



LIBRARIES

UNIVERSITY OF WISCONSIN-MADISON

Review of the mining and milling waste materials and interaction of the tailing leachate with the mine waste disposal facility liner and subsoils for a zinc-copper mine proposed by Exxon Corporation n...

Helmke, Philip A.

[s.l.]: [s.n.], December 7, 1984

<https://digital.library.wisc.edu/1711.dl/CY4SFXES3ZLL68M>

<http://rightsstatements.org/vocab/InC/1.0/>

For information on re-use see:

<http://digital.library.wisc.edu/1711.dl/Copyright>

The libraries provide public access to a wide range of material, including online exhibits, digitized collections, archival finding aids, our catalog, online articles, and a growing range of materials in many media.

When possible, we provide rights information in catalog records, finding aids, and other metadata that accompanies collections or items. However, it is always the user's obligation to evaluate copyright and rights issues in light of their own use.

LOWER STACKS

REFERENCE

Local Materials Collection

REVIEW OF THE MINING AND MILLING WASTE MATERIALS
AND INTERACTION OF THE TAILINGS LEACHATE
WITH THE MINE WASTE DISPOSAL FACILITY LINER AND SUBSOILS
FOR A ZINC-COPPER MINE
PROPOSED BY EXXON CORPORATION NEAR CRANDON, WISCONSIN

Submitted by
Philip A. Helmke, PHD

December 7, 1984

TABLE OF CONTENTS

LIST OF DOCUMENTS	PAGE i
COPY OF CONSULTING CONTRACT	ii
LEACHATE GENERATION	1
Sources of data	1
Reactions of Tailings in the MWDF During Active Filling Operations	4
Reasonableness of the Predicted Leachate Composition	7
Potential Range in the Leachate Composition	8
Appropriateness of the Composition of the Synthetic Leachate Used in the Column Experiments	9
Potential for Differing Synthetic Leachate Compositions to Affect Retardation Factors Determined in the Column Studies	11
Stability of the Composition of the Synthetic Leachate Solution	14
ADEQUACY OF THE POTENTIAL RANGE OF REACTION ENVIRONMENTS	15
ADEQUACY OF PREDICTED REACTIONS AFTER FACILITY ABANDONMENT	18
Complete Exposure of the Tailings to the Atmosphere	18
Enclosure Under a MWDF Cap	19
Enclosure Under a Cap that Completely Eliminates Ingress of Oxygen	20
POTENTIAL FOR PRECIPITATION OF GYPSUM IN THE UNDERDRAIN SYSTEM	20
CARBONATE CONTENT OF MWDF SOILS	23
COMPATIBILITY OF THE MWDF LINER WITH POTENTIAL LEACHATES	26
ROLE OF MWDF LINER AND UNDERLYING SOILS IN ATTENUATING THE TAILING LEACHATE	28
EVALUATION OF LABORATORY STUDIES ON TAILINGS	32
Desirability of Conducting Leach Tests of Tailings	36

Desirability of Conducting Studies of Reaction Kinetics	36
Concentrations of Radioactive Elements in Mine Tailings and Slurry Water	37
COMPUTER MODELING OF LEACHATE-SOIL INTERACTIONS	38
Table One	40
Literature Cited	41
APPENDIX A	

The following documents were reviewed in this report.

- | | |
|------------------|---|
| Document 1 BCR | Waste Characterization Studies of Typical Waste Rocks From the Crandon Mineral Deposit by B. C. Research, July, 1982. |
| Document 2 CSMRI | Characterization of Crandon Mill Tailings by the Colorado School of Mines Research Institute, October 12, 1982. |
| Document 3 DACE | Volume I - Final Report Soil Attenuation Study by D'Appolonia Consulting Engineers, 1982. |
| Document 4 DACE | Volume II - Appendix H, Laboratory Data, Soil Attenuation Study by D'Appolonia Consulting Engineers, 1982. |
| Document 5 GA | Laboratory Testing Programs, Crandon Project, Waste Disposal System, Project Report 5, by Golder Associates, May, 1982. |
| Document 6 KP | Report on Preliminary Design: Volume I - Main Report, and Volume II - Appendices for the Tailings Storage Facility, by Knight and Piesold, LTD, December 3, 1982. |

I. AUTHORITY

This contract is entered into by and between the State of Wisconsin Department of Natural Resources, Box 7921, Madison, Wisconsin 53707 (hereinafter referred to as "the Department") and Dr. Philip A. Helmke (hereinafter called "the Consultant"), under the authority of Section 23.40 (5), subject to the requirements of Section 16.87 (2), Wisconsin Statutes.

II. PURPOSE

The purpose of this contract is to have the Consultant provide the Department with technical assistance in reviewing and verifying data concerning the mining and milling waste materials (tailings) and interaction of the tailings leachate with the mine waste disposal facility (MWDF) liner and subsoils for a zinc-copper mine proposed by Exxon Corporation (hereinafter referred to as "Exxon") near Crandon, Wisconsin. This information will be utilized in the environmental and regulatory reviews of Exxon's submittals and in preparing the draft (DEIS) and final (FEIS) environmental impact statements and mine permits for the proposed Crandon mine project.

III. SCOPE OF WORK

A. The Consultant shall perform for the Department in connection with its environmental impact analyses of the zinc-copper mine proposed by Exxon (hereinafter referred to as "the Project"), the following services:

1. Project Familiarity: The Consultant shall become familiar with the general aspects of the proposed Project through discussions with Department staff and reading Project-related documents which will be made available by Department staff.
2. The Consultant shall review and evaluate the tailings testing protocols and data in documents a, b, and c, and the relevant portions of documents d and e regarding waste characterization listed below:
 - a. Waste Characterization Studies of Typical Waste Rocks from the Crandon Mineral Deposit - Final Report, by B. C. Research, July, 1982;
 - b. Characterization of Crandon Mill Tailings, Colorado School of Mines Research Institute, October 12, 1982;
 - c. Soil Attenuation Study, Crandon Project, Volumes I and II, by D'Appolonia Consulting Engineers, 1982;
 - d. Laboratory Testing Programs, Crandon Project, Waste Disposal System, Project Report 5, by Golder Associates, May, 1982;
 - e. Report on Preliminary Design: Volume I - Main Report, and Volume II - Appendices for the Tailings Storage Facility, by Knight and Piesold, Ltd., December 3, 1982.

3. Utilizing information contained in the documents listed above, the consultant shall evaluate and address the following specific topics:
 - a. Leachate generation, including:
 - (1) adequacy of the description of the reaction of the tailings in the MWDF during active filling operations;
 - (2) reasonableness of the predicted leachate composition;
 - (3) the potential range in the leachate composition;
 - (4) the appropriateness of the composition of the synthetic leachate used in the column experiments;
 - (5) the potential for differing synthetic leachate compositions to affect retardation factors determined in the column studies, and its significance; and
 - (6) the stability of the composition of the synthetic leachate solution at equilibrium conditions (the Consultant shall utilize geochemical models such as WATEQ, PHREEQE, or others to help evaluate synthetic leachate stability);
 - b. Adequacy of the potential range of reaction environments, including possible pH adjustment of the tailings with lime which were used by Exxon for the prediction of the MWDF leachate characteristics and acid production;
 - c. Adequacy of Exxon's evaluation of the predicted reaction of the tailings in the MWDF after facility abandonment. The full range of containment scenarios shall be addressed, including, at a minimum:
 - (1) Complete exposure of the tailings to atmospheric elements due to erosion of the capping materials;
 - (2) Enclosure under a MWDF cap as described in Exxon's submitted documentation (ie., .60 to .74 inches per year of percolation into the tailings through the cap as documented by "Waste Disposal Facility Reclamation Cap", by Owen Ayres and Associates, November, 1982); and
 - (3) Enclosure under a MWDF cap that completely eliminates ingress of oxygen and water to the tailings;
 - d. The potential for precipitation, and approximate amounts of gypsum within the tailings, the underdrain system, and the liner. This shall include reference to changes in pressure, redox potential, and/or pH, which would affect gypsum precipitation in these areas.
 - e. Carbonate content of the tailings and underlying soils of the disposal site area as proposed by Exxon. This may require recommendations for laboratory testing to confirm the

neutralizing capacity predicted by Exxon. Determination of the size distribution and mineralogy of the carbonate rock may also be important in assessing the ability of the underlying soils to neutralize acidic leachate passing through them.

