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D'APPOLONI

Volume I - Final Report

Soil Attenuation Study

Crandon Project
Crandon, Wisconsin

Exxon Minerals Company
Rhinelander, Wisconsin

Volume I - Final Report

Soil Attenuation Study

D'APPOLONIA

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SOIL ATTENUATION STUDY
EXXON-CRANDON PROJECT

EXECUTIVE SUMMARY

Exxon Minerals Company (Exxon) is planning to mine zinc, copper, and lead bearing sulfide minerals near Crandon in northeast Wisconsin. Portions of the mine waste materials will be disposed in a mine waste disposal facility (MWDF). Exxon has selected the area designated as Area 41, located east and southeast of the mine/mill site, as the primary candidate area for the MWDF site. Extensive studies (Golder, 1980) have identified Area 41 as possessing the best combination of characteristics to prevent and mitigate potentially adverse effects to the existing environment while meeting waste disposal design requirements.

The proposed mine/mill facility will generate three general solid waste types including ore tailings, backfill sands, and wastewater treatment sludge. The coarse size fraction of the tailings (backfill sands) will be used to fill in underground mined-out areas. The ore tailings will have a high sulfide content and, considered in conjunction with their fine particle size, will have a potential for acid leachate generation. The process wastewater sludge is expected to contain free lime and have a high acid-neutralization capacity.

Current plans indicate that the MWDF will be constructed in stages and will eventually cover several hundred hectares. Key components of the proposed MWDF design relative to the soil attenuation study are depicted in Figure EX-1 and include:

- Pond embankments will be constructed using MWDF site glacial till soils and lined with modified glacial till which may have bentonite clay additions to further reduce seepage.
- An underdrain system will be installed to reduce pond seepage.

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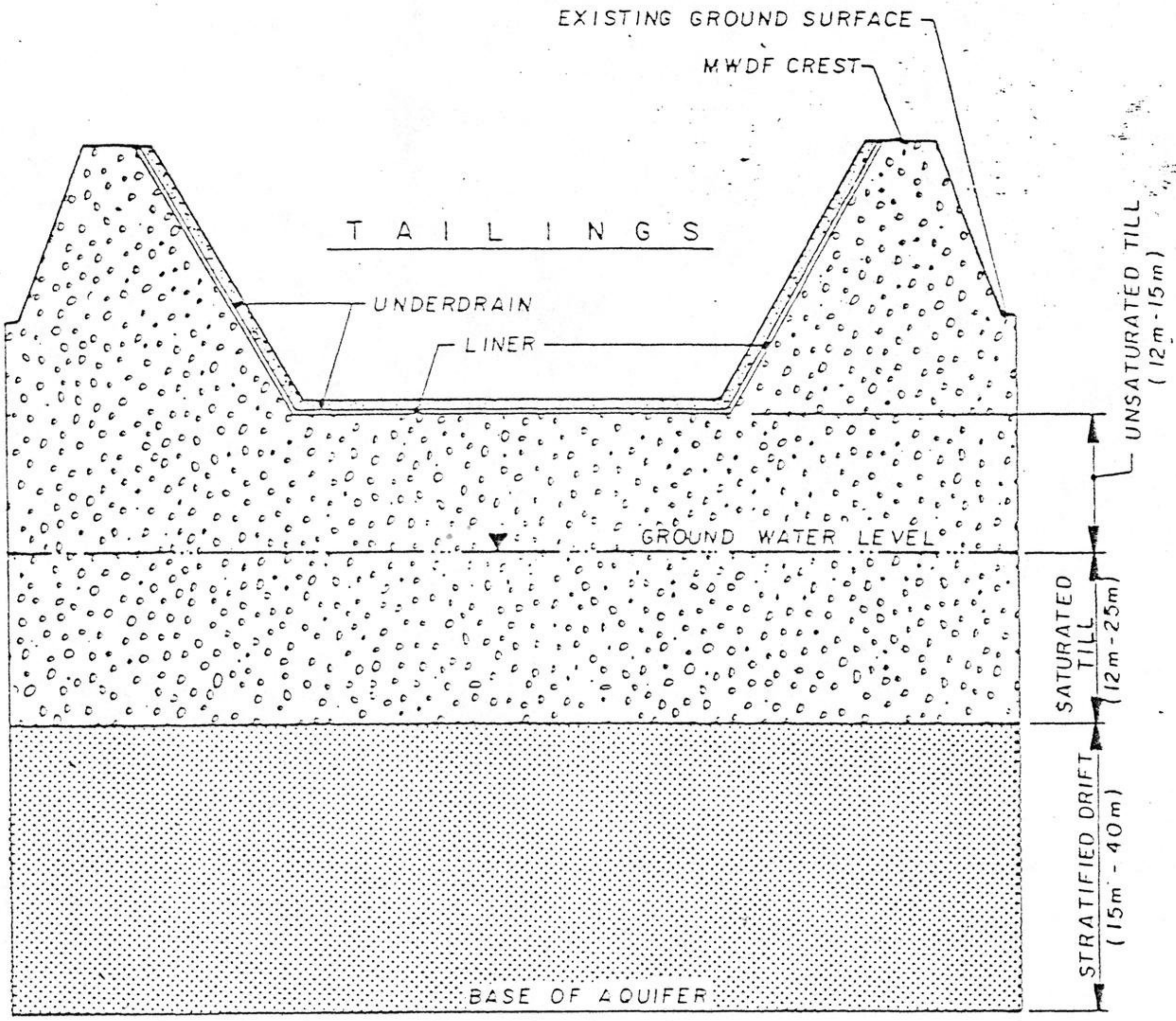

FIGURE EX-1

GENERALIZED VERTICAL CROSS SECTION OF MWDF TAILING POND AND UNDERLYING SOILS

PREPARED FOR

EXXON MINERALS COMPANY
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D'APPOLONIA

(NOT TO SCALE)

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- Pond bottoms will be located about 12 to 15 meters above the ground water surface to enhance soil attenuation of potential seepage chemical species in the unsaturated zone.
- Once a pond is filled to capacity with tailings, a cap will be placed on its surface to reduce precipitation infiltration into the pond.

The objective of this study was to determine the chemical attenuation characteristics of a potential liner material and underlying soils of MWDF site Area 41. Varying seepage pH conditions were considered for those chemical parameters with the highest potential to be present at the Crandon MWDF site. This study also meets the requirements of the Wisconsin Administrative Code, NR 182.075.

The results of the attenuation study were evaluated relative to the present or anticipated conditions of the Crandon site to predict the behavior and potential migration of chemical parameters from the MWDF. The study scope did not include predicting the hydrological impacts of the MWDF. However, the results of the study provide the necessary chemical attentuation data to perform a hydrological/geochemical impact study.

The study scope included:

- Generation of soil composites and soil liner admixture representative of MWDF site soil conditions.
- Characterization of the composite and liner test samples.
- Generation of synthetic (spiked) tailings leachates to encompass the widest range of possible leachate quality that could be related to MWDF operations.
- Determination of attenuation characteristics for the test samples to chemical parameters of the leachates.

To evaluate the chemical attenuation characteristics of the MWDF site soils and MWDF liner for the chemical parameters of interest, both batch and column test retardation factors (R_d) were determined. Retardation factors are used in mass transport models to determine the velocity of chemical solutes (species) of interest relative to the advancing ground water front. The retardation factor for a particular solute is defined as follows:

$$R_d = \frac{\text{average linear ground water velocity}}{\text{solute migration velocity}}$$

where R_d is a dimensionless ratio and the sorption isotherm is assumed to be linear.

When $R_d = 1$, the solute of interest migrates at the same velocity as that of the advancing seepage front. As the solute is more strongly influenced by sorption phenomena, its velocity diminishes and R_d becomes greater than 1. Therefore, if a solute has an $R_d = 100$, its migration velocity is 100 times less than the seepage front.

Two major stratigraphic units have been identified as potential leachate migration routes from the MWDF site Area 41: a poorly sorted glacial till and a coarse-grained stratified drift (Figure EX-1). The glacial till has a typical saturated permeability of 10^{-7} meters per second and directly underlies the MWDF. Most vertical migration of leachate from the MWDF is expected to occur in this unit, as it is largely above the ground water table. The stratified drift has a saturated permeability of 10^{-4} to 10^{-5} meters per second and typically underlies the glacial till. Lateral migration of potential leachates from the MWDF will occur in this saturated zone. Typically, a less permeable fine-grain stratified drift also underlies the coarse-grain stratified drift but is not expected to be an important leachate migration route.

Because of the heterogenity of each stratigraphic unit, composite samples were created to better represent their overall physical and chemical characteristics. In addition to these two composite samples, a representative liner material as might be considered for the MWDF (a four percent bentonite/glacial till admixture) was also tested in this attenuation study.

The grain-size distribution of the test samples reflects the geologic origin of the materials and their relative ability to transmit seepage. The glacial till composite and the bentonite/till admixture exhibit a relatively well-graded distribution of particle sizes. The well-graded nature of the material indicates the permeability should be moderate to low. In contrast, the stratified drift composite reflects the glaciofluvial origin of the material. Over 80 percent of the drift is fine and medium sand as a result of water sorting of materials.

