POLYPROPYLENE SPHERES

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
3255	FRP TANK	1	EA					39000				
5100	VALVES, Saddle collar	1	L-					16000				
	Rex No 55000							6000				
								61000				

MAIN ITEM NO. C-18

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 – A

Sheet _____ of _____

Made by BMD Date 10-1-77

QUANTITY: (2)

ESTIMATE FOR: MIST COTTRELL 14,000 Nm³/HR 40°C.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	MIST COTTRELL	2	ea	140000				280000				
								280000				

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

QUANTITY: (1)

Made by [illegible] Date 10-2-79

ESTIMATE FOR: STACK BLOWER 28,000 N M³/HR 18" H₂O SUCTION.
= 20,000 ACFM

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	FAN	1	Ea					20000				
	elbow											
								20000				

MAIN ITEM NO. C-20

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by Earl Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: STACK - 150' HIGH. 3'-0" & 2'-0"

Acct	Item	Quantity	U/M	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3705		20	Ton	1500				30000				
								30000				

MAIN ITEM NO. C-21

S EST-9 REV. 6/78

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by [illegible] Date 10-1-78

QUANTITY: (2)

ESTIMATE FOR: SOLUTION COOLER - E.R.P. 2.7M Ø x 9.0M HIGH W/2 STAGES TUBE 8.2' 29Ø 0.25 M HIGH BAFFLES W/1½" Ø ALLOWANCE FOR BAFFLES

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5795	ERP TANK COOLER	2	EA.	70000				140000				
								140000				

MAIN ITEM NO. C-22

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 23014

Sheet _____ of _____

Made by DM Date 10-1-71

QUANTITY: (1)

ESTIMATE FOR: PUMP (FOR GAS COOLING TOWER RECYCLING) 3,000 GPM - 150' head 150 HP. R.L.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	PUMP	1	Ea					20,000				
								20,000				

S EST-8 REV. 8/78

MAIN ITEM NO. A-23

350

McKee Wka

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by DMP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: PUMP, (WASH TOWER EFFLUENT) SAME AS C-23

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
6100	PUMP	1	ea					10000				
								10000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-24

351

McKee Wkg

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DZP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: PUMP (FOR WASH TRUCK RECYCLING) SAME AS C-23

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5100	PUMP	1	ea					10000				
	Same as C-23											
								10000				

9 EST-9 REV. 6/78

MAIN ITEM NO. C-25

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by AHP Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: BLOWER FOR COOLER AIR BLOWER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5070	BLOWERS	2	EA	40,000				80000				
								80000				

S EST-9 REV. 6/78

MAIN ITEM NO. C-26

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC



Estimate No. 2301 A

Sheet _____ of _____

Made by AMO Date 10-1-79

QUANTITY: (1)

ESTIMATE FOR: RECYCLE SETTLER R.L. STEEL

Acct	Item	Quantity	U/M	Unit Cost	Manhours Unit	Manhours Total	Manhours S/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R TANK SHELL	15	TON	1,300					19500			
3254	R.L.	1700	#	5.00					8500			
									28000			

Avg. 39000.

MAIN ITEM NO. C-27

Rec'd 9-27-79 SMD

PROCTOR & SCHWARTZ INC.
SUBSIDIARY OF SCM CORPORATION

7TH STREET & TABOR ROAD, PHILADELPHIA, PENNSYLVANIA 19120

REPLY TO:
PROCTOR & SCHWARTZ, INC.
6455 Almaden Expressway
San Jose, California 95120
Phone: (408) 997-1766

PHONE: (215) 329-6400
(TWX): 710-670-8886
CABLE: "PROCTOR"

September 19, 1979

Arthur G. McKee Co.
2700 Campus Dr.
San Mateo, CA 94403

Attn: Armondo Lonzo, Project Manager

Subject: Budget Estimate for Drying Iron Pyrite Pellets

Dear Mr. ALonzo:

Thank you for calling PROCTOR & SCHWARTZ, INC. yesterday requesting budget estimates for drying Iron Pyrite Pellets. It was good to talk with you again.