- f. The compatibility of the MWDF liner with the range of potential leachates, including the short- and long-term permeability of the MWDF liner;
 - g. The role of the MWDF liner and the underlying native soils in regard to the attenuation of the tailing's leachate, including the accuracy of the retardation coefficients as proposed by Exxon, including examining and discussing the range of potential retardation coefficients; and
 - h. The Consultant shall provide the Department with a written summary, acceptable to the Department, of his review and evaluation of the documents and topics listed above.
4. The Consultant shall evaluate and recommend laboratory studies on tailings samples characterization.
- a. The Consultant shall evaluate laboratory studies, conducted by Exxon, on representative tailings samples from Exxon's pilot plant milling studies. The Consultant shall also determine the suitability of the use of the tailings samples for mineral analyses. The Consultant shall recommend which analytical tests the Department should conduct in order to determine all of the major, minor, and trace elements, with special regard given to toxic elements and species potentially present in the tailings. This may include evaluation of the sampling of the supernatant accompanying the stored tailings for determination of in-field redox potential, dissolved oxygen content and pH of the supernatant upon opening of the tailing storage barrels.
 - b. The Consultant shall prepare a proposed plan for any additional laboratory work which needs to be conducted, whether by Exxon or by the Department, in order to complete any of the evaluation activities described above. The proposed plan shall indicate which laboratory analyses the Consultant is able to provide. The Consultant shall evaluate the following items, as necessary, in order to develop the proposed plan for additional laboratory work:
 - (1) the desirability of conducting leach tests of the tailings, including manipulation of the pH, Eh, and buffering capacity of the system, ranging from highly acid oxidizing conditions to a buffered reducing environment;
 - (2) desirability of conducting studies of the reaction kinetics in various reaction environments, in order to correlate lab studies with possible field conditions (this would be connected with verification of retardation factors of the leachate species);
 - (3) desirability of determining the presence and concentration

of radioactive elements in the mine tailings and slurry water, compare those concentrations to general levels known to exist in soils, rocks, and other natural features in Forest, Lincoln, and Oneida Counties; and

- (4) desirability of reproducing and evaluating the biological confirmation test developed by B. C. Research to evaluate acid generating potential of sulfide ore wastes.
5. The Consultant shall review and evaluate the additional testing protocols and data performed by Exxon or the Department in response to recommendations made by the Consultant under Scope of Work Item III. 4 above, and shall provide the Department with a written summary, acceptable to the Department, of this review.
6. The Consultant shall use the leachate test results, soil analyses, and saturated and unsaturated conditions of the soils as described in the reports listed above as the basis for utilizing computer models to determine:
 - a. Interaction of the leachate and slurry water with the MWDF the MWDF liner material;
 - b. Attenuation potential of the MWDF subsoils;
 - c. Impact of the carbonate content of the MWDF subsoils on attenuation of contaminants found in the tailings leachate.
 - d. The Consultant shall provide the Department with a written summary, acceptable to the Department, detailing the results of any computer modeling he conducts under this section.
7. The Consultant shall perform literature surveys of and prepare written summaries, acceptable to the Department, of the state of scientific knowledge and its potential application to engineering considerations on the subjects listed below. This shall include the reproduction or acquisition of technical and journal publications which support the written summaries, which shall become property of the Department.
 - a. Leach test data and leach test protocols for sulfide ore body mining and milling wastes;
 - b. Use of mining and milling wastes disposal liners (with an emphasis on amended soil liners), including site designs, quality and construction control, monitoring data and other instrumentation used to evaluate site performance and waste characteristics;
 - c. Waste characterization data related to sulfide ore processing wastes.
 - d. Biological degradation of sulfide ore tailings and associated control mechanisms;
 - e. Tailings slurry water and tailings thickener overflow water

constituents and concentrations.

8. DEIS: Following review and acceptance of the EIR, the Department will prepare the DEIS on the proposed Project. The Consultant shall be available for consultation with Department staff during the Department's review of the EIR and subsequent preparation of the DEIS.
 9. The FEIS will be written following a comment period and informational meeting on the DEIS. The Consultant shall be available to review comments germane to the Consultant's area of expertise and provide a written response to those comments, suitable for Department use, if directed by the Department to do so.
 10. The Consultant may be required to attend informational meetings held for the public and governmental agencies in the Crandon area during the DEIS and FEIS process.
 11. The Consultant shall be available to attend meetings with Exxon and Exxon's consultants on topics related to the Consultant's area of expertise.
 12. The Consultant shall be available to testify as necessary at the master hearing (s. 144.836, Wisconsin Statutes) concerning the portions of the analysis prepared by the Consultant which are utilized by the Department for inclusion in the EIS and regulatory decisions.
- B. Except as otherwise specifically provided in the contract, the consultant shall provide technical, professional, and other services necessary to perform all the services listed in III. A. 1 - 12 above.

IV. WORK PRODUCTS

- A. The chief work product will be written reviews of Exxon's documents and written analysis of mine waste tailings, liner compatability, leachate characteristics and interaction with the liner as described by Scope of Work Items III. A. 1 - 7 for Department review and inclusion into the DEIS and FEIS. The Consultant shall provide the Department the written reviews, analyses and recommendations described in Work Items III. A. 1 - 7 by July 30, 1984. Any reviews, analyses and recommendation of additional waste tailings characterization, liner compatability, and leachate interaction work to be performed by Exxon will be due within 90 days of written notification by the Department to proceed with such work.
- B. The Consultant shall provide assistance to the Department, as requested, during the Department's preparation of drafts of impact analyses and other aspects of the waste tailings characterization, liner compatability, and leachate interaction discussions in Exxon's EIR and related documents, for use in the DEIS and FEIS and for consideration in determining the issuance of a mining permit as described by Scope of Work Items III. 8 & 9. This assistance will be provided within 30 days of written notification by the Department to provide such assistance.

SECTION III A 3 a Leachate Generation

Sources of Data

Data on the composition of waters in contact with the proposed tailings and various mined materials from the Crandon mine are found in several of the documents submitted by Exxon. The various sources and types of experiments and dates they were conducted are summarized here to help synthesize a coherent trend in the data.

Document 1 BCR Waste Characterization Studies of Typical Waste Rocks From the Crandon Mineral Deposit by B. C. Research.

This report contains data on the composition of waters that were reacted with samples of hanging wall rock, foot wall rock, and samples of high sulfide content massive and stringer wastes. Two different tests were done to estimate the potential of the samples to generate acid leachates. A titration test was done to determine if the acid neutralizing capacity of the sample was greater than the sample's capacity to generate acid, based on a chemical analysis of its sulfide content. In addition, a confirmation test was done on each sample. This involved a shake flask test of the sample with an active culture of Thiobacillus ferrooxidans to determine the sample's potential for acid production.

The leaching characteristics of the samples were determined by column leaching studies. One group of columns was acidified with sulfuric acid before being inoculated with T. ferrooxidans while the second group received no pretreatment before inoculation. After 126 days of leaching, the columns were put to rest on March 31, 1980, but they were kept continually moist. In October, 1980, the columns were washed several times and the collected solutions analyzed for pH, Cu,

Fe and sulfate. A second set of samples were studied in a similar fashion except that the columns were pretreated with ammonium sulfate as a bacterial nutrient for one week before they were inoculated with T. ferrooxidans. After 233 days of leaching, the columns were put to rest on February 16, 1982, and then washed after 7, 14 and 21 day rest cycles.

Report one also contains the results of the EPA toxicity tests. Document 2CSMRI Characterization of Crandon Mill Tailings by the Colorado School of Mines Research Institute.

This report contains data on zinc tailings fines from massive and stringer ore, combined mine backfill, unclassified zinc tailings from massive ore, pyrite concentrate fines and pyrite tailings fines from massive and stringer ore. The EPA toxicity extraction test was done on all of the samples as well as the same biological confirmation test as was done in document one. All of the fines and tailings were analyzed by agitated leach tests. The samples were agitated with either an acid solution (sulphuric acid), pure water, or alkaline (calcium hydroxide) solutions for 48 hours. These data are useful to access the behavior of the sample materials under different pH conditions but they do not reflect the effects of T. ferrooxidans.

Column seepage studies were also done on three samples (zinc tailings fines from the massive ore, zinc tailings fines from the mixture of massive and stringer ore, and the combined mine backfill) under four different conditions. The conditions were tailings submerged under alkaline water (pH 10), tailings submerged under de-ionized water (pH 5.6), tailings submerged under acidic water (pH 3), and tailings alternately submerged under deionized water and exposed

to air. Twelve columns, one sample under each condition, were operated for 31 weeks. Every two weeks, one pore volume was drained from each column and an equal amount of makeup water was added. All samples were analyzed for pH and Eh and selected samples were analyzed for conductivity, Cu, Fe, Pb, Na, Ca, K, Mg, sulfate, and total sulfur. These studies provide information on the characteristics of the seepage water and on potential changes in the physical and chemical properties of the samples due to leaching.