The glacial till composite, stratified drift composite, and bentonite/till admixture all contain predominantly quartz and feldspar, with clay minerals comprising less than 15 percent of the samples. The dominant carbonate mineral present in the samples is dolomite. The dominant clay minerals in the samples include kaolinite, mica/illite, chlorite, mixed layer clays, and smectites. The mixed layer clays are an irregularly, interstratified two-component mixture of chlorite and vermiculite. Quartz and feldspar also constitute more than 50 percent of the clay-size fraction of these samples. The reaction pH for all samples is strongly alkaline ranging from 8.75 to 9.80. Neutralization capacities of the samples are moderate to high and range from 0.7 to 2.3 percent calcium carbonate equivalent.

The MWDF leachates will likely be alkaline with a pH ranging between 10.5 and 7.0. The air oxidation of thiosalts generated during flotation in the mill could cause the tailings pond waters to decrease to a pH of 7.0, even with the planned excess lime addition. Therefore, 9 and 6 were chosen as representative leachate pH conditions to study soil chemical attenuation characteristics for the anticipated MWDF site soil environment. However, if excessive sulfide-mineral oxidation should occur, the pH of the tailings leachate may decrease. To study an extreme case, a pH 3 leachate was also chosen to examine soil attenuation characteristics. Therefore, both the anticipated and possible "worst-case" leachate pH and chemistry range in the MWDF were included in the attenuation study.

Synthetic leachates were prepared by spiking leachates generated from a constant pH 2 modified ASTM (1981) 1:4 leachate of the Crandon Pilot Mill tailings. The leachates were also spiked to simulate mill reagents or increase solute levels to significantly above analytical detection limits to aid in their analytical determination for this attenuation study.

Generalized results of the attenuation testing are presented in Table EX.1. This table of relative mobility for leachate chemical constituents represents the combined results of the bulk and column attenuation testing, which were in agreement.

The attenuation test results can be used to estimate field hydraulic seepage rates and concentration of various chemical parameters with time for the anticipated field soil conditions. The accuracy of the estimate is influenced by the test limitations and assumptions. However, the test results provide sufficient information to estimate the time variability of seepage quality.

Based upon the anticipated field soil conditions discussed in Chapter 4.0, Table EX.2 shows the approximate time for chemical parameters with known retardation factors to migrate through the various individual and combined soil units to half their source concentration. As can be seen from this table, any chemical parameter with a retardation factor of five or above will require about 950 years or more for its concentration at the 366 meter (1,200 foot) compliance boundary to equal half of its source concentration. Even if a chemical parameter has a retardation factor of 1.0, no chemical attenuation, it still will require 188 years

TABLE EX.1

GENERAL MOBILITY OF LEACHATE CONSTITUENTS(1)

PARAMETER	LEACHATE pH		
	pH 3	pH 6	pH 9
Filterable Residue(2)	Very Mobile	Very Mobile	Very Mobile
Chloride	Very Mobile	Very Mobile	Very Mobile
Fluoride	Solubility Controlled	Solubility Controlled	Solubility Controlled
Nitrate-Nitrogen	Mobile	Mobile	Mobile
Sulfate	Very Mobile	Very Mobile	Very Mobile
Total Sulfur	Very Mobile	Very Mobile	Very Mobile
Cyanide	Slightly Mobile	Solubility Controlled	Slightly Mobile
Arsenic	Slightly Mobile	Slightly Mobile	Immobile
Barium	Solubility Controlled	Solubility Controlled	Solubility Controlled
Cadmium	Mobile	Immobile	Immobile
Chromium	Slightly Mobile	Solubility Controlled	Immobile
Copper	Mobile	Slightly Mobile	Immobile
Iron	Mobile	Mobile to Slightly Mobile	Solubility Controlled
Lead	Slightly Mobile	Solubility Controlled	Solubility Controlled
Manganese	Very Mobile	Very Mobile	Immobile
Mercury	Slightly Mobile	Solubility Controlled	Immobile
Selenium	Solubility Controlled	Slightly Mobile	Slightly Mobile
Silver	Solubility Controlled	Slightly Mobile	Slightly Mobile to Immobile
Zinc	Mobile	Slightly Mobile	Immobile

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(1) Very mobile - moves at same velocity as water seepage front ($R_d = 1$)
Mobile - $R_d < 10$
Slightly mobile - $R_d > 10$, < 100
Immobile - $R_d > 100$
Solubility controlled - chemical parameters in synthetic-spiked leachate at or below analytical detection; thus is not a measure of soil attenuation characteristics.

(2) Filterable residue = total dissolved solids.

TABLE EX.2

APPROXIMATE MIGRATION TIME FOR CHEMICAL PARAMETERS AS RELATED TO SOIL ATTENUATION

CHEMICAL PARAMETERS RETARDATION FACTOR (R_d)	YEARS TO REACH $C/C_o = 0.5$(1)			
	BASE OF MWDF LINER	BASE OF GLACIAL TILL	COMPLIANCE BOUNDARY IN STRATIFIED DRIFT(2)	TOP OF LINER TO COMPLIANCE BOUNDARY(2)
1	4	134	50	188
5	20	669	250	940
10	39	1,338	500	1,880
25	98	3,345	1,250	4,700
50	195	6,690	2,500	9,400
100	390	13,380	5,000	18,800

---

(1) Approximate years to reach half concentration of source for probable MWDF site soil conditions, as presented in Chapter 4.0. Calculation assumes fully saturated conditions and a constant source concentration above each soil unit; i.e., soil units are not connected. Calculation ignores dilution, dispersion, and variation in source concentration. Therefore, values shown are considered to be more conservative than expected for the design conditions of the probable MWDF site operations.

(2) 366 meters (1,200 feet).

for its concentration to increase to one half of its source value. For alkaline leachates nearly all of the heavy metals have retardation factors greater than 10, many either greater than 100 or are so insoluble as to be analytically undetected. These calculations conservatively assumed fully saturated conditions in all units. Additionally, the calculation also ignored the effects of dilution and dispersion and possible variation in the source concentration or seepage flow rates during operational and postoperational conditions.

Estimates of how pH will change with time in various soil units were based on the column attenuation test results. For instance, for a pH 3 MWDF leachate, the number of years for the soil unit's seepage pH to decrease from normal background (approximately pH 8 to pH 7) to pH 5 for the anticipated field conditions is summarized as follows:

SOIL UNIT	FIELD TIME (years)
Four percent bentonite/ till admixture liner	30
Glacial till	223 to 910
Stratified drift	255

The above analysis of the attenuation data, along with potential dilution and dispersion calculations, can be used to identify the parameters where further analyses are not required to perform a hydrological impact study. The selection of the final parameters for use in any impact study must, however, also consider their potential source concentration variation over time, i.e., will the concentration diminish, remain constant, or increase over time.

The significance of this leachate-soil attenuation program for the MWDF siting, construction, and operations can be briefly summarized as follows:

- Most of the chemical attenuation of any MWDF seepage occurs in the glacial till as a result of the permeability and thickness of this stratigraphic unit (Table EX.2). Also, the glacial till typically has higher retardation factors than the stratified drift (Chapter 3). A MWDF with the greatest thickness of till beneath the tailing pond has the greatest attenuative potential.

- The mobility of chemical parameters decreases with increasing pH of MWDF leachate. Thus, the pH of the tailing pond should be maintained in the alkaline range.

- U.S. EPA primary drinking water standard elements in alkaline MWDF leachate are typically very effectively chemically attenuated by glacial till. Chemical parameters such as sulfate or filterable residue (total dissolved solids) on the U.S. EPA secondary drinking water standards list exhibit little chemical attenuation, R_d <2.0, thus these parameters depend upon mechanical attenuation, dilution, and dispersion for control. A MWDF design that reduces seepage rate during operation (underdrain) and during postreclamation (tailing cover) will also minimize, by chemical and mechanical attenuation, potential impacts at the 366 meters (1,200 feet) compliance boundary.

- Selection of chemical parameters for any monitoring program for pre, post, and operational phase of the MWDF would benefit by designating which chemical species are likely to be mobile or immobile.

1.0 INTRODUCTION

Exxon Minerals Company (Exxon) retained D'Appolonia Consulting Engineers, Inc. (D'Appolonia), to perform a soil attenuation study for the preferred MWDF area. The objectives of this study were to:

- Determine the chemical attenuation characteristics of a potential MWDF liner material and underlying soils for varying seepage pH conditions and those chemical parameters with the highest potential to effect the existing ground water quality.
- Evaluate the chemical attenuation data relative to the present or anticipated conditions of the Crandon Project MWDF.
- Supply the necessary attenuation data for the evaluation of any hydrological/geochemical impact study of the MWDF.

The study scope did not include evaluating the potential hydrological impacts of the MWDF. However, the results of the study do aid the selection of seepage chemical parameters for possible future computer simulation studies.

This study was limited to a laboratory investigation. To accomplish the project objectives, the following tasks were performed:

- Review of previous Crandon Project reports for their relevancy to the design of the study and evaluation of the study results.
- Selection of samples from four borings penetrating the major stratigraphic units potentially affected by MWDF seepage for physical and chemical index testing. Results of the index testing were used to generate soil composites which represent MWDF site conditions for further analyses and subsequent laboratory attenuation studies.
- Generation of a bentonite/till admixture, approximating a potential liner material for the MWDF.

- Generation of synthetic tailing leachates at three test pH's (3, 6, and 9) to encompass the range of possible leachate quality within the MWDF.