For the budget estimate you requested, I utilized the specifications you gave me by phone which are listed below. I also made two assumptions from the data: (1) The drier length and width of the unit you saw in Japan were the conveyor dimensions, and (2), the bulk density of the Iron Pyrite was given at a Bone Dry weight. The estimated prices of the units follow the specifications.

Specifications:

Japanese Drier Size:	2-1/2 meters x 30 meters (assumed conveyor dimension)
Total Capacity:	12-1/2 metric tons/hr. (on above machine) 25 metric tons/hr. total required
Bulk Density:	3.0 kilograms/liter = 187 lbs./ft.^{3}
Maximum Air Temp.:	250°
Initial Moisture Control:	12%
Final Moisture Content:	0.3 - 0.5%
Load Depth:	150 mm 6 inches

Job Lexington, N.C.
weight

September 19, 1979

C-10

Estimated Budget Prices

Description	12.5 Metric Tons/Hr.	25 Metric Tons/Hr.
Overall length, ft. (includes dryer feed and delivery end extentions	approx. 93'	approx. 145'
Overall width, ft.	approx. 12' - 7"	approx. 14' - 7"
Conveyor Belt Width	10' - 6"	12' - 6"
Total Estimated Base Price including circulating fans gas burners, exhaust fans and motors	$251,000.00	$420,000.00
Oscillating spreader conveyor at feed end, hydraulically operated	$ 13,000.00	$ 13,000.00
Power/Control Cubical	$ 18,000.00	$ 24,000.00 ~~$ 24,000.00~~
Quantity required for 25 metric ton/hr. capacity	2	1

The units priced above include the following features:

1. Special heavy duty construction of 3" square tubular steel with all metal 16 gauge or lighter of aluminized steel and all metal 14 gauge or heavier covered with epoxy.

2. Dryers have our "all door" construction for easy accessability to the internal body for periodical cleaning.

3. Insulation provided throughout the dryer of 4" fiberglass including the doors, subfloor, ceiling and dryer end panels.

4. Gas burners with indicating temperature controllers and burner safety controls.

5. Circulating and exhaust fans, centrifugal type, with motors.

6. Variable speed conveyor drive for mild steel constructed perforated conveyor.

7. Oscillating conveyor feeder at the feed end to distribute product evenly across the perforated conveyor bed.

8. Power/Control Cubical including recording temperature controllers, flame safety devices, motor starters, main power disconnect, all prewired internally.

Again, thank you very much for calling PROCTOR & SCHWARTZ to request our pricing for this equipment. If we can be of service to you in answering any questions, please do not hesitate to call us.

Very truly yours,

PROCTOR & SCHWARTZ, INC.

John M. Michalec
Sales Engineer

JMM:pf

Encl.: Bulletins: 563/75
492-1/74

cc: Craig Schoeller
Philadelphia

SUBJECT: Nonferrous - EQUIPMENT SHEET: 2 OF 3
CLIENT: EXXON DATE:
COMPUTED BY: FP CHKD. BY: AA JOB: 2489 CONTRACT NO.:

D-6 Gypsum Filter

Belt Filter 316 SS & Vacuum System

D-7 Metals Solution Surge Tank
same as D-2

D-8 Copper Precipitation System

D-9 Cement Copper Filter (TWO)
Filter Press - Plate & Frame

D-10 Lead Precipitation Tank w. Agitator

4. m^3 - 5.5'ϕ x 6'H, closed top
Rubber lined mild steel, baffled
22" diam. axial type turbine -
1 HP

D-11 Lead Sulfide Thickener
same as D-1

D-12 Lead Filter (TWO)
same as D-9

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: NONFERROUS · EQUIPMENT · Cap. Cost SHEET: 1 OF 3
CLIENT: EXXON DATE:
COMPUTED BY: FP CHKD. BY: AA JOB: 2489 CONTRACT NO.:

D-1 Iron Plant Bleed Thickener

24' ϕ - rubber lined, steel construction

D-2 Clarified Solution Surge Tank
20 m³
9' ϕ x 11' H - PVC lined, mild steel - covered

D-3 Limestone Addition Tank (TWO)
with agitator
7.5 m³ each - 7' ϕ x 7' H
PVC lined mild steel construction, cosed top
4 baffles each tank
Top mounted 28" diam. radial type turbine
220 RPM, 50 HP each

D-4 Gypsum Precipitation Tank with agitator
150 m³ volume - 18' ϕ x 21' H, closed top
PVC lined mild steel construction
Baffles: four
Top mounted, 6' diam. axial type turbine
agitator - 50 RPM - 50 HP motor

D-5 Gypsum Thickener
24" ϕ - Mild Steel, rubber lined
Same as D-1

Davy McKee
ENGINEERS AND CONSTRUCTORS

ENGINEERING COMPUTATION SHEET
DAVY McKEE LAKELAND INC.
LAKELAND, FLORIDA

Form # 624

SUBJECT: Non Ferrous - EQUIPMENT - C.C. SHEET: 3 OF 3
CLIENT: EXXON DATE:
COMPUTED BY: FP CHKD. BY: AA JOB: 2989 CONTRACT NO.:

D-13 Iron Precipitation Tank (THREE) with Agitator

8.0 m³ each - 7'Φ x 7.5'H
Rubber lined mild steel, closed top, baffled
Top mounted 28" diam. axial type turbine
1 HP each

D-14 Iron Thickener
same as D-1

D-15 Iron Filter (TWO)
same as D-9

D-16 Zinc Precipitation Tank w. Agitator (ONE)
same as D-13

D-17 Zinc Thickener
same as D-1

D-18 Zinc Filter

8'Φ x 8'W Rotary drum filter
with vacuum system

D-19 Calcium Chloride Solution Surge Tank
same as D-2

Davy McKee
ENGINEERS AND CONSTRUCTORS

ESTIMATE SUMMARY
(DIRECT COST BY EQUIPMENT)

Estimate No. 2301 A
Sheet 1 of 2
Made by DRS Date 12-12-79

ESTIMATE FOR: AREA D - NON FERROUS METALS

F.S. No.	Item	Unit	Quantity	Manhours	* Process Equipment	Material	Labor	Subcontract	Total
D-1	THICKENER-FOR IRON PRECIP	EA	1		100000				
D-2	TANK-FOR CLARIFIED SOLUTION SURGE	EA	1		10000				
D-3	TANKS W/AGGIT. FOR LIMESTONE ADDITION	EA	2		20000				
D-4	TANK W/AGGITATOR FOR GYPSUM PRECIP	EA	1		50000				
D-5	THICKENER-GYPSUM	EA.	1		100000				
D-6	FILTER FOR GYPSUM	EA	1		75000				
D-7	TANK-METALS SOLUTION SURGE	EA	1		10000				
D-8	COPPER PRECIPITATION	EA			80000				
D-9	FILTERS FOR CEMENT COPPER	EA	2		24000				
D-10	TANK W/AGGIT FOR LEAD PRECIP.	EA	1		10000				
D-11	THICKENER FOR LEAD SULFIDE	EA	1		100000				
D-12	LEAD FILTERS.	EA	2		24000				
D13	IRON PRECIP. TANKS	EA	3		30000				
					633000				

S-ESI-10 REV. 8/78

THICKENER TANKS RING

Davy McKee

ESTIMATE SUMMARY

(DIRECT COST BY EQUIPMENT)