Document 3 DACE Volume I - Final Report Soil Attenuation Study by D'Appolonia

Document 4 DACE Volume II - Appendix H, Laboratory Data, Soil Attenuation Study by D'Appolonia

These documents present data on the synthesis of potential leachates from the MWDF and on their interactions with the proposed liner material and the soils from the MWDF site. Most of this research was done during the first half of 1982 as judged by the dates recorded on the data sheets in document four. Each of these reports appears to be technically sound and correct, except for some small areas discussed in later sections. The procedures used are contemporary, the quality control for the analytical procedures are adequate to good, and it is evident that a great deal of planning went into the design of the different experiments.

The major deficiency of the reports is that little effort was made to correlate the results from the studies to synthesize a generalized result of the most probable and extreme situations that may be encountered with the MWDF. A cohesive description of such situations seems to be the intent of the the various studies but no one apparent-

ly had the responsibility to put all of the results together. This inadequacy probably resulted because all three of the studies mentioned above were conducted almost simultaneously by different organizations. The charge given to each organization is very clearly stated in their reports but there is little evidence that their experimental approaches evolved during their investigations to consider the results found by the other investigators. The result is that the collective data bases have some gaps, which if filled, will enhance the certainty of any predictions concerning the effects of the MWDF.

III A 3 a (1) Reactions of Tailings in the MWDF During Active Filling Operations.

The portion of the reports that comes closest to dealing with this topic is located in document 2 CSRMI but no section specifically mentions this topic. This may be intentional because of the difficulty of making such predictions, but the capability of predicting those reactions along with the reactions that will occur after the MWDF is closed is central to evaluating the geochemical impact of the MWDF. The data in the reports that is applicable to such predictions are summarized and compiled below. The biological confirmation tests reported in documents 1 BCR and 2 CSRMI confirm that the ores and tailings are susceptible to sulfide oxidation by T. ferrooxidans and that they are capable of generating acid leachates when the base neutralizing capacities of the materials are exceeded. The data in Tables 10, 12, 14-17, 39 and 42-51 in report 1 BCR and especially those in Tables 6-11, H-1 - H-6, I-1 - I-4, I-6 and J-3 - J-14 in report two are relevant.

The column seepage studies reported in document 2 CSRMI pp 36-42, and the associated appendices are the most relevant. The columns were operated for 31 weeks. From appendix J, the pH of the leachates were in the range of about 7 to 9 when the leachates were submerged in neutral, alkaline or acidic solutions, although it tended to be towards the low side of this range for the acidic solutions. The concentrations of Cu, Fe and Pb were low under these conditions, which is expected for moderately alkaline conditions, while those of Zn and sulfate were moderate, especially when compared to those present in leachate solutions from ores that were inoculated with Thiobacillus ferrooxidans (e.g. compare this data to the data in Tables 46-51 in document 1 BCR).

The absence of Thiobacillus ferrooxidans in the column studies is perhaps the greatest uncertainty in predicted the reaction of the tailings in the MWDF. This bacteria thrives only in acid environments and under aerobic conditions. The MWDF and the associated waters is proposed to be kept slightly alkaline to meet the requirements of the process water in the flotation process. Also, the influx of oxygen into the tailings pile should be very limited because the bulk of the tailings will be continually submerged. As such, this should reduce or even eliminate the effects of Thiobacillus ferrooxidans except in portions of the MWDF where the tailings are exposed to the atmosphere.

A question that is related to the oxidation of sulfide and the potential formation of polythionates is the value of the Eh in the MWDF. Some of the data in Appendix J, especially those in Table J-1, need to be clarified. This table shows that the Eh of the acid water, pH 3 sulfuric acid, is -360 mv. This value is lower than the reduc-

tion stability limit of water. The lowest value of Eh that an aqueous solution can theoretically have is about 59 mv times the pH, and the reported value is well below that. The data in Table I-3 also show a more negative value of Eh than can theoretically exist and the Eh data in table I-1 is missing. Also, it is unusual that the alkaline and deionized water solutions used in the column seepage studies also initially had very reducing values of Eh. These apparent discrepancies in the Eh data of the initial solutions causes one to question the validity of the Eh data for the sample solutions (Tables J-3 - J-9), which also were very reducing.

At least some of the columns appeared to be under reducing conditions because a surface layer of rust-like material coated the surfaces of the columns in the acid leach (Page 39). This indicates reducing conditions within the columns but oxidizing conditions in the solution covering the columns. The disappearance of thiosulfate that was initially generated in the alkaline leach (Figure 2) is also evidence of the oxidizing conditions that must have prevailed during the tests. An additional inconsistency is that the redox potential of the leachates from report 1 BCR never reached negative values (Appendices 10 and 23). The data in report 1 BCR appear to be correct while those in report 2 CSRMI are suspect. Although these discrepancies in the reported data are unsettling, the results are sufficient to make firm conclusions.

The composition of the MWDF seepage was predicted by CH₂M/Hill with a computer analysis using WATEQ. The results are given in data column six in Table 3.5 of document 3 DACE. The reported values agree qualitatively with the concentrations reported for alkaline leachates

in document 2 CSMRI, tables I-6 and J-4. The major difference is that the concentration of zinc is much higher in the alkaline leachates than calculated. For the results in Table I-6, this probably occurs because the samples were leached for only 48 hours and the pH was more alkaline than the computed value. Under slightly more acid conditions, the concentration of zinc decreased to lower values than calculated after seven pore volumes of leachate (Table J-4). Some of the difference also results because the calculated concentration of Ca is lower and that for sulfate is higher than reported in Tables I-6 and J-4. These characteristics will tend to increase the concentration of dissolved zinc because of its complexation with sulfate.

The worst case composition for the MWDF seepage is given in Tables 46-51 and others in document 1 BCR. These represent the values obtained under oxidizing conditions in the presence of T. ferrooxidans.

III A 3 a (2) Reasonableness of the Predicted Leachate Composition

From the discussion above it is apparent that the composition of the MWDF leachate is highly dependent upon the reduction-oxidation status of the tailings and the pH. Slightly alkaline values of pH and flooded conditions that limit the flux of oxygen into the tailings will result in leachate with the lowest concentrations for most dissolved materials. The results given in the various studies show the advantages of maintaining those conditions. The predicted composition given in Table 3.5 of document 3 DACE is reasonable if one accepts the values as typical of a range of compositions of the leachate and not as absolute representations of the final actual values. The concentrations of some of the dissolved materials cannot be predicted with

precision from geochemical data alone and the actual concentrations may also be sensitive to the specific operations during the filling of the MWDF and the geophysical characteristics of the MWDF. For example, the concentration of sulfate is generally limited in the MWDF leachate by the solubility of gypsum, which in turn is influenced by the balance of calcium in the system, which is also affected by the partial pressure of carbon dioxide and the precipitation of calcite, and the input of water undersaturated with these compounds.

III A 3 a (3) Potential Range in the Leachate Composition

The potential range in the concentrations of elements in the leachate is within the limits set by those experiments that were done under acid, oxidizing conditions and those done under alkaline conditions as reviewed above in document 1 BCR and 2 CSMRI. Examples of the environmentally worst case compositions include the data in Tables 48 and 50 and appendices 10 and 23 in document 1 BCR and the data in Tables 8, J-10 and J-11 in document 2 CSMRI. The least environmentally hazardous compositions are those generated under near neutral to slightly alkaline conditions. Examples are the data in Tables 47, an intermediate case, in document 1 BCR and those in Tables J-3 through J-8 in document 2 CSMRI. It is important to note that with respect to the range in leachate compositions the pH is the most important variable. The trend is that under acid conditions the leachate will have relatively high concentrations of most elements and that the leachate will have the lowest concentrations of most elements under slightly alkaline conditions. The presence of oxygen is important mostly because of its potential effect on the acidity of the leachate resulting from the oxidation of sulfide. The availability of oxygen will gen-

erally have only small effects on the concentrations of most elements in the leachate when sufficient alkaline material is present to maintain the pH near neutral or slightly alkaline. The greatest effect of allowing oxidation to occur will be on the concentration of sulfate in the leachate, which will increase with increasing sulfide oxidation. Reducing conditions will also affect the speciation of some elements that can exist as oxyanions or as reduced species, such as the elements arsenic and selenium.

III A 3 a (4) Appropriateness of the Composition of the Synthetic Leachate Used in the Column Experiments.