- Determination of constant pH batch retardation factors (R_d's) for selected metals at pH 3, 6, and 9.

- Determination of soil column attenuation characteristics for the tailing leachates and their effect on the permeability of the compacted soil columns.

- Determination of the acid neutralization capacity and distribution of carbonate minerals in the soils beneath and surrounding the MWDF site Area 41.

- Evaluation of the laboratory results relative to the physical and geochemical environment of the Crandon MWDF site Area 41.

In addition to the above technical tasks, a Quality Control Program was established for this project to insure the correctness of the work conducted. The Quality Control Program used in this study is discussed in Appendix A.

The remaining chapters and appendices of this report describe the study MWDF site soil characteristics and laboratory and analytical methods, results, and conclusions specific to the study objectives discussed above.

2.0 SITE AREA DESCRIPTION

This chapter provides the background information on the Crandon Project site area used in formulating the assumptions and conditions used in the design of the laboratory attenuation studies and the evaluation of the study results. The Crandon Project site area is located in the Northern Highlands region of northeastern Wisconsin in Forest County. This area is characterized by glacial landforms of moderate relief consisting of rolling hills and intervening valleys. Generally, Precambrian bedrock containing the ore deposit is overlain by as much as 90 meters of glacial deposits. The resulting surface water drainage system consists of lowland and upland wetland areas, and several lakes and streams. The region is sparsely populated and contains extensive deciduous forest stands. As shown in Figure 2-1, the ore deposit occupies portions of both Nashville and Lincoln townships, while the mine support and mill facilities are expected to be located in Lincoln Township. The preferred MWDF Area 41 is located east and southeast of the ore body and occupies portions of Lincoln and Nashville townships.

Section 2.1 of this chapter provides a description of the existing site area environment; specifically, site geology and ground water hydrology. Section 2.2 provides a spatial and conceptual layout of a MWDF operation and description of the waste characteristics.

2.1 EXISTING MWDF SITE ENVIRONMENT

2.1.1 Site Geology

The Crandon Project site area consists of Precambrian metavolcanic tuff bedrock overlain by as much as 90 meters of glacial deposits. The bedrock is a southern extension of the Canadian Shield and within the project area has an irregular surface. Regionally, the bedrock surface trends downward to the southeast and east at approximately 1.3 to 2 meters per kilometer (Golder, 1981b).

Glacial deposits at the site area consist principally of soil or sediment materials deposited during the Wisconsin stage of the Pleistocene Epoch. The Wisconsin stage represents the most recent of the major ice advances during the Pleistocene and began about 75,000 years ago. The bulk of surficial material in the site area is most likely the result of the Woodfordian substage lasting from about 22,000 to 12,500 years ago. During this period, ice from the Green Bay Lobe advanced from the southeast and ice from the Langlade Lobe flowed from the northeast. These ice advances met in northeastern Wisconsin, resulting in complex interfingering and overlapping of materials (Dames and Moore, 1981a).

The glacial stratigraphy of the MWDF site is complex but can be characterized by three general units as shown in Figures 2-2 and 2-3. Glacial till/fine-grained stratified drift typically overlies the bedrock surface and is in turn overlain by coarse-grained stratified drift and a finer-grained unit of glacial till. As discussed later, most lateral ground water flow from beneath the MWDF site area occurs in the coarse-grained stratified drift. Additionally, the glacial till/fine-grained stratified drift underlying the coarse-grained stratified drift has a permeability of two to three orders of magnitude lower than the coarse-grained stratified drift (Golder, 1982b). Therefore, the lower glacial till/fine-grained stratified drift is essentially a hydrological barrier and this unit and the lower bedrock will not be discussed further.

Thicknesses of the upper glacial till and coarse-grained stratified drift (hereafter termed stratified drift) units vary considerably across the site area, ranging from only a few meters to tens of meters but are typically on the order of 20 to 40 meters for each unit (Figure 2-4). Discontinuous lenses of lacustrine and glaciofluvial deposits occur principally within and below the stratified drift unit and at the glacial till/stratified drift interface. Surface lacustrine deposits are also present predominantly surrounding and beneath present-day lakes and wetlands. More detailed characterization of site area glacial stratigraphy has been discussed in reports prepared by Dames and Moore (1981a) and Golder (1982b).

The glacial till materials generally consist of a poorly sorted heterogeneous mix of silt, sand, gravel, cobbles and boulders, and traces of clay. They are classified as sand-silt mixtures, are predominantly nonplastic, and possess variable permeabilities due to variation in the content of fine particles (Golder, 1981b).

Stratified drift materials in the MWDF site area consist predominantly of well-sorted sand, with some gravel and a low percentage of fine particles. These materials are present to depths of 30 to 65 meters under MWDF site Area 41 and represent the principal aquifer through which most lateral ground water flow occurs.

2.1.2 Ground Water Hydrology

On a regional and site-specific basis, the glacial deposits overlying the Precambrian bedrock contain the principal aquifers. The glacial deposits typically consist of permeable sands, gravels, cobbles, and boulders with variable but small amounts of clay, while the bedrock is generally of low or very low permeability.

In the Crandon Project site area, ground water occurs under both unconfined and confined or semiconfined conditions. Confined or semiconfined conditions exist due to the contrasting permeability between the glacial till and stratified drift deposits. Locally, perched aquifers of limited areal extent occur above the main ground water table.

Configuration of the potentiometric surface or ground water table is, in general, a subdued reflection of the surface topography. The potentiometric surface tends to be higher beneath the upland areas, including MWDF site Area 41, and is present at or close to ground surface in the lowland areas. Upland lakes are generally above the potentiometric surface, suggesting that these lakes function as ground water recharge areas. In contrast, many low-lying lakes receive ground water discharge from the surrounding area.

Ground water flow is outward from MWDF site Area 41. Ground water flow within the stratified drift tends to be mainly horizontal. The hydraulic gradient in the stratified drift is in the range of 0.002 to 0.006 (Golder, 1982b).

The permeability of the glacial till and stratified drift units has been estimated by several field and laboratory investigations (Golder, 1982b). Generally, saturated permeability is on the order of 10^{-6} to 10^{-7} meters per second in the glacial till and 10^{-4} to 10^{-5} meters per second in the stratified drift.

Domestic water well yields in the site area were compiled in a well survey (Dames and Moore, 1982). Yields range from 0.032 to 0.063 cubic meter per second in the stratified drift.

Appendix B of this report lists sources of additional information on MWDF site conditions.

2.2 CONCEPTUAL MINE WASTE DISPOSAL FACILITY OPERATIONS

Exxon has selected the site area designated as Area 41 (Figure 2-1), located east and southeast of the mine/mill site, as the primary candidate site for the MWDF. Extensive siting studies (Golder, 1980) have identified Area 41 as possessing the best combination of characteristics to mitigate potential impacts to the existing environment while meeting MWDF design requirements.

2.2.1 Mine Waste Material Properties

The general waste types to be disposed at the MWDF include ore tailings, backfill sands, and wastewater treatment sludge. The fine fraction of the ore tailing materials will be less than about 30 microns in effective diameter (i.e., silt and clay size), while the coarse size fraction that will be backfilled consists of sand-size materials. Coarse waste rock from the mine may also be placed in the disposal area. The ore tailing will have a high sulfide content and, considered in conjunction with their fine particle size, will have a potential for acid leachate generation. The process wastewater sludge is expected to contain free lime and calcium carbonate and have a high acid-neutralization capacity.

2.2.2 Mine Waste Disposal Facility Operations

Current plans indicate that the MWDF will be constructed in stages with wastes slurried and pumped to the disposal ponds through a pipeline system (Golder, 1982a). These tailing disposal ponds will eventually cover several hundred hectares. Components of the proposed tailing pond design relative to the soil attenuation study are depicted in Figure 2-4 and include:

- Pond embankments will be constructed using site compacted till which may have bentonite clay additions to further reduce seepage.
- An underdrain (leachate collection) system will be installed to reduce pond seepage.
- Pond bottoms will be located approximately 12 to 15 meters above ground water to maximize soil attenuation of seepage species in the unsaturated zone.
- Once a pond is completed, a cap will be placed on its surface to reduce infiltration into the pond.

Additionally, the leachate of the mine waste material (hereafter termed tailings) are expected to have a pH of about 10.5. Considering seasonal variations, a minimal pH of 7.0 may occur in the summer months, especially at the tailing pond surface, due to the oxidation of thiosalts. Exxon currently plans to add excess lime, in addition to the process wastewater sludge to maintain the alkalinity of the tailing's pore volume water.

3.0 LABORATORY STUDIES

3.1 SAMPLE COMPOSITING AND COMPOSITE SAMPLE CHARACTERISTICS

3.1.1 Introduction

As discussed in Chapter 2.0, two major stratigraphic units have been identified as potential leachate migration routes from the MWDF site Area 41: (a) a poorly sorted glacial till and (b) a stratified drift (Figure 2-4). The glacial till has a typical saturated permeability of 10^{-7} meters per second and directly underlies the MWDF. Seepage leaving the bottom of the MWDF will migrate vertically through this unit toward the underlying ground water table. The stratified drift has a saturated permeability of 10^{-4} to 10^{-5} meters per second and typically underlies the glacial till (Golder, 1982b).