Estimate No. 2301 A

Sheet 2 of 2

Made by DMP Date 10-12-79

ESTIMATE FOR: AREA D - NON FERROUS METALS

F.S. No.	Item	Unit	Quantity	Manhours	Process Equipment	Material	Labor	Subcontract	Total
D-14	IRON THICKENER	EA	1	120000					
D-15	IRON FILTER	EA	2	240000					
D-16	TANK W/AGITATOR	EA	1	10000					
D-17	THICKENER	EA	1	100000					
D-18	ZINC FILTER	EA	1	75000					
D-19	TANK FOR CACL. CHLORIDE	EA	1	4000					
	TOTAL PAGE 1			319000					
	TOTAL FROM PAGE 2			633000					
	TOTAL AREA D FACTOR (3)			952000	X(3)				2856000
	TOTAL D.C.							10%	2860000
	ADD 25% FOR IND COST								720000
	TOTAL D.C. + IND COST								1580000
								10%	1600000

S EST 10 REV. 0/78

362

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DJP Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: THICKENER (FOR IRON PLANT BLEED)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	24' THICKENER. T&K QUOTE.	1	Ea					100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-1

303

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DDP Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: TANK-(FOR CLARIFIED SOLUTION SURGE) 9'ϕ x 11' HIGH W/CLOSED TOP MILD STEEL W/FRP LINING.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL & TANK	35	Lbs	1.30					$450			
3260	PVC LINING	440	ϕ'	5.00							2200	
									$600		2200	

19000

S EST-9 REV. 6/78

MAIN ITEM NO. D-2

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DPL Date 10-2-79

QUANTITY: (2)

ESTIMATE FOR: TANKS W/AGGITATOR - 7'ØX7' HIGH W/CONICO TOP - MILD STEEL W/PVC. LINING.
4-BAFFLES - 8" X 6'-6" - AGITATOR - 2'-0"Ø RAD. TURBINE - 50HP.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL & TANK	4	TON	1300					5200			
37	PVC LINING	600	SF	500							3000	
5100	AGGITATOR - 50HP 4500 1500 MOTOR ADJ 6000	2	EA	6000				12000				
								12000	5200		3000	

20,000

9 EST-9 REV. 6/78

MAIN ITEM NO. D.3

365

McKee Wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A-

Sheet _____ of _____

QUANTITY: (1)

Made by RWD Date 10-2-79

ESTIMATE FOR: TANK FOR GYPSUM PRECIPITATION W/AGITATOR - 18'8" X 21' HIGH W/CLOSED TOP MILD STEEL, P.V.C. LINED, CLOSED TOP - 4 BAFFLES 1'-8" X 20' - 6'8" DIA SIDE TURNING SOLE

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL TANK	18	TON	1300					23400			
3700	P.V.C. LINING	2000	S.F.	.05/S.F.							10000	
5100	AGITATOR	1	EA					15000				
								15000	23400		10000	

50,000

MAIN ITEM NO. D-4

S EST-9 REV. 6/78

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by DRP Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: THICKENER FOR GYPSUM.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKENER 24'ϕ	1	EA					100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-5

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: GYPSUM FILTER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	Gypsum Filter Delt Fellon 316 SS + Vac Pump.	1	ea					75000				
								75000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-6

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by RMD Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: TANK FOR METALS SOLUTION SURGE (SAME AS D-2)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL B TANK	3.5	TON	1300					4600			
3760	PVC. LINING	440	SF	@5.50							2200	

add'l - 10,000

MAIN ITEM NO. D-7

S EST-9 REV. 8/78

369

McKee Wke

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. _____

Sheet _____ of _____

Made by DJP Date 10-11-78

QUANTITY: (1) COPPER PRECIPITATION

ESTIMATE FOR: KENNECOTT (ONEA)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
600V	COPPER PRECIPITATION SYSTEM	1	EA					80000				
								80000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-8

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by RAP Date 10-12-79

QUANTITY: (2)

ESTIMATE FOR: FILTERS FOR CEMENT CRUSH

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	FILTERS CR CRUSH	2	EA	12,00				24000				
								24000				

5 EST-9 REV. 8/78

MAIN ITEM NO. D-9

371

McKee WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A -

Sheet _____ of _____

Made by DRP Date 10-2-79

QUANTITY: (1)

ESTIMATE FOR: TANK W/AGITATOR FOR LEAD PRECIPITATION - 5'5"R 6' HIGH W/CLOSED TOP (1470 # AXIAL TURBINE HP) 4-BAFFLES 6"x 5'-10" LONG ; MILD STEEL W/RUBBER LINED.