The compositions of the leachates used in the column studies are given in Tables 3.5 through 3.8 of document 3 DACE and the compositions of the effluents are given in document 4 DACE. These reports do not discuss the rationale behind the selection of the leachate composition except to state that the spiked leachate target concentrations given in Table 3.5 were specified by Exxon (Section 2.2 of Appendix 2). It seems logical that the synthetic leachate should have a composition close to that expected of the leachate from the MWDF, with other cases bracketing the range of potential compositions. The actual concentrations of the trace or minor elements is probably not very important for the attenuation experiments done here as long as their concentrations are sufficient to be accurately measured while still being low enough that they are much smaller than the concentrations of the dominant or matrix elements. This occurs because within a limited concentration range the reaction of a dissolved element with a solid phase, such as a soil, is nearly independent of its concentration but very dependent upon the concentrations of the matrix elements

and the environmental conditions. It is thus most appropriate to compare the concentrations of the matrix elements in the synthetic leachate to their expected concentrations and to evaluate the environmental conditions.

With respect to the their effects on the measured values of the retardation factors, the most important cations in the leachate are Ca, Mg, Fe, K and Na. The most important anions are sulfate and other sulfur species and carbonate. Sample number 2 reported in document 1 BCR was recommended by Exxon as being the most representative of the materials that will be deposited into the MWDF (Meeting with DNR and Exxon, May 22, 1984). Table 1 compares the range of concentrations of several elements and environmental conditions in the synthetic leachate to those measured in the column leachate from sample 2 (Tables J-4, 7, 10 and 13 in document 1 BCR). It is important to note that the data reported for the column attenuation experiment is the starting composition of the solution used to estimate values of the retardation factors while the data for the tailings leachate is the composition of the leachate obtained from columns of tailings. Comparison of the two sets of data shows that the composition of the synthetic leachate used to measure the retardation factors is reasonable and appropriate.

If any criticism is to made about the selection of the synthetic leachate composition it would be that none of the synthetic leachate compositions approached that expected from the worst case condition where the tailings would be exposed to acidic, oxidizing conditions in the presence of T. ferrooxidans. The leachate could then have a pH of near 2, sulfate concentrations of over 30,000 mg/L and iron

concentrations of almost 9,000 mg/L. Under the proposed plans for the MWDF, this environment could only occur after the facility is abandoned and somehow the tailings became exposed to the atmosphere.

III A 3 a (5) Potential for Differing Synthetic Leachate Compositions to Affect Retardation Factors Determined in the Column Studies.

The most important parameters of the leachate that can affect the measured values of the retardation factors are the concentrations of the dominant cations, especially Ca and Mg, the concentration of sulfate or other sulfur species, the concentration of iron, pH, and the redox status.

The concentrations of Ca and Mg affect the values of the retardation factors because the cations of these elements compete for adsorption and exchange sites with the cations of the trace elements (heavy metals). High concentrations of Ca and Mg in the leachate will saturate a greater proportion of the available sites with Ca and Mg ions, leaving fewer sites to be occupied by the ions of the trace elements. This will occur even though the trace cations generally have much greater adsorption affinities than do the ions of Ca and Mg. The much higher concentrations of Ca and Mg offset the adsorption advantage that most trace cations have. The synthetic leachate used in the column experiments had Ca and Mg concentrations that are towards the highest values expected for the leachate from the MWDF. Lower values of Ca and Mg will tend to produce higher values for the retardation factors of the trace cations.

The concentration of sulfate and thiosalts is important in two ways. The most important is probably the effect sulfate has on the

speciation of dissolved trace elements. Most of the heavy metals of concern are transition group elements and they commonly occur as divalent cations in solution. As such, they tend to be strongly adsorbed by soils because most soils, including those under the MWDF and its liner, have a net negative charge. Several of the trace elements of concern, especially Zn, Cd, Cu, Pb and Mn, readily form dissolved complexes with sulfate that have a net charge of zero (ion pairs). These neutral complexes are only weakly adsorbed by soils. Any interaction of the complexes with the soil occurs mostly as a result of any slight dipole moment of the sulfate complex. The net result is that high concentrations of dissolved sulfate will decrease the measured values of the retardation factors. The concentrations of sulfate used in the synthetic leachate solutions are as high or higher than those expected during the operation and filling of the MWDF but are lower than those that could occur if the capping material is eroded away after the facility is abandoned.

The second way that the concentration of sulfate could affect the values of the retardation factors is its affect on the adsorption of anions onto the soil. This would be most important for As, Se, Cr(IV) and cyanide. Arsenic, Se and Cr can form oxyanions under oxidizing, acid conditions, and their adsorption by the soil will be decreased if the concentration of sulfate is high because of the limited positive charge on the soil. The concentrations of total cyanide in the leachate are expected to be less than 0.1 mg/L (Table 3.5 in document 3 DACE). This compares to concentrations of 0.003 to 0.020 mg/L of free cyanide and values of up to 0.06 mg/L total cyanide found in river waters (Leduc, 1981). Most of the cyanide in the leachate will

occur as soluble complexes with the transition elements, especially under alkaline conditions where HCN is appreciably dissociated. Cyanide in the form of such complexes is much less toxic than the free form. Because cyanide and most of its complexes are anions, and because the value of the retardation factor for cyanide was measured to be near one, the concentration of sulfate should have little effect on the value of its retardation factor.

The importance of dissolved iron is its hidden effect on pH. Acidic leachates can have high concentrations of dissolved iron. Percolation of such leachates into less acidic environments can result in much greater pH effects than predicted by the pH and volume of the percolating fluid alone because precipitation of each Fe^{+++} ion as ferric hydroxide releases three protons. This pH effect will tend to decrease the values of the retardation factors for the trace elements, however, this will be partially offset by the adsorption capacity of the precipitated iron hydroxide for cations and by the cementing action of the iron hydroxide, which will reduce the permeability of the soil. The concentrations of Fe used in the column studies cover the expected range of concentrations except those which may occur if the tailings are completely exposed to the atmosphere.

The pH is important because hydrogen ions compete with the metal cations for adsorption sites on the soil. Low values of pH will result in low values of the retardation factors. Also, at pH values slightly less than neutral and higher, the concentrations of many of the trace elements in the leachate will be in equilibrium with their hydroxides. As long as the pH buffering capacity is not exceeded by the influx of acidic leachate, such precipitation reactions will

result in very high values of measured retardation factors. The pH values of 3, 6 and 9 used for the synthetic leachate are reasonable except that under complete exposure of the tailings to the atmosphere the pH could be as low as almost 2.

Values of Eh are important because of their effect on the speciation of dissolved Fe, Se, Cr and Sb. Selenium, Cr and Sb can form oxyanions under acid, oxidizing conditions and these forms of the elements will be adsorbed less strongly, that is smaller retardation factors, than the cationic forms of these elements. Divalent Fe is the dominant form of dissolved Fe expected in the leachate under all conditions except the most acid and oxidizing conditions and so the Eh variable for Fe is only important if the tailings are exposed to the atmosphere.

III A 3 a (6) Stability of the Composition of the Synthetic Leachate Solution.

The best indicators of the stability of the synthetic leachate solutions are the data from the weekly analyses of the leachate given in Tables D.2 through D.4 in document 3 DACE. These indicate that the composition of the leachate was stable for the four month duration of the phase I research and the two month duration of the phase II research. The values for dissolved Fe fluctuate slightly, probably in response to changes in the Eh. This is a difficult parameter to control, and it is doubtful if it can be improved upon.

Computer analyses of some of the data were also done utilizing the program GEOCHEM (Sposito and Mattigod, 1980). The data for the leachates analyzed from 2/16/82 from Tables 3.6 through 3.7 from document 3 DACE were used as input. The data for the effluent given in document

4 DACE indicates that the pH of the pH 3 leachate increased to about 6 and that the Eh decreased to about 200 mv. A similar decrease in the Eh for the effluents for the pH 6 and 9 studies also occurred and the pH of the pH 9 column decreased to about 7. Therefore the pH 3 data from 2/16/82 was run at its original pH and Eh and at pH 6 and at Eh 200 mv to assess what may happen as the leachate reacts with the soil column. The change in Eh increased the amount of divalent iron but it did not affect any of the other elements. Increasing the pH to 6 indicated that the solution became saturated with a copper carbonate but this may be an artifact of the calculations because not all potential Cu compounds and dissolved complexes are in the data base. Changing the values of Eh to 200 mv for the pH 6 case and holding the pH constant at 5.82, had no affect on the composition of the leachate. For the pH 9 case, reducing the pH to 7 indicated that the solution will be saturated with calcium carbonate, cadmium carbonate, and zinc carbonate. The partial pressure of carbon dioxide was held at $10^{-3.5}$ atmospheres for all of the calculations.