Soil samples for use in this attenuation study were obtained from four borings in the MWDF site Area 41 (Figure 2-1). The borings were drilled by Golder Associates (Golder) in May and June 1981. One-hundred twenty-one samples were collected from these borings (Golder, 1981d). Samples were selected by Golder to represent the stratigraphic units encountered during the drilling program. Golder's sampling procedures are discussed in Appendix C.

To prepare samples for laboratory testing, compositing was done. The compositing attempted to provide samples with geochemical and hydrogeologic characteristics similar to the major stratigraphic units in the area. Due to the complex glacial stratigraphy of the region, and heterogeneous nature of each stratigraphic unit, testing of individual samples for each minor statigraphic variation was not feasible.

3.1.2 Sample Compositing

Since composite samples were to represent the stratigraphic unit characteristics, index testing was initiated to assess typical ranges of site sample characteristics. Thirty (30) samples of the 121 samples available for use in this study were chosen for index testing. Samples for index testing were chosen based upon a representative physical appearance for the two major stratigraphic units of concern, the spatial distribution across the MWDF site, and a wide range of carbonate effervescence results. Carbonate effervescence was used as a method of chemical characterization differentiation for initial sample selection. Carbonate content can affect pH of MWDF seepage and chemical species migration.

Index tests on the selected samples included grain-size analyses, reaction pH, and neutralization capacity determinations. The grain-size distribution is an indication of permeability (a geohydrologic parameter) and can indicate chemical species migration mitigation potential. Reaction pH and neutralization capacity are both indices of many heavy metal species migration mitigation potential. A detailed discussion of the criteria used for selecting the samples for index testing and the results of the index tests are presented in Appendix C.

The index testing showed that the following three composite samples would adequately represent the site geochemical and geological characteristics for the purpose of this study:

- Composite Sample No. 1. "Fine-grained" glacial till with low neutralization capacity.
- Composite Sample No. 2. "Coarse-grained" stratified drift with low neutralization capacity.
- Composite Sample No. 3. Glacial till with high neutralization capacity.

Figures 2-2 and 2-3 show the location of samples used for compositing on geologic profiles of the MWDF site Area 41. The grouping of the samples for compositing was accomplished by visual inspection, grain-size feel of the samples, and estimated neutralization capacities. Regarding grain-size compositing, the "fine-grained" samples for Composite No. 1 were defined as having the feel of clays present in the sample. This grouping into fine-grained samples did not consider the amount of coarse-grained materials present in the sample, only that clays were present. Conversely, the "coarse-grained" samples for Composite Sample No. 2 were defined as having the feel of an absence of clays in the sample. This grouping did not consider the amount of silts and fine sand material in the sample, only that clays were absent in large quantities.

The neutralization capacity of the samples was estimated from a correlation of the 30 neutralization capacity and carbonate effervescence results presented in Appendix C. Basically, six categories of carbonate effervescence were established representing estimated neutralization capacities (in percent calcium carbonate equivalent) from less than 1.5 to greater than 9. For Composite Samples No. 1 and No. 2, all samples selected had calcium carbonate equivalents estimated at less than three percent. For Composite Sample No. 3, all samples selected had calcium carbonate equivalents greater than three percent. Grain size was not a criteria used in the generation of Composite Sample No. 3.

In addition to physical and geochemical characterization (grain size and neutralization capacity), samples for compositing were selected with the following considerations:

- Vertical distribution within each borehole and spatial distribution over the MWDF site.
- Position of the sample above and below the water table. Vertical migration of the MWDF seepage will occur through the unsaturated zone in the glacial till and this migration will continue downward through the glacial till below the water table until the MWDF seepage encounters the regional stratified drift aquifer, where lateral migration will occur (Figure 2-4). However, it is expected that most chemical attenuation will occur above the water table. Glacial till samples from above the water table and stratified drift samples from beneath the water table were preferred.

Detailed discussions of the criteria used for selecting the 66 samples for compositing and the samples and procedures used in generating the composites are presented in Appendix C.

Composite Samples No. 1 and No. 2 were used in all phases of the laboratory attenuation testing. Composite Sample No. 3, the glacial till with high neutralization potential, was selected only for characterization of calcium carbonate equivalent and long-term acid buffering capacity. To maintain a conservative (worst case) testing program, low neutralization capacity samples (Composite Samples No. 1 and No. 2) were chosen for testing both the glacial till and stratified drift for chemical species attenuation. A high neutralization capacity sample (Composite Sample No. 3) would neutralize acidic leachate better and show more chemical parameters attenuation potential. "Fine-grained" stratified drift would be expected to have a higher attenuation capacity than the "coarse-grained" stratified drift. However, most lateral ground water flow should be through the coarse-grained materials. The "fine-grained" glacial till composite allowed determination of the probable range of MWDF site soil attenuation characteristics.

3.1.3 Liner Sample Generation

A representative liner soil material for the proposed MWDF tailing ponds was also generated for use in the attenuation study. This liner sample was composed of a glacial till sample collected by Exxon from Golder's (1982c) Test Pit No. 22 (Figure 2-1) and sodium bentonite available from American Colloid (product name Volclay). Both of these materials are identical to those used in Golder's (1981a) liner engineering studies. A four percent (dry weight bentonite to dry weight till) bentonite/till admixture was prepared. The four percent bentonite/till admixture was chosen so as to represent the middle of the range, 0-8 percent, used in Golder's (1981a) liner engineering studies. For the sample characterization and batch attenuation studies, the bentonite and till were mixed dry. For the column attenuation and long-term permeability study, the bentonite and till were mixed wet, as described in Appendix F, to simulate probable field mixing conditions.

3.1.4 Composite and Liner Sample Characteristics

Since larger grain-size particles could not be present in the column test samples (would not allow proper compaction of the columns), the coarse and fine gravel fractions (plus No. 4 sieve material) of each composite were separated, removed, and weighed for grain-size distribution. Except for being separately characterized for its carbonate effervescence (Table 3.4), the gravel fraction of each sample was not used in any other characterization or attenuation test. This provided identical composite samples for all tests.

Composited samples (minus No. 4 sieve material) were physically and chemically analyzed for grain-size distribution, mineralogy, reaction pH, neutralization capacity, exchangeable cations and cation exchange capacity (CEC), anion exchange capacity (AEC), and organic matter content. Results of these analyses are discussed below.

3.1.4.1 Grain-Size Distribution

Grain-size distribution of the composite samples (Table 3.1) reflects the geologic origin of the materials, its probable permeability and, to some extent, chemical parameter attenuation. The glacial till (Composite No. 1) exhibits a relatively well-graded distribution of particle sizes with 35 percent gravel, 51 percent sand, and 14 percent undifferentiated silt and clay (minus No. 200 mesh fines). The well-graded nature of the material with 14 percent fines indicates the permeability should be moderate to low. ,Once the gravel fraction is removed, the till is essentially a medium and fine sand with approximately 20 percent undifferentiated silt and clay (fines). This increase in fines will reduce its permeability. With compaction, this material can have a very low permeability.

When four percent bentonite is added to the glacial till (Test Pit No. 22) sample to generate a liner soil material, the material is still well graded with 23 percent gravel, 57 percent sand, and 20 percent fines. Removal of the gravel increases the fines content to 26 percent. This bentonite/till admixture, when compacted, exhibits very low permeabilities; as evidenced by the permeability testing discussed later herein.

The stratified drift (Composite No. 2) reflects its glaciofluvial origin. Over 80 percent of the drift is fine and medium sand as a result of water sorting of materials. Only eight percent of its mass was lost when the gravel fraction was removed for the attenuation tests.

3.1.4.2 Mineralogy

Mineralogy can be used to help predict reactions of soil particles with leachates. Tables 3.2 and 3.3 present the results of semiquantitative X-ray diffraction analyses of bulk (minus No. 4 sieve material) and clay fractions of the precolumn test composite and liner samples. All three samples, the glacial till (Composite No. 1), stratified drift (Composite No. 2), and bentonite/till admixture, contain predominanly quartz and feldspar, with clay minerals accounting for 15 percent or less. The dominant carbonate mineral present in the samples is dolomite. Calcite was also detected in each sample, but only at trace levels. As shown in Table 3.3, the dominant clay minerals in the samples include kaolinite, mica/illite, chlorite, mixed layer clays, and smectites. The mixed layer clays are an irregularly interstratified two-component mixture of chlorite and vermiculite. As would be expected for these three samples, the bentonite/till admixture sample contained the most smectite (5 to 10 percent). Quartz and feldspar also constitute more than 50 percent of the clay-size fraction of these samples.

Dames and Moore (1981b) analyzed 18 samples from 14 borings in the Crandon Project environmental study area for mineralogy by X-ray diffraction analysis. Most of the samples were glacial till materials. Their results generally confirm the findings of this investigation, except they found smectite to be the dominant clay mineral present and kaolinite to be present in only minor amounts compared to the other clay minerals.

The mineralogy indicates that most of the soil will be rather inert to even low pH seepage. The clay minerals, especially the smectites and mixed layer clays, could enter into exchange or adsorption reactions with certain chemical species in the leachate (see Section 3.2 for leachate makeup). The carbonate minerals will react with low pH leachates, if such seepage is present and occurs beneath the MWDF.