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R TANK	1	EA	1300					2000			
3754	R. L	200	LF	8.00							1600	
5100	AGITATOR.	1	EA					3200				
								3000	2000		1600	
									6600			

SAY 10,000

MAIN ITEM NO. D-10

372

5 EST-9 REV. 6/78

McKee Wiko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by BMP Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: THICKENER - FOR LEAD SULFIDE

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKENER	1 ea						100000				
								100000				

9 EST-9 REV. 6/78

MAIN ITEM NO. D-11

McK WKo

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by _____ Date 10-12-79

QUANTITY: (2)

ESTIMATE FOR: FILTERS - FOR LEAD

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	FILTERS	2	Ea					24000				
								24000				

MAIN ITEM NO. D-12

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (3)

ESTIMATE FOR: TANKS W/AGITATORS - M.S. R.L.; CLOSED TOP; 7'Ø x 7'5" HIGH; AGIT 2-4" AXIAL FLOW

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R TANKS	5	Tnk	*1,300					6500			
3754	RUBBER LINER	650	SF	8.00							5200	
5100	AGITATORS	3	Ea	6010				18000				
								18000	6500		5200	

3,200

30,000

MAIN ITEM NO. D-13

S EST-9 REV. 6/78

375

McKee wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by RMP Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: IRON THICKENER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKENER	1	ea					100000				
								100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-14

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301-A

Sheet _____ of _____

Made by DRP Date 10-12-79

QUANTITY: (2)

ESTIMATE FOR: IRON FILTERS

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
50000	FILTERS	2	ea	12000				24000				
								24000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-15

McKee Wko

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A-

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: TANK W/AGITATOR FOR ZINC PRECIPITATION (SAME D-13)

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
3210	STEEL R TANK	2	Ea	1300					2600			
3754	RUBBER LINED	210	ft²	8.00							1700	
5100	AGITATORS	1	Ea.	4000				4000				
								10,000				

MAIN ITEM NO. D-16

McKEE WKG

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301A

Sheet _____ of _____

Made by DMD Date 10-12-78

QUANTITY: (1)

ESTIMATE FOR: ZINC THICKENER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	Manhours $/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	THICKENER	1 ea						100000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-17

McKee wka

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A -

Sheet _____ of _____

Made by DMS Date 10-12-79

QUANTITY: (1)

ESTIMATE FOR: ZINC FILTER

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	$/MH	Process Equipment	Material	Labor	Subcontract	Total
5000	ZINC FILTER 8'x8' Rotary Drum - filter + Vac Pump	1	EA					75000				
								75000				

S EST-9 REV. 6/78

MAIN ITEM NO. D-18

380

McKee WKO

ESTIMATE WORKSHEET

DOMESTIC

Estimate No. 2301 A

Sheet _____ of _____

Made by _____ Date _____

QUANTITY: (1)

ESTIMATE FOR: TANK FOR CALCIUM CHLORIDE SOLUTION SURGE TANK SAME AS D-2

Acct	Item	Quantity	Unit	Unit Cost	Manhours Unit	Manhours Total	S/MH	Process Equipment	Material	Labor	Subcontract	Total
3240	STEEL A TANK	3	TAN	1001					4600			
3760	PVC LINING	440	#	5[illegible]							2200	
								19000				

MAIN ITEM NO. D-19

S EST-9 REV. 6/78

381

UW-STEVENS POINT
3 1775 621733 8