In summary, the analytical data reported in document 4 DACE and the results of the computer calculations indicate that the synthetic leachate solutions were stable. Some compounds are likely to have precipitated in the columns during the attenuation experiments, especially in those experiments that started with acidic leachates. This is to be expected.

III A 3 b

ADEQUACY OF THE POTENTIAL RANGE OF REACTION ENVIRONMENTS

The reaction of the tailings under various leaching conditions is reported in document 2 CSMRI (Pages 23-36 and associated appendices).

Samples of the tailings were subjected to agitated leach tests using pH 3 sulfuric acid, deionized water, and pH 10 calcium hydroxide slurry. The pH 3 and water tests were done three times with 48 hours for each cycle and the pH 10 test was done for only one cycle for 48 hours. The ratio of solid to liquid ranged from 1 to 4 for the pH 3 and water tests and 1 to 1 for the pH 10 test.

The concentrations of elements leached during the first cycle were always higher than they were in successive cycles, indicating that a portion of the ions leached were already dissolved in the interstitial solution of the tailings, or weakly sorbed to the tailings, or minor amounts of readily soluble minerals were present. The highest degree of leaching resulted from the acid leach. Leaching under alkaline conditions resulted in an initial concentration of thiosulfate that was then oxidized to near zero concentration within 50 hours.

The main value of these test is to establish concentrations of dissolved sulfate, iron and pH of water when it is reacted with fresh tailings. Zinc was the only trace element that was leached appreciably of the elements analyzed. The tests were done open to the atmosphere but the short, 48 hours, duration of the test would have minimized the amount of oxidation that could occur. The samples were not inoculated with T. ferrooxidans.

A more relevant series of tests is a series of column studies where samples of tailings were submerged in pH 3 sulfuric acid, pH 5.6 deionized water, and pH 10 calcium hydroxide slurry for 31 weeks (Pages 36-42 and associated appendices). Every two weeks the columns were removed, allowed to drain, and the leachate collected and analyzed. The results are summarized in Table 11. The mixture of the

tailings from the massive/stringer ore is the most relevant. The most important feature of these data is that the pH of the leachates was almost always between 7 and 8. Sulfate concentrations ranged up to 2400 mg/L, which is about the concentration used for the soil attenuation experiments.

A major question concerning these data is the reported values of Eh, as discussed in section (III A 3 a (1)) earlier. Oxidation was minimized in these tests because the columns were always covered with water and they were not inoculated with T. ferrooxidans. Oxygen is also proposed to be excluded in the MWDF. If the column data are to be used to approximate the conditions existing in the MWDF, then it would be helpful to know the Eh values for these experiments. Also, the description of the column test does not indicate if the redox status of the leachate was preserved during the collection of the leachate and how the samples were preserved for analysis. These are deficiencies that should be clarified.

An additional question concerns the production of thiosalts. They apparently form readily under alkaline conditions in tailing ponds as discussed in document 2 CSMRI (Page 31). Oxygen is required for their production. It also appears that they are readily oxidized to sulfate under oxidizing conditions. The question concerns what levels of Eh are needed for thiosalts to form and to be stable. This may be important in an evaluation of the retardation factors because some of the trace metals form soluble complexes with thiosulfate.

III A 3 c

ADEQUACY OF PREDICTED REACTIONS AFTER FACILITY ABANDONMENT

III A 3 c (1) Complete Exposure of the Tailings to the Atmosphere

None of the submitted material specifically addresses this question. Many of the tests gave results that are useful to address this question but it would be informative if Exxon would give their thoughts. Complete exposure of the tailings to the atmosphere due to erosion of the capping materials will result in reactions similar to those reported in document 2 CSMRI (Pages 20-22 and Appendix H) and in document 1 BCR.

Almost all of the tailing samples, including the sample of mixed zinc tailings fines (massive/stringer ore) which is the most representative of the proposed tailings, are confirmed acid producers (Table 5, document 2 CSMRI). Also, the literature survey reported in document 2 CSMRI confirms that high sulfide tailings deficient in basic material for neutralization will generate acids if oxidative conditions are present. All of the evidence indicates that exposure of the tailings to the atmosphere resulting from the erosion of the capping material will produce acid leachates.

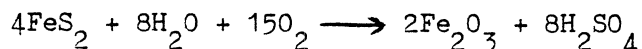
The composition of the leachates will most likely be similar to those reported in Tables 16 and 17 and Tables 42-51, especially those for columns 102, 104 and 105, in document 1 BCR. This report also gives estimated loadings of leached elements based on these results and a 50 meter high pile of unprotected material (Tables 27, 28 and 53). There may be room for argument about the values used for the scaling factor from laboratory to field conditions but this will have little effect on the composition of the leachate.

One factor that may mitigate the effect of complete exposure of the tailings to the atmosphere is the additional neutralization capacity of the tailings resulting from the addition of lime during the operation of the facility to maintain a slightly alkaline pH. If both calcite and gypsum precipitate in the tailings pond, the pH will be buffered at about 7.8 at atmospheric values of the partial pressure of carbon dioxide. This pH will be maintained until either the gypsum or calcite is totally dissolved.

III A 3 c (2) Enclosure Under a MWDF Cap

None of the submitted documents address this question directly. The column studies reported in document 2 CSMRI are the most appropriate to use as indicators of the leachate characteristics because the columns were submerged during the tests except for every two weeks when the leachate was collected. The Eh data is suspect in these studies as discussed earlier. The pH values of the leachate were generally in the range of 6 to 8, which indicates the neutralization capacity of the tailings is sufficient to maintain the pH near neutral under conditions where oxidation is minimized.

The approximate effect of 0.6 inches of percolation into the tailings on the pH environment can be calculated. The acid neutralization capacity of the combined zinc tailing (massive/stringer ore) is about 32 pounds of H_2SO_4 per ton (16 mg/Kg) (Table H-2, Page 88, in document 2 CSMRI). The density of this tailing is 3.46 g/cm^3 (Page 6 in document 6 KP). The exact stoichiometry of the oxidation of sulfides to sulfuric acid is slightly dependent upon the environmental conditions and reactions pathways. For the following reaction;



the production of sulfuric acid will be about 17 mg/L if the influx of oxygen due to percolation of oxygen saturated water is about 10 mg of O_2 /L, which is the solubility of oxygen in water at 15 C. This is a somewhat arbitrary but reasonable value. This amount of acid requires the neutralization capacity present in 1030 g, or about 300 cm³, of tailings to be neutralized to pH 3.5. An infiltration rate of 0.6 inches (1.5 cm) will thus produce enough acid to consume the neutralization capacity of a layer of tailings about 0.45 cm thick per year. This calculations exemplifies the importance of maintaining the integrity of the MWDF cap to limit the influx of oxygen.

The situation is likely to be better than illustrated above if an active ecosystem is maintained above the cap because the concentration of oxygen in waters from soils supporting active plants is much lower than that used in the calculation. Document 6 KP gives an infiltration rate of 0.31 inches/year, which is essentially identical within the errors allowed by such estimations with the value used above.

III A 3 c (3) Enclosure Under a Cap That Completely Eliminates Ingress of Oxygen

This topic is also not covered by any of the submitted reports. However, the case is essentially identical to the one discussed above which allowed almost no oxidation.

III A 3 d

POTENTIAL FOR PRECIPITATION OF GYPSUM IN THE UNDERDRAIN SYSTEM

The underdrain system consists of perforated pipes laid directly on the underseal in a herring bone pattern. These will feed into larger diameter collector drains. The intent is to reduce the hydrostatic head on the underseal to minimized seepage from the MWDF.

Analysis of the collected leachate will also provide valuable information on the performance of the MWDF. The underdrain system will be inaccessible after the MWDF starts to be filled. None of the submitted documents address the potential of these pipes being blocked by precipitation of materials from the leachate.

To study the potential for precipitation, data representing the composition of various leachates were run with the GEOCHEM computer model at various values of Eh, pH, and partial pressures of carbon dioxide. GEOCHEM is an extension of REDEQL2 and it was designed to model the behavior of dissolved elements in the soil-water system (See Appendix A).

The potential for precipitation occurs because the transition from the tailings drainage blanket to the underdrain pipes represents a potentially abrupt change in the environmental conditions of the leachate. For precipitation to occur, the concentration of one or more ions must change enough so that the solubility product of some mineral is exceeded. This can occur because of evaporation, which is unlikely in the drain system, or because of chemical reactions that are induced because of changing chemical or physical conditions.