3.1.4.3 Chemical Characteristics

Chemical characterization data are presented in Table 3.4 for the composite and liner samples. The reaction pH for all samples is strongly alkaline ranging from 8.75 to 9.80. Neutralization capacities of the samples are moderate to high and range from 0.7 to 7.2 percent calcium carbonate equivalent. The "low neutralization capacity" glacial till and stratified drift composite samples had substantial neutralization capacities of 2.3 and 1.6 percent calcium carbonate equivalent, respectively. The "high neutralization capacity" glacial till had a neutralization capacity of 7.2 percent calcium carbonate equivalent. These values represent 23, 16, and 72 tons of calcium carbonate equivalent per 1,000 tons of soil, respectively. As presented in Footnote 4 of Table 3.4, the gravel fractions of the samples had neutralization capacities similar to the composite samples, as estimated from carbonate effervescence results.

The cation exchange capacity (CEC) for all samples ranges from 4.2 to 7.4 milligram equivalents per 100 grams of soil. These CEC values reflect, in part, the low clay content of the soils, since CEC resides principally in clay minerals and collodial materials. Field condition CEC values may be greater than indicated in Table 3.4. The analytical procedure for CEC determination utilizes a pH 7.0 buffered solution, while soil reaction pH is 8.75 or higher. CEC tends to increase at higher pH and in soils with substantial amounts of variable charge clay minerals present (e.g., kaolinite). Thus, an increase in field condition CEC may result, especially for alkaline seepage.

Calcium is the most prevalent exchangeable cation followed by magnesium and sodium in the three samples tested. Levels of potassium and exchangeable acidity (hydrogen) are 0.1 milligram equivalent per 100 grams of soil or less. The relative proportions of exchangeable cations, considered in conjunction with adsorption affinities and solution concentrations, can be used to evaluate the potential for exchange reactions to occur between the MWDF seepage and cation exchange sites of the soil. A small but important amount of exchangeable sodium occurs and is highest in the bentonite/till admixture sample. Since sodium is generally more weakly adsorbed on cation exchange sites than potassium, calcium, magnesium, and other divalent and trivalent cations, the potential exists for MWDF seepage cations with greater adsorption affinities to enter into exchange reactions with sodium and be retained on soil particles.

Anion exchange capacity (AEC) values range from 1.5 to 1.7 milligram equivalents per 100 grams of soil. The principal source of AEC in soils typically resides in sesquioxides (e.g., goethite and amorphous compounds). Anion exchange capacities exist at low pH's where there is adsorption of H^+ ions resulting in a positive charge on the soil surface. As a result of these positively charged sites, anions can be attenuated.

Organic matter affects ion attenuation by exchange reactions and the formation of chelates and organometallic complexes. Organic matter may attenuate cationic species but typically has a low capacity for anion retention. Organic matter content in the three samples is low, ranging from 0.22 to 0.96 percent. The highest organic matter content occurred in the four percent bentonite/till admixture, which was composed of a glacial till sample collected near ground surface. Due to the low levels of organic material in the site soils, ion retention by organic matter is not anticipated to be a major reaction in the site soils.

3.2 LEACHATE SYNTHESIS, TESTING, AND STABILITY

3.2.1 Introduction

The overall philosophy of the leachate synthesis was to create a solution which was (a) representative of any MWDF tailing liquors yet (b) conservative in the estimated concentration of chemical species available for migration. The pHs of the leachates were selected from conditions of possible worst case (pH 3) to values which bracketed the probable MWDF operating and reclamation conditions (pH 6 and pH 9). An attempt was made to maintain the leachates under similar environmental conditions (i.e., reduced state) that are anticipated in and eventually below the MWDF.

The synthetic leachates were prepared by spiking leachates generated from the Crandon Project pilot mill tailings. The leachates were spiked to simulate mill reagents or to increase solute concentrations significantly above analytical detection limits to aid in solute detection during the attenuation study. The tailings were leached at pH 2 to generate a "worst-case" chemical matrix of the major metals (e.g., Ca, Mg, Na, K, Al, Si) for the synthetic leachates. A "worst-case" chemical matrix was desired because soil attenuation of heavy metals generally decreases with increasing ionic strength (Griffin, et al., 1976a, 1976b, and 1977).

The pHs for the synthetic leachates were selected to approximate typical and worst-case conditions. For typical conditions, the MWDF leachates will likely be alkaline with a pH ranging between 10.5 and 7.0. The tailings will contain a high sulfide content and the tailings water is expected to contain reduced sulfur species, especially thiosulfate. The oxidation of thiosalts in the tailing ponds may cause the tailings leachate to decrease to a pH of approximately 7. Oxygen for this chemical reaction will come from unsaturated pore spaces within the tailings, the subsoil, and from the pond surface. As the oxygen is consumed, anoxic conditions are expected to eventually occur beneath the MWDF. To bracket these probable pH values, synthetic leachates were prepared at pHs of 6 and 9.

A lower pH could result if sulfide-mineral or chemical species oxidation occurs within the pond or subsoils. Although long-term oxygen presence in an MWDF or its subsoils appears unlikely, a synthetic leachate with a pH of 3 was generated to simulate an extreme "worst-case" acid condition.

3.2.2 Synthetic Leachates Generation

The synthetic leachates utilized tailings from the Crandon Project pilot mill as a base. The pH was adjusted to the three target values (3, 6, 9), the matrix was stabilized, filtered, oxygen removed, spiked to target chemical concentrations, and aged under a nitrogen atmosphere. The salient aspects of the leachate generation procedure were as follows:

- Generate chemical matrix - The Crandon pilot mill tailings were leached at pH 2 (H_2SO_4) using the ASTM (1981) shake extraction of solid waste with water method.
- Adjust pH - The leachates were filtered and the pHs of three separate aliquots were adjusted to 3, 6, and 9 with lime. Lime was used to neutralize the leachates as it will be present in the process wastewater and sludge (Chapter 2.0).
- Leachate oxidation—matrix stabilization - The three different pH leachates were periodically stirred for 24 hours to oxidize the leachates and induce precipitation. This procedure was employed to promote the long-term stability of the leachates by removing solutes in the leachate chemical matrix which were at a state of saturation with readily formed mineral phases as a result of leaching the tailings in an oxidizing environment.
- Precipitate removal - The leachates were filtered through 0.45 μm filters.
- Oxygen control - The leachates were purged of oxygen by bubbling nitrogen through the leachates for 60 hours in an attempt to obtain semi-anoxic conditions.

- Leachate synthesization - Each leachate was spiked to target concentrations (Table 3.5).
- Leachate stabilization - To obtain a more stable chemical composition, the leachates were aged for one week under a nitrogen atmosphere before the start of leachate analyses and attenuation testing.

Details of the leachate synthesization and maintenance are presented in Appendix D. Throughout the study, a nitrogen atmosphere was maintained over each leachate. Also, pH was periodically monitored and maintained in each leachate, and any precipitates which formed after the leachates were spiked were allowed to remain in contact with the leachates.

3.2.3 Results and Discussion

Table 3.5 presents a summary of the synthetic tailings leachate chemistry after the various steps of generation. The chemical compositions of the pH 2 and spiked leachates are in good agreement, considering the spike concentrations added to the pH 3, 6, and 9 leachates.

Two leachates were generated for each pH and have been termed Phase I and Phase II leachates. The Phase II leachates were generated after the supplies of Phase I leachates were exhausted so that the column attenuation tests could be conducted for a longer time period. The same procedures were used to generate both the Phase I and Phase II leachates. The concentrations shown in Table 3.5 for the pH 3, 6, and 9 leachates are the highest representative values for duplicate Phase I and Phase II leachate analyses. Tables 3.6 through 3.8 present the results of the initial and final analysis for each of the Phase I and Phase II leachates.

As shown in Tables 3.5 through 3.8, the general chemical quality of the leachates improves with increasing pH even though the three different pH leachates were identically spiked (Appendix D). For the pH 3 leachates, cyanide, mercury, selenium, and silver, were lower in the leachate than concentrations added from spiking. As pH increased to 6, arsenic, cadmium, chromium, copper, and lead, in addition to the above four species, were also below target levels in the leachates. At pH 9, iron, manganese, and zinc were also below target concentrations, in addition to the above nine species. However, as is evident from Table 3.5, the leachates used in the attenuation study at all pH's had higher concentrations of all species than predicted from mass balance equilibrium modeling for estimated tailing pond water conditions (CH_2M/Hill, 1982).

3.2.3.1 Cation/Anion Balance

The cation/anion balance, numerical summation of the milliequivalents for a given sample, indicates the completeness of analytical determinations (they should be equal). The following results were obtained for the pH 2 and October 26, 1981 analyses of the different pH synthetic-spiked leachates:

	pH 2	pH 3	pH 6	pH 9
cations (meq/ℓ)	107.4	144.2	106.5	69.0
anions (meq/ℓ)	62.0	130.9	84.5	65.8

From these results, it appears the leachate analyses were numerically deficient in anions. Sulfur species account for approximately 90 percent of the anions present. Leachates were analyzed only for sulfate, thiosulfate, and total sulfur. Thiosalts are known to disproportionate or interconvert among themselves. Because thiosulfate is unstable at low pHs, tetrathionate was substituted for thiosulfate as the spike for the pH 3 leachate (Appendix D). However, no analyses of tetrathionate were made for the leachates, which may account for some of the numerical deficiency in anions, especially for the pH 3 leachate. When thiosulfate (in equivalent SO_4) and sulfate analyses are totaled, excess total sulfur is present in all the leachates. Other unmeasured sulfur species are, therefore, present in the leachates. When total sulfur as sulfate is substituted for sulfate and thiosulfate in the milliequivalents per liter calculation for anions, the values for the pH 2, 3, 6, and 9 leachates change to 97.5, 175.9, 135.5, and 90.3, respectively. These values, however, by not considering the mix of sulfur species present, may be higher than the actual anion milliequivalent per liter in the leachates. Therefore, except for the pH 2 leachate analysis, which still has nine percent more cations than anions, there is reasonable agreement in the cation/anion balances for these leachate analyses considering the uncertainty in sulfur specification.

The results of the other leachate analyses, Tables 3.6 through 3.8, are similar to analyses for which the cation/anion balances were calculated. Therefore, the other leachate analyses should also have reasonable cation/anion balances.

3.2.3.2 Leachate Stability Evaluation

The leachate stability was assessed in two ways: (a) by leachate equilibrium modeling using a chemical equilibrium model (WATEQ), and (b) monitoring the leachates during the attenuation testing program.

Equilibrium Modeling: The leachate stability and possible equilibrium/ mineral precipitation reactions which could occur in the pH 2 and synthetic leachates was assessed using a modified version of Truesdell and Jones (1974) chemical equilibrium model, WATEQ. The modified WATEQ model enables predictions as to the chemical species distribution in solution and what minerals are soluble or stable within the given environments of each leachate. WATEQ calculates the equilibrium distribution of aqueous chemical species (complexes) of major and minor elements using chemical analysis and measurements of temperature, pH, and redox potential. From this model, the states of reaction of the water with solid (mineral) and gaseous phases are calculated.

Table 3.9 presents the results of the WATEQ analyses for the equilibrium distribution of the aqueous chemical species in the pH 2 and synthetic leachates as of October 26, 1981; approximately seven days after spiked leachates were generated. Salient results of this analysis are as follows:

- Little evidence of anionic metal complex formation. Neutral ion pairs were more prevalent than anionic complexes.
- Ferrous iron is the dominant form of soluble iron in the pH 2, 3, and 6 leachates while, in the pH 9 leachate, ferric is the dominant form of iron present.
- Sulfate forms complexes, at important levels with aluminum, cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, and zinc in almost every leachate pH, especially in the lower pH leachates.
- Oxides or hydroxides of chromium, copper, iron, lead, and zinc replace the sulfate complex in the pH 9 leachate.

WATEQ does not include a thiosalt data dose. However, as suggested by Davis and Leckie (1978), Benjamin and Leckie (1982), and The Chemical Society (1971), thiosulfate forms strong complexes with cadmium, copper, silver, and mercury.

Table 3.10 presents the results of the WATEQ analyses for the state of leachate solution equilibrium with possible solution chemistry controlling mineral phases. Salient results of the above equilibrium modeling follow:

- Calcium and sulfate levels in the leachates will be controlled by gypsum precipitation reactions since gypsum ($CaSO_4 \cdot 2H_2O$) is predicted to be at saturation in all four leachates (pH 2, 3, 6, and 9). (Although not modeled by WATEQ, thermodynamic data also suggest that sulfate, by the precipitation of barite [$BaSO_4$], is probably also controlling barium solution levels.)
- Fluorite (CaF_2) is at a state of saturation in the pH 9 leachate and unsaturated in the pH 2, 3, and 6 leachates. Fluorite levels in the pH 9 leachate will be controlled by fluorite precipitation.
- Amorphous iron hydroxide [$Fe(OH)_3$] is at or above saturation in the pH 3, 6, and 9 leachates.

Additionally, most crystalline iron hydroxides are at a state of super saturation. Therefore, the precipitation of iron hydroxide mineral phases is controlling iron levels in these pH leachates.

- Sulfate minerals or amorphous precipitates, especially in the lower pH leachates, may be controlling solution levels of aluminum and lead.
- Carbonate and/or hydroxide minerals or amorphous precipitates may be controlling the solution levels of cadmium, calcium, chromium, copper, manganese, and zinc in the pH 9 leachate.

The above results indicate that some of the heavy metals in the leachates may continually be removed from solution. This is because sesquioxides of iron, which were shown to be stable in the leachates, tend to adsorb substantial amounts of other metals. Additionally, concentrations of other metals may increase in solution with time as amorphous precipitates begin to age and crystallize, releasing elements adsorbed onto the mineral (Tables 3.6 through 3.8).

Stability Monitoring: Tables 3.6 through 3.8 show the results of the leachate analyses at generation and at completion of testing. Appendix D (Tables D.2 through D.4) presents the results of periodic monitoring of the leachate quality during the course of the attenuation testing program for specific indicator parameters. Regarding stability, the tables show, as predicted by the WATEQ analysis, that increases and decreases occur in several elements with leachate aging. But, in general, the concentrations remained fairly stable. However, fluctuations in the Eh and sulfur species were observed in all three synthetic leachates.

Since the leachate influent to the bentonite/till admixture columns (Columns K-1 and K-2) could not be mechanically sampled during testing, the leachates were analyzed at the beginning and completion of testing. Appendix D (Table D.5) presents the results of these analyses. In general, the leachate chemistry of both the pH 3 and 9 leachates remained fairly stable. The major exception was that the pH of the pH 9 leachate decreased to approximately 7.0 and 6.5 during the course of the column testing.

3.3 DISTRIBUTION RATIOS AND RETARDATION FACTORS

3.3.1 Introduction

The main purpose of this study was to assess the ability of the soils at the MWDF site to attenuate chemical species which may be present in the tailing leachate. The data would be used for further evaluation and design considerations and planning of the MWDF operations and reclamation.

Sorption attenuation capacities of soils can be expressed in terms of a distribution ratios (K_r) and/or retardation factors (R_d). These expressions are often used in mass transport models to determine the velocity of solutes (chemical species) of interest relative to the advancing ground water front.

The distribution ratio (K_r) for a specific chemical species may be defined as the ratio of (a) the mass sorbed onto a solid phase to (b) the mass remaining in solution. As expressed by Freeze and Cherry, 1979:

$$K_r = \frac{\text{mass of solute on the solid phase per unit mass of solid phase}}{\text{concentration of solute in solution}}$$

The dimensions of this expression reduce to cubic length per mass (L^3/M). It is conventional to express K_r in units of milliliters (cubic centimeters) of solution per gram of sample.

Distribution ratios are dependent upon solute concentration, competing ion effects, pH, oxidation-reduction potential (Eh), temperature, time of contact between the solute and "sorbing" soils, and the geomedia characteristics, such as mineralogical composition and texture. The distribution ratio for a given chemical species generally assumes a different value when any of the above conditions are altered.

The retardation factor (R_d) for a particular solute is defined as the dimensionless ratio of the average ground water velocity to the solute migration velocity in the absence of dispersion effects. For a particular geomedia, the retardation factor is related to a distribution ratio by the following expression (Freeze and Cherry, 1979):

$$R_d = 1 + (\rho/n_e)\,K_r = \frac{\text{average linear ground water velocity}}{\text{solute migration velocity}}$$

where

K_r = distribution ratio (cm^3/g),
ρ = bulk density (g/cm^3) of the geomedia, and
n_e = effective porosity.

When $R_d = 1$ (i.e., $K_r = 0$), the solute of interest migrates at the same velocity as that of the advancing waterfront. The K_r value increases as the solute migration is more strongly influenced by sorption phenomena and, hence, causes R_d to become greater than one. The retardation factor, when calculated from K_r values, assumes that at a specific pH, the adsorption isotherm is linear and does not involve attentuation by chemical precipitation.

The laboratory methods used to assess these parameters, R_d and K_r, are (a) batch tests and (b) column tests. The batch tests were used to define the distribution ratios, K_r, and consequently the retardation factors for those chemical species which exhibit adsorption potential for soils. Appendix E presents the details of batch test procedures used in this study.

For more mobile chemical parameters, the retardation factors were determined directly by column tests. The column tests also provided a means of comparing the retardation factors obtained by the batch tests for the chemical parameters exhibiting slight mobility. Appendix F presents the details of column testing for determination of retardation factors.

3.3.2 Batch Attenuation Tests

3.3.2.1 Experimental

A short-term constant pH batch method was used to determine distribution ratios of the glacial till, stratified drift, and bentonite/till admixture. The process of batch testing involves (a) disaggregating representative soil samples; (b) placing a specified amount of soil and leachate (of known chemical characteristics) in a reaction bottle; (c) letting the contents react for 48 hours; (d) centrifuging the bottle to separate sediments and liquid; and (e) removing the clear supernatent and analyzing the chemical characteristics.

The attenuation characterizations of the following chemical species were analyzed by batch testing in accordance with the proposed ASTM (1981) method:

- Arsenic
- Cadmium
- Chromium
- Copper
- Iron
- Lead
- Manganese
- Mercury
- Selenium
- Silver
- Zinc
- Cyanide

The above distribution ratios were determined for pH 3, 6, and 9 leachates to assess and enable modeling of the pH dependence upon the migration rates of the above solutes. During testing, pH was adjusted to remain a constant. In addition, distribution ratio determinations were conducted under a nitrogen atmosphere to simulate the expected semi-anoxic state of percolating leachates. Appendix E contains full details on the batch test method and presents the results of the distribution ratio, including duplicate, determinations.