It appears from the computer models that gypsum precipitation may not be as significant as precipitation of calcite and dolomite. This appears reasonable because the transition from the drainage blanket to the underdrain will be accompanied by a pressure drop that depends on the hydrostatic head. A decrease in pressure allows carbon dioxide to escape from solution, which results in the precipitation of calcite analogous to that which occurs during the formation of stalagmites and stalactites in limestone caves.

Calcite will control the solubility of Ca above pH values of about 8 if the partial pressure of carbon dioxide is about $10^{-3.5}$ and the concentration of sulfate is about 0.01 M or less. Gypsum will control the concentration of Ca at lower values of pH if the sulfate concentration is sufficient. The solubility of gypsum should be insensitive to changes in Eh unless thiosalts, which are easily oxidized, or sulfides, which react more slowly, are oxidized to sulfate at the interface of the drainage blanket and the pipes. This would require the influx of oxygen from the atmosphere into the drainage system, which is unlikely. A qualified expert should give an opinion on the design of the system to determine if air from the atmosphere will circulate through the drain system.

The results from GEOCHEM indicated that the predicted MWDF leachate given in Table 3.5 of document 3 DACE is over saturated with calcite and dolomite at its natural pH of 9.48 with a partial pressure of CO_2 of $10^{-3.5}$, the value for the atmosphere. This result is also predicted by the WATEQ analysis given in Table 3.10 of the same report. Decreasing the pH to 7.0 indicates that no solid phases were in a state of over saturation. Variations of pH, Eh, and P_{CO_2} for several of the leachates given in Tables 3.6 through 3.8 (those used in the column studies) did not result in the precipitation of gypsum.

These results indicate a potentially important deficiency in several of the submitted studies. All of the experiments were done open to the atmosphere, and presumable at a partial pressure of CO_2 of $10^{-3.5}$ atmospheres. The potential exists for significantly higher partial pressures of carbon dioxide within the tailings in the MWDF. The source of the carbon dioxide could be the dissolution of the minor

amounts of calcite and dolomite in the tailings and liner material by the leachate. The carbon dioxide variable was not considered in any of the leach or column tests. Exxon should consider the effect of variable concentrations of carbon dioxide on the potential for precipitation of minerals or show why this variable is not important.

There is also a potential that leachates coming from different parts of the MWDF will have different values of pH and other parameters and that these leachates could intermix in the underdrain system with the result that the mixed leachates would be over saturated with several mineral phases. This would result in localized precipitation of minerals.

III A 3 c

CARBONATE CONTENT OF MWDF SOILS

The concentration of calcium carbonate and dolomite in the tailings and underlying soils of the disposal site are discussed in Pages 3-38 through 3-42 in document 3 DACE. The concentration of carbonate minerals in the tailings is given in Table 4 of document 1 BCR. The concentration of carbonate minerals in the tailings is so small that it is not a significant factor in the design considerations of the MWDF. Most of the tailings sample were confirmed as net acid producers.

The content of carbonate minerals in the soils from the MWDF site were estimated by a "fizz test". Soil samples were tested for carbonate effervescence with 10 percent HCl and assigned a numerical rating ranging from 1 to 4 based on the observed reaction. A range of 1 to 5 was used for the samples from the four borings that provided the composited samples. A subgroup of 105 samples was also analyzed for their ability to neutralize acidity by reacting them with an ex-

cess of standardized acid which was then back titrated. The results are reported in percent calcium carbonate equivalent but this does not imply that all of the acid neutralization potential of the sample is the result of carbonate minerals.

The data from this subgroup of samples were then used to calibrate the results of the "fizz" test. X-ray diffraction analysis of the composite samples used for the attenuation tests were also done (Table 3.2), and these results confirm that carbonate minerals are present, mostly dolomite with traces of calcite.

Reaction of the sample with excess acid followed by titration with base is an accurate way of measuring the acid neutralization capacity of soil samples. The measured values include the acid neutralization capacity that results from any carbonate minerals plus the neutralization capacity that results from the base saturation of any ion exchange sites. The carbonate minerals, or any other minerals that will dissolve by reacting with hydrogen ions, comprise the nonexchangeable basicity of the sample. Exchangeable cations, such as calcium and magnesium, can also be displaced by hydrogen ions with the corresponding consumption of acidity. The titration test will measure both forms if sufficient time is allowed during the titration for the minerals to react or dissolve. The "fizz" test will give an indication only of the content of carbonate minerals in the sample.

The "fizz" test is very subjective and it is sensitive to several environmental variables. The most important of these is that dolomite reacts slowly with dilute HCl and that it probably makes a minor contribution to the amount of fizz observed. The results are obviously sensitive to the interpretations of the observer and the effects of

this variable would be minimized if the same technician did all of the "fizz" tests. The data for the "fizz" test on the samples used for the attenuation study (document 4 DACE) were gathered by three different individuals. This may have increased the scatter of the data but probably no more than the inherent semiquantitative nature of the "fizz" test.

The time needed to do titration analyses for all of the samples, and the resulting high levels of accuracy in the results, is probably not warranted because of the natural variations in the soil samples. The correlation established between the numerical ratings from the "fizz" test and the titration data allows one to predict the approximate acid neutralization capacity of a group of samples, although the accuracy of such a prediction for a single sample could have a very large error. For the data reported in Table G.1 of document 3 DACE, the correlation is percent carbonate equals $3.97 \times \text{carbonate effervescence rating} - 1.59$. The correlation coefficient is 0.72. Only those samples that were tested with a 1 to 4 "fizz" rating were used. The composited samples were rated 1 to 5 and they were not included in the above correlation.

The reported data clearly establish that the soils do have some acid neutralization capacity. The content of that capacity shows spatial variability, which is very normal. The conclusions given on page 3-42 of this section of the report are acceptable and correct. No additional testing is recommended.

III A 3 f

COMPATIBILITY OF THE MWDF LINER WITH POTENTIAL LEACHATES

The MWDF liner will consist of the local soils, glacial till, mixed with bentonite, a montmorillonite clay. The grain size distribution of the glacial till is given in Table 3.1 of document 3 DACE. The mineral composition of the samples before and after the column tests was determined by semiquantitative X-ray diffraction and the results are given in Tables 3.2 and 3.3. The reaction pH, neutralization capacity, and exchangeable ions are given in Table 3.4. These data are discussed in pages 3-25 through 3.31.

The x-ray diffraction data indicated no change in the mineralogy of the samples as a result of the column studies except for the formation of gypsum in the pH 3 columns. However, this is not a very rigorous test because mineral phases present at less than about five percent are often not detected by this technique. The main conclusion that can be made from the X-ray diffraction data is that no large changes in mineralogy occurred.

The conclusions given on page 3.29 are reasonable and expected. A typo in the first line of the third conclusion, "chloride" almost certainly should be "chlorite". The potassium concentration in the MWDF leachate is indicated to be lower than that used in the column studies, which will diminish the conversion of smectite clays to mica/illites. This interaction should have little affect on the retardation factors or on the permeability. The minerals present in the samples are generally and widely accepted to be stable in the pH 6 to 9 environments of the column experiments. The major changes that will occur at these pH values are the reaction pH, neutralization capacity,

and content of exchangeable ions. Except for the neutralization capacities given in Table 3.22, these data were not gathered after the column studies, which is unfortunate because they could be more sensitive indicators of the stability of the materials and potential changes in the mineral composition than are the X-ray diffraction data.

The bentonite clay added to the proposed liner is a natural montmorillonite. Most of the base exchange sites will be occupied by sodium. Exposure of this material to the high calcium concentrations that will be present in the leachate will convert most of the exchange sites to calcium. This will cause a slight decrease in the volume of the montmorillonite, which will have the tendency to increase the permeability of the material.

The data presented here can not be used to evaluate the stability of the liner under prolonged exposure to acid leachates. Montmorillonites are unstable under acid conditions, being converted to kaolinite and soluble silica. There is no single pH at which montmorillonites become unstable because their stability depends on the concentrations of other elements in solution as well. However, pH values lower than 4 are cause for concern. Soil materials containing the minerals studied here will have a large buffer capacity for pH when the pH drops to 4 or lower, but this occurs at the expense of structural cations as Fe and Al are dissolved. None of the pH 3 columns were run long enough so that the pH of the effluent dropped below 5 (Data in document 4 DACE) and Tables 3.16 and 3.17. The statement made on page 3.31 that no perceptible soil elements (Al, Ca and Si) were observed in the effluent would be expected if the effluent was

always above 5. Such elements dissolved from the top of the column, where the pH was most likely lower, would be precipitated or adsorbed in the lower portions of the columns where the pH was not yet reduced to such low values by the leachate. The design of the MDWF facility is such that acidic leachates should never reach the MWDF liner. But If the integrity of the MWDF is to be questioned to the extent that very acid leachates will reach the MWDF liner, then longer term column studies of the liner material and acid leachates should be done. Such studies may show sufficient degradation of the liner material that its' permeability will be significantly affected. Procedures are available to determine the long-term effects of leachates on liners and soils (Haji-Djafari and Wright, 1982).