3.3.2.2 Results and Discussion

Table 3.11 presents the resulting constant pH retardation factors from the distribution ratios calculated from duplicate batch tests as set forth in Appendix E (Tables E.6 through E.8). Table 3.12 presents the retardation factors which take into account the effects of leachate neutralization, i.e., assumes the pH 3 leachate concentration at the start of testing. The effects of leachate neutralization on solute removal can be evaluated because the pH 3, 6, and 9 leachates were prepared identically, except for the amount of lime added to adjust pH (Appendix D).

General findings of the batch attenuation testing include:

- Retardation factors (R_d) for the metals, chromium (pH 6), iron (pH 9), lead (pH 6, 9), mercury (pH 3, 6), selenium (pH 3, 6, 9), and silver (pH 3, 6, 9), are lower than what would be anticipated to occur under field conditions. This is because their concentrations in solution were limited by their solubilities.

- Attenuation of the metals, arsenic, cadmium, chromium, copper, manganese, and zinc, increased with increasing pH.

- No metal retardation factors increased with decreasing pH. Except for the pH 9 leachate mixtures, manganese was leached from the soils.

- Retardation factors for both the bentonite/till admixture and glacial till materials generally were higher than the coarse-grained stratified drift materials.

- Duplicate attenuation batch tests were in agreement.

Special findings of the batch attenuation testing include:

- For the pH 3 leachate, the metals arsenic, chromium, lead, and mercury were noticeably attenuated with R_d's in the approximate range of 20 to 150. Selenium and silver were limited in solution by their very low solubility in the leachate solutions.

- For the pH 6 leachate, the metals arsenic, cadmium, and copper were noticeably attenuated with R_d's in the approximate range of 30 to 160. Chromium, lead, mercury, selenium, and silver were limited in solution by their solubility in the leachates.

- For the pH 9 leachate, the metals arsenic, cadmium, chromium, copper, manganese, mercury, selenium, silver, and zinc were noticeably attenuated with R_d's in the approximate range of 100 to 1,600. Lead was limited in solution by its solubility in the leachate.

- Results for cyanide attenuation were analytically inconsistent (leachate solutions near detection limit), but it appears cyanide is attenuated (R_d's less than 20) by the bentonite/till admixture and glacial till sediments.

As shown in Table 3.12, the effect of leachate neutralization has very pronounced effects on the attenuation of the following metals: arsenic; cadmium; chromium; copper; iron; lead; manganese; and zinc. Mercury, selenium, and silver largely remained limited in solution by their very low initial solubility in the leachates. These results indicate major attenuation when percolating acidic leachates can be neutralized by the MWDF soils.

As a check on the results of the batch tests, a review of the general soil attenuation mechanisms and trends for heavy metals, as extracted from the literature, was made. Table 3.13 summarizes this information. The results of this study, Tables 3.11 and 3.12, generally conform to the findings of past investigations. The soil attenuation of anionic complexes, such as cyanide and selenium oxides, did not increase as pH decreased. This may have been due to the very low concentrations of these species in solution, which made accurate R_d determinations difficult.

3.3.3 Column Attenuation Tests

3.3.3.1 Introduction

Retardation factors for mobile, $R_d = 1$ to 5, chemical parameters such as sulfates, or total dissolved solids and acidity, all of which may exist in tailings liquid, cannot be as accurately determined by batch tests and the conversion of distribution ratios. Direct measurement from column tests are preferred. Column tests can also be used to measure the retardation of slightly mobile chemical parameters.

The column test consists of permeating the leachate (containing the solutes or chemical parameters of interest) through the soil sample and measuring the resultant retardation directly. The retardation factor is determined by comparing the rate of movement of the chemical species being studied to a completely mobile tracer species such as chloride.

When the concentration of the chemical parameters of interest was observed as half the value in the leachate reservoir, the retardation factor was calculated as:

$$R_d = \frac{\text{pore volumes accumulated at half concentration for the chemical parameter of interest}}{\text{pore volumes accumulated at half concentration of tracer}}$$

The selection of the half concentration for determining chemical species column breakthrough and calculation of "sorption" retardation factors is based on the assumption that dispersion influences the movement of chemical parameters through the soil columns (idealized plug flow chemical breakthrough). When the test system is more dynamic (chemical reactions such as mineral/chemical precipitation or dissolution are occurring), then the determined retardation factors are specific only to the half concentration of the chemical species being investigated. This is because the chemical breakthrough plots (concentration versus time) show variations and fluctuations in the curve shapes, as a result of the chemical reactions occurring in the columns. When the test system is dynamic, "nonsorption," then the results can be appropriately evaluated by methods as discussed in Chapter 4.0.

3.3.3.2 Experimental

The procedure for column testing includes (a) compacting the composite samples to near field densities and permeabilities; (b) covering the sample with an impervious membrane; (c) placing the samples in a triaxial pressure cell and applying consolidating pressure; (d) saturating the samples with MWDF site ground water; (e) applying a resevoir of leachate to the sample; and (f) collecting and analyzing the effluent from the sample.

The column tests were conducted using split fractions of the same three complisted soil samples and leachate sources used in the batch attenuation tests. A total of 10 column tests were conducted. Table 3.14 presents the experimental design for the program. Duplicate column tests of the glacial till and stratified drift were conducted using the pH 9 leachate as a permeant to examine the reproducibility of the hydraulic and chemical attenuation tests and because the tailings leachate will likely be alkaline in the MWDF.

An attempt was made during the study to have no more than one pore volume (void space in a dry soil column) of flow from each column per week to allow sufficient time for chemical reactions to occur. The glacial till and stratified drift soil samples were, however, too permeable to achieve this flow rate with a static leachate-reservoir head. A peristaltic pump was, therefore, used as the leachate permeant driving force. The bentonite/till admixture samples were tested under a constant hydraulic gradient so that changes in their permeability could be continually monitored.

Effluents from the columns were monitored for the following primary parameters:

- Chloride (As the water tracer assuming $R_d = 1$.)
- Specific conductance/total dissolved solids
- Sulfate
- Total sulfur
- Available acidity
- Arsenic
- Iron
- Zinc
- pH
- Eh

Other parameters (specifically those potentially in the MWDF tailing seepage) were periodically analyzed in the column effluents and retardation factors calculated. Tables 3.15 through 3.19 list the other parameters and determined retardation factors.

The chemical data were normalized (measured permeant concentration divided by source concentration) and related to pore volumes of flow from each soil column. Plots of the normalized concentration versus the number of pore volumes (chemical breakthrough curves) were constructed for each column so that solute front advancement R_d values could be calculated.

Source concentrations were determined from representative monitored leachate concentrations (Appendix D) during the column test period. As previously discussed, the source concentration for most of the monitored parameters remained fairly constant.

An anomalous situation occurred in the pH 3 leachate column tests. Chloride concentrations in seepage effluent were two to four times higher than in the influent leachate permeant. The reason for this increase is unknown, but is speculated to be an analytical problem. To keep the test results conservative, the maximum effluent chloride concentration was used as the tracer source concentration for calculating the solute retardation factors.

Other parameters (total sulfur, sulfate, and specific conductance) measured in the column effluents were sometimes observed to also exceed the leachate source concentration. These differences were likely due to analytical interferences and are discussed in Appendix D.

The plots of normalized concentration versus pore volumes for each column effluent were maintained throughout the test. Figures 3-1 through 3-10 present these results. The plots allow the half concentration pore volume displacement to be quickly determined and the R_d value to be calculated.

Detailed discussions of the testing methodology and results of the chemical monitoring are presented in Appendices F and H, respectively.

3.3.3.3 Results and Discussion

Table 3.15 presents half concentration R_d values for the continuously monitored parameters. Salient findings of the solute front advancement attenuation study are as follows:

- The retardation factor for sulfate, total sulfur, and specific conductance/total dissolved solids are essentially 1 for the three leachate pHs and soil samples tested, including duplicate pH and leachate columns (glacial till and stratified drift). This implies, as was assumed for chloride, that these parameters will have minimal chemical attenuation by the MWDF site soils. Some minor retardation of sulfur species was evident in the columns permeated with pH 3 leachate, which was probably due to the formation of gypsum in these columns (Section 3.4.2).

- Retardation factors for iron and zinc with pH 3 and 6 leachate were higher for the glacial tills than for either the stratified drift or bentonite/till admixture.

- Retardation factors for arsenic are in excess of the values shown in Table 3.15, since half concentration breakthrough did not occur in any of the columns permeated with pH 3 and 6 leachate.

The behavior of pH through the column provides an assessment of the leachate neutralization reactions with the soil. For the column tests, the following observations from Figures 3-1 through 3-10 were made:

- The effluent pH of the pH 3 leachate columns decreased to approximately pH 5 and remained there until the conclusion of the test.
- The effluent pH of the pH 6 leachate columns decreased to pH 6 in the glacial till and stratified drift column after approximately seven and five pore volumes, respectively.
- The effluent pH of the pH 9 leachate columns remained at about pH 7 throughout the test. (As discussed in Section 3.2.3, the pH 9 leachate reservoir for Column K-2 decreased to approximately pH 7. However, the reservoir pH for the four other pH 9 leachate columns remained near pH 9 throughout the test.)
- The effluent pH profile of the duplicate pH 9 leachate columns for the glacial till and stratified drift were similar.

Further discussion of pH movement through the columns and assessment of acid retardation are presented in Section 3.5.

Tables 3.16 through 3.19 present the half concentration column retardation factors for the other chemical species studied in this investigation. These retardation factors were calculated from:

- Two effluent analyses from each soil column (Tables 3.16 through 3.19); the
- Ratio of (a) pore volumes required for the source half concentration of chloride to breakthrough (Figures 3-1 through 3-10); to (b) pore volumes required for the half concentration for the chemical parameters of interest to breakthrough each column; and
- Influent leachate permeant analyses (Tables 3.16 through 3.19). An attempt was made to measure these influent characteristics at about the time the analyzed effluent would have first entered

the sample; i.e., leachate reservoirs were sampled and analyzed about one week before the column seepage was collected and analyzed.

3.3.4 Comparison of Batch and Column Attenuation Results

Table 3.20 summarizes the results of the batch and column retardation factor determinations. Generally, the results of the two methods are in excellent agreement. However, the following differences in the results of the two methods were observed:

- The retardation factors for the column attenuation study showed that cadmium, copper, and zinc are attenuated more by the MWDF site soils than predicted from the batch test results for the pH 3 leachates. However, the batch tests were conducted at constant pH 3, while the column tests effluent from the pH 3 column leachate permeant was about pH 5 (retardation of pH).
- The pH 9 column tests indicate that manganese is attenuated less than what would be predicted by the pH 9 batch test. However, the column effluent pH was not pH 9, but approximately pH 7. Manganese results for the pH 6 batch test and leachate influent pH 9 column tests are in agreement.

3.4 EFFECTS OF LEACHATE-SOIL INTERACTIONS WITH SOIL CHARACTERISTICS

The column tests were also used to determine variations in permeabilities, mineralogy, and chemical characteristics during water and leachate permeation. A discussion of pertinent observations and results is presented below.

3.4.1 Permeability

Table 3.21 presents permeabilities measured in the ten soil columns. Permeabilities are shown (a) as initially measured by passing MWDF site area ground water through the samples and (b) as finally measured by passing leachate permeants through the samples. Permeabilities were determined under steady-state flow conditions and calculated from final sample dimensions. Heads and sample confining pressures were identical for the initial and final permeability determinations. Appendix F presents the details of the permeability measurements.

Glacial Till: The initial permeabilities (with ground water as permeant) for three of the four glacial till samples were near 5 x 10^{-8} meters per second. The fourth sample (Column I-4) showed initial permeabilities near 4 x 10^{-7} meters per second. All of the glacial till samples showed permeabilities on the order of 1 x 10^{-7} to 5 x 10^{-7} meters per second after leachate permeation.

The increase in permeability of three of the four glacial till samples is attributed to initial measurements at partial saturation. The fine-grained texture of the samples could have prevented complete initial saturation. All of the glacial till columns were similarly compacted during preparation (Appendix H). Steady-state flow was achieved in all columns. Complete saturation may not have occurred in Columns I-1 through I-3. This explanation of low initial permeabilities is further supported by no observed physical changes in the samples at the conclusion of the tests (Appendix F). If partial saturation was the cause of the initial low permeabilities, then initial saturated permeabilities of Columns I-1, I-2, and I-3 would be on the order of 10^{-7} meter per second, i.e., very similar to Column I-4. The initial and final column permeability data would then be in agreement with field permeabilities (Table 3.21) measured by Golder (1982b).

Stratified Drift: Table 3.21 shows permeabilities for stratified drift near 1 to 2 x 10^{-5} meters per second for initial and final permeabilities. Saturation in these coarse-grained samples was more readily attained. The column permeability values are in agreement with field measured data (Golder, 1982b).

Bentonite/Till Admixture: The bentonite/till admixture tests showed very low initial permeabilities (10^{-10} meters per second) with only a slight increase after leachate permeation. These permeabilities are for partially saturated conditions. The fine-grained, clayey texture of the sample prevented complete saturation during the test. The saturation at final condition was approximately 83 percent. The percent saturation was determined by measuring the specific gravity and water content at several longitudinal points along each column. The average moisture content in each sample was 12.1 percent, which was fairly constant along the length of the samples. It is anticipated that complete saturation would not increase the permeability substantially above these values.

The bentonite/till admixture, if incorporated in the MWDF design, is anticipated in the long term to be near the percent saturation achieved in the column tests; and consequently to have a permeability near those measured. The test method simulated the liner overlying the unsaturated glacial till, in that only atmospheric pressure was present on the seepage effluent of the sample. The underlying till has a higher permeability than the bentonite/till admixture and will allow drainage of permeating water. Thus, the measured values are considered representative of anticipated MWDF site conditions. Therefore, no significant change in the permeability should be expected in the soil liner material from potential MWDF leachate interactions.

3.4.2 Mineralogy

Tables 3.2 and 3.3 present the results of bulk and clay pre and post-column test mineralogy from representative column samples of the glacial till and bentonite/till admixture. Semiquantitative X-ray diffraction analyses were used for these determinations. The analyses were conducted to assess whether the leachate reactions would change the mineralogy and consequently the chemical retardation or permeability characteristics of the soil. No postcolumn mineralogical analyses of the stratified drift or columns permeated with pH 6 leachate were performed because no major interaction was expected.

Results of these analyses follow:

pH 3 Leachate Columns

- The glacial till and bentonite/till admixture column samples showed a significant decrease in the carbonate mineral content (dolomite). Concomitantly, gypsum (calcium sulfate) formed in these columns. (Similar results would be expected for the stratified drift).

- A reduction of smectite and mixed layer clays in the glacial till and bentonite/till admixture samples was noted. Concomitantly, there was an increase in the mica/illite clay fractions in the samples. This was most likely caused by cations (especially potassium) in the higher ionic strength leachates causing the collapse of the expanded clay layer minerals (i.e., smectites and mixed layer clays) into a mica/illite type clay structure. (Similar results would be expected for all leachate pHs and soil at the MWDF site.)

- The chloride content of the glacial till and bentonite/till admixture increased in the columns permeated with the pH 3 leachate. This was probably the result of aluminum hydroxide precipitation in clay interlayer regions, forming chlorite type clay mineral structures. This reaction is common in the pH range of 3 to 6. As shown in Figures 3-1 through 3-3, the seepage pH from these columns was approximately 5. Additionally, from Table 3.10, aluminum hydroxide is at an equilibrium state of saturation with the pH 6 leachate. Also, the seepage chemistry results shown in Tables 3.16 and 3.17, which show that aluminum is removed from the pH 3 solution, support the above conclusion.

pH 9 Leachate Columns

- The glacial till and bentonite/till admixture columns permeated with the pH 9 leachate showed no change in carbonate minerals and no gypsum precipitation occurred. (The same results would be expected for the stratified drift column.)

- A reduction of smectite and mixed layer clays was noted in the glacial till and bentonite/till admixture as would be anticipated from the above discussion.

The above-noted changes are consistent with the previously discussed permeability and column and batch attenuation test results. The gypsum precipitation at low pH leachate values will increase the retardation factor for sulfate above 1. The changes in the expanded clay layers (which constitute only a trace amount of the bulk soil) are on a small scale and will not cause preceptible variations in permeability or attenuation characteristics.

A black precipitate observed forming in many of the columns (especially those permeated with the pH 9 leachate - Appendix H) was analyzed for its chemical composition. No new mineral phases were detected in the postcolumn test mineralogical analyses; however, it was anticipated that this was an amorphous precipitate. X-ray diffraction will not detect amorphous precipitates. To identify the material, an analysis was performed using an energy dispersive X-ray analyzer attached to a scanning electron microscope. The results of this analysis indicated that the black amorphous precipitate was predominately an iron-sulfur (ferrous sulfide) compound. Similar precipitates can be expected within the tailings, liner, and soils at the MWDF site for similar environmental conditions (i.e., anoxic environment) and could act to retard iron and sulfur movements.

3.4.3 Chemical Characteristics

Table 3.22 presents the pre and postcolumn test reaction pH and neutralization capacity results for the 10 test columns. For all 10 column samples, the reaction pH decreases from strongly alkaline (8.75 to 9.80) to the neutral range (6.53 to 7.62). The lower reaction pHs were present in the samples permeated with the pH 3 and 6 leachates. The reaction pHs of the samples permeated with the pH 9 leachate were similar to the column effluent pHs (Figures 3-6 and 3-10). The observed decrease in reaction pH may have resulted from the loss by dissolution of the detected trace amounts of calcite, which is more basic than dolomite.

All column samples, except the bentonite/till admixture permeated with pH 9 leachate (Column K-2), showed an appreciable decrease in neutralization capacity. The K-2 column showed a 0.1 percent increase in neutralization capacity. This result and the discussion of lost neutralization capacity to acidity passed through the columns, presented in Section 3.5.1.4, indicate a possible heterogeneous distribution of carbonate minerals in the column and bulk composite samples.

The permeant effluent of the column tests was also chemically analyzed during two periods of the column testing. The presence of principal soil elements in the effluent could indicate loss of soil structure and associated increases in permeability or changes in attenuation characteristics. Tables 3.16 through 3.19 present the results of these analyses.

For the columns permeated with pH 3 and pH 6 leachates, no preceptible principal soil elements (aluminum, calcium, and silicon) were observed in the effluent