A black precipitate was observed in many of the columns (Page 3.30). While this compound could not be conclusively identified, it most likely was ferrous sulfide. If so, this observation indicates that the Eh conditions within the tailings can become low enough that sulfide concentrations are significant. This reinforces earlier indications that the Eh conditions within the tailings need to be clarified.

III A 3 g

ROLE OF THE MWDF LINER AND UNDERLYING SOILS IN ATTENUATING THE TAILING LEACHATE.

The retardation factors were measured by batch distribution ratios and by column techniques. The retardation factors for species that have large values can not be easily measured by column experiments because the dissolved species are so effectively sorbed by the column that an inordinatly large volume of leachate must be passed

through the column. This length of time is unreasonable for materials that have a low permeability, such as the liner material and the native soils. Measurement of distribution ratios and the calculation of retardation factors is the only reasonable option for these cases. Column experiments will give the most accurate values for species that have relatively small values of retardation factors. The two methods and the results are discussed on pages 3.16 - 3.26, 4.1 - 4.10 and Appendices E and F of document 3 DACE.

Most of the values of the distribution coefficients determined from the duplicate experiments agree (Tables E.6-E.8). The few pairs of duplicates that do not agree, such as those for As in the pH 6 glacial till, Cd in the pH 6 stratified drift, Mn in the pH 9 glacial till and stratified drift, Ag in the pH 9 stratified drift, and Zn in pH 9 glacial till are usually the result of one of the pairs having a solution concentration somewhat higher than the trend found in the other samples at the same pH, especially when the concentrations were near the detection limit. The values for cyanide are highly variable and are often reported to be zero. This occurred because the concentration of cyanide in the leachate was near the analytical detection limit. The reports, Table E.7, assume that no chemical attenuation of cyanide occurs. This is probably correct because anions in general are weakly attenuated, and singly charged anions are especially so.

The values of the distribution ratios that were calculated using the composition of the pH 3 leachate as the initial leachate and the measured values of the pH 6 or 9 from the batch test should be used with caution (Table 3.12). This kind of calculation implicitly implies that the mass of soil is large enough that the properties of the

soil are not changed as a result of the neutralization of the acid in the pH 3 leachate plus the adsorption or precipitation of the metals in the pH 3 leachate. I think that the intent of these calculations is to show the potential of the soils to attenuate the pH 3 leachate if the volume of soil is large, such as in field conditions. More exact estimates of the potential negative effects of acidic leachates on the soil can be derived by considering the number of moles of acidity contained in the leachate and the number of moles of acid neutralization capacity consumed in the soil to neutralize that acidity. This requires consideration of the permeability of the soil and the number of pore volumes of leachate that pass through the material.

The conclusions given on pages 3-19 and 3-20 are generally valid and reasonable. For conclusion 3, Mn was probably leached from the soils because the redox status of the batch tests was low enough to reduce Mn to the more soluble Mn^{++} form. With respect to cyanide, its retardation factor is expected to be small because of the small anion exchange capacity of these soils, which when coupled with the high concentration of sulfate that will occupy most of the exchange sites, indicates that much of the cyanide should stay in solution.

The column experiments were used to determine the retardation coefficients for those species that have values of about one. All of the values are based on the assumption that the value for the chloride ion is one, which is reasonable. The concentrations of chloride in the effluent from the pH 3 columns was higher than the leachate permeant. Analytical difficulties and leaching of chloride from the soil were both considered as potential explanations but the anomaly was not

resolved (Page D-6). The retardation factors were calculated using the highest values of chloride measured in the effluent as representative of the permeant, which will tend to make the reported values of the retardation coefficients from these columns smaller than their probable real values.

Problems were also encountered with the sulfate analyses. It too was sometimes higher in the effluent than in the permeant, especially for the pH 3 columns (Page D-6). This was thought to result from an analytical problem. My opinion is that the interaction of the reduced sulfur species and sulfate with oxygen from the atmosphere during the analysis produced elemental sulfur (milk of sulfur) in the solution. A turbidimetric procedure was used and colloidal sulfur would produce a positive result. These anomalies affected the values of the retardation coefficients for individual cases but the overall trend is very clear that the retardation coefficient for sulfate is about one.

The conclusions given on pages 3-24 and 3.25 are reasonable and valid. Comparison of the results obtained from the batch and column experiments shows that they are similar (Page 3-26) except that the column results for several of the metals are larger than those obtained from the batch experiments. This is expected because the batch experiments were done at constant pH while the effluent from the pH 3 columns had a pH of about 5.

Attempts to treat acidity as a dissolved species met with mixed success (Pages 3.31 - 3.37). In reality only H^+ can be treated similarly to the calculation of retardation coefficients for the other dissolved species, and then only in very simple systems. This is because H^+ occurs as part of the solvent, water, and it can be pro-

duced and consumed by a wide variety of reactions in systems as complex as those used in these studies. Its solution concentration is not controlled by the relatively simple adsorption-desorption or precipitation reactions that are common for the other dissolved species. The soil titrations discussed on page 3-37 are probably a suitable alternative to retardation factors as they give the effect a given number of pore volumes of each leachate has on the pH of the soil.

The values of the retardation coefficients for the proposed bentonite/till liner are generally larger than those for the glacial till and stratified drift. The differences are inconsequential when the seepage of the MWDF leachate is considered because the liner is so much less massive than the underlying soils. The purpose of the liner is to form a low permeability layer to retard seepage. It does not need to attenuate the composition of the seepage. That it does is a bonus.

III A 4 a

EVALUATION OF LABORATORY STUDIES ON TAILINGS

These studies are reported in document 2 CSMRI. Sample number 2, which is zinc tailings fines from mixed massive/stringer ore, is recommended to be the sample that best represents the proposed tailings that will fill the MWDF. The mineralogical examinations are reported in pages 15-18. X-ray diffraction and optical microscopy of polished sections to determine the sulfide mineralogy were the two techniques used. Pyrite and quartz were the two dominant minerals. Sphalerite (ZnS) and chalcopyrite (CuFeS_2) were present at less than one percent, which is what one would expect in material that had these minerals

removed by flotation processes. These analyses seem adequate and no additional studies are recommended.

The EPA toxicity extraction test was negative for all of the inorganic parameters and it does not need to be repeated.

All of the samples except one tested positive as potential acid producers. No additional tests are recommended, especially since Exxon proposes to treat all of the tailings as potential acid producers.

Semi-quantitative and quantitative spectrographic analyses were done on the samples of tailings. The accuracy of the semi-quantitative analyses is reported to be ± 50 percent. The accuracy of the quantitative analyses is not given but it is probably in the range of ± 10 to 20 percent. The values measured by spectrographic analysis are reported with a precision of one part per thousand (Appendix E), which is unrealistic. One part in ten is more reasonable. The samples were washed five times with deionized water, dried, and pulverized before analysis. The water washes could have removed small amounts of some elements but the quantities removed should be insignificant, especially when one considers that the material was already through a water based flotation process. Some of the particles ranged in size up to 37 micrometers before they were pulverized for analysis and this will also have had minimized leaching losses. The advantages of the water washes is that they would have removed any soluble salts that may have precipitated in the tailings during storage and transport.

The elements Be, Bi, Cl, Li, Se, Sb, and Tl were below the detection limits of the spectrographic analyses. Except for Cl, they are potentially toxic and accurate values of their concentrations in the

tailings should be available for the preparation of the environmental impact statement.

Additional analyses of the tailings are recommended to provide values for the above elements and to confirm the values obtained by the spectrographic analyses. Duplicate analyses of sample number 2, the mixed zinc tailing from massive/stringer ore would be adequate. A combination of analytical techniques would be best. Inductively coupled plasma emission spectroscopy for Al, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Hg, Mg, Mo, Ni, Tl, and V. Neutron activation analysis for Al, Sb, As, Ba, Cd, Cs, Cl, Cr, Co, Cu, Ga, Au, Hf, Fe, Mn, Ni, K, Rb, Ag, Na, Se, Sr, Th, U, and Zn. Values for Be, Bi, Li, Hg, and Tl may also need to be checked by other techniques such as atomic absorption spectrophotometry.

The concentrations of many of these elements are likely to be very low. I do not think that measured values for every element are needed. However, analysis of a sample by the technique recommended for each element will establish the upper limit of concentration of each element with a high degree of certainty. All three of these techniques have sensitivities for their respective elements in the range of about 1 to 1000 nanograms/gram with an accuracy of usually better than five percent.

Neutron activation analysis services are available at the University of Wisconsin Nuclear Laboratory. Inductively coupled plasma emission spectroscopy and atomic absorption spectrophotometry analyses are available at the University of Wisconsin Soil and Plant Analysis Laboratory and at the State Laboratory of Hygiene. All three

of the techniques are also available and used routinely in my laboratories at the University of Wisconsin.

Several times the question of the redox status of the tailings arose in this review of the documents. The behavior of the tailings under oxic conditions is well determined and needs no additional studies. However, the behavior of the tailings under slightly anoxic or anoxic conditions has not been clearly defined. Many of the tests were done under a nitrogen atmosphere which resulted in slightly anoxic conditions, but the conditions expected in the MWDF are not projected so one can not evaluate the relevance of the results to field conditions. Also, some of the reported values of Eh were questioned. Some of the experiments will need to be repeated if these ambiguities can not be clarified during a conference of the concerned parties. Especially important is the composition of the MWDF leachate under the conditions expected in the MWDF and the nature of the leachate-liner and leachate-soil interactions under the conditions expected in the field, and the potential for precipitation of gypsum in the underdrain system resulting from changes in the concentration of sulfate from a variable redox status.

The partial pressure of carbon dioxide is also an important variable that was not addressed in the submitted documents. Changes in the partial pressure of carbon dioxide can cause precipitation or dissolution of carbonate phases with resulting changes in the attenuation potential of the MWDF subsoils. The most important aspect is the impact of carbon dioxide on the potential of precipitating calcite or dolomite in the underdrain system. Leachates generated under anoxic conditions with elevated partial pressures of carbon dioxide

should be analyzed and their reactions to reduced pressures of carbon dioxide studied. Appropriate specialists should be consulted concerning the composition and pressure of any atmosphere in the underdrain system to help evaluate the potential of carbonate compounds in the drainage pipes.

An analysis under carefully controlled conditions of the supernatant in the tailing storage barrels would give useful information if the seals on the barrels could be verified to be air tight. These analyses should include Eh, pH, dissolved elements including speciation of the sulfur compounds. An instrumental technique, such as inductively coupled plasma emission spectroscopy capable of analyzing in the ultraviolet region should be used for the total sulfur analyses to eliminate the problems reported in these documents. This is not an EPA approved technique yet but it is much more accurate and less sensitive to interferences than the standard spectrophotometric and turbidimetric techniques.

III A 4 b (1) Desirability of Conducting Leach Tests of Tailings.

Additional leaching tests are probably not necessary, unless the results of conferences between the concerned parties indicate that additional information is necessary on anoxic environments. One should keep in mind that even with all of the publicity about acid mine drainage, most of the action will occur under low oxygen concentrations if the MWDF operates as planned.

III A 4 b (2) Desirability of Conducting Studies of Reaction Kinetics.

I did not find any evidence that any of the results were limited by reaction kinetics. Oxidation of the tailings and waste rock by T.ferrooxidans occurred within a few days. The effluents from the

column leaching studies of the tailings reached nearly constant values within the time of the studies. The effluents from the column attenuation studies were nearly constant towards the end of these studies.

Verification of the retardation factors will need to be done only if the concerns about the redox status discussed above show that the present studies were done under too high a value of Eh.

III A 4 b (3) Concentrations of Radioactive Elements in Mine Tailings and Slurry Water.

The concentration of thorium is given in Appendix 20 of document 1 BCR. The values found are on the low side of typical values found for rocks and soils. The radioactivity from ^{226}Ra and ^{228}Ra and from ^{230}Th and ^{232}Th is given in appendix F, page 72 of document 2 CSMRI. The results are discussed on pages 13 through 14 of document 2 CSRMI and they are compared with typical values for soils in Table 3, page 14. The most comprehensive discussion of the radiological properties of the ore, waste rock, and soils is in pages 3.38 through 3.44 in Crandon Project, Mine Waste Disposal Facility Feasibility Report NR 182.08.

Their conclusions that the radioactivity in the proposed tailings are typical of that found for ordinary crustal materials and that no additional tests are needed are very reasonable. The concentrations of Th and U, which are the ultimate parents of the radioactive isotopes of Ra and Th, are lower than those commonly found for typical soils. The values for ^{40}K are also very low. The isotope ^{137}Cs occurs only as a fallout product in nature and its concentration is expected to be near zero for all of the materials except the very surface of the soils.

The concentrations of Th and Ra in the slurry water are difficult to predict. Alkaline solutions having high concentrations of dissolved carbonate tend to dissolve the highest concentrations of Th but the relatively low concentrations in the tailings mitigate against significant concentrations occurring in the slurry water.

III A 4 b (4) Reproducing Biological Confirmation Test.

The biological confirmation test was used to evaluate the acid production potential of the tailings as reported in documents 1 BCR and 2 CSMRI. The procedures are essentially identical and the results confirmed the chemical acid production tests in most cases. I see no need to repeat these tests.

III A 6

COMPUTER MODELING OF LEACHATE-SOIL INTERACTIONS

Some of the computer models produced within the last few years have potential for application in an evaluation of the interaction of leachates with soils. Their main value is to assess the impact of changing environmental conditions such as pH, Eh, P_{CO_2} , and P_{O_2} on the stability of a given solution and the potential of the solution to precipitate mineral phases. The models can also be applied to assess the effectiveness of soils to attenuate the concentration of dissolved species in seepage because they can calculate the speciation of the dissolved elements. This is helpful because the reaction of dissolved species with soils is highly dependent upon the ionic charge of the dissolved species.

One of the programs that may be helpful here is GEOCHEM (Appendix A). It calculates the concentrations of dissolved species and considers environmental variables such as CO_2 , Eh, and pH similar to

the WATEQ programs. An advantage of GEOCHEM to this study is that it contains a sulfate, sulfide, and thiosulfate (only the common form of thiosulfate) data base. The model also includes subroutines for cation adsorption onto constant potential surfaces such as metal hydroxides and for cation exchange equilibria. The latter subroutine applies only to mono- and divalent cations interacting with a montmorillonite surface.

Six of the leachates reported in the documents were run under various values of pH, Eh, and P_{CO_2} for a total of about 30 cases. The major finding is that several of the solutions can easily become supersaturated with Ca and Mg carbonates. They also confirmed the speciation of the MWDF leachate predicted by WATEQ and which was used in the column attenuation studies.

A copy of the output of a run based on the proposed MWDF leachate is included with the original copy of this report as an example.

Additional studies can be done if this is necessary and appropriate.

Table 1. The range of concentrations for selected elements in the leachate used as the input for the column attenuation experiments are compared to those measured in the effluent of the column leach studies of the tailings.

Column attenuation experiment ¹		Tailings leachate ²
Element	Range	Range
	-----mg/L-----	
Ca	440-660	25-600*
Mg	66-240	2-NR**
Na	495-770	NR
K	15-120	<1-NR
Fe	0.4-1456	<0.01-0.02
SO ₄	2000-6000	1400-2000
S ₂ O ₃	42-510	NR
pH	2.98-9.05	7.29-8.96
Eh	246-586 mv	-98--103*** mv

1. Data from Tables 3.6 - 3.8 Volume I - Final Report Soil Attenuation Study by D'Appolonia.
 2. Data from Tables J-4, 7, 10, 13 Characterization of Crandon Mill Tailings by the Colorado School of Mines Research Institute.
- * Values not measured during early part of experiment when they would be the highest.
- ** NR Not Reported
- *** These values may have been incorrectly measured. See text for discussion.

Literature Cited

- Haji-Djafari, S. and J. C. Wright. 1982. Determining the long-term effects of interactions between waste permeants and porous media. Am. Soc. Testing Materials (ASTM) 2nd Symposium on Testing of Hazardous and Industrial Solid Wastes.
- Leduc, Gerard. 1981. Ecotoxicology of cyanides in freshwater. in Cyanide in Biology. B. Vennesland, E. E. Conn, C. J. Knowles, J. Westley, and F. Wissing eds. Academic Press, London. pp 478-494.
- Sposito, G. and S. V. Mattigod. 1980. GEOCHEM: A computer program for the calculation of chemical equilibria in soil solutions and other natural water systems. The Kearney Foundation of Soil Science, University of California-Riverside.

**Page Image
not Available**

**Missing
Appendix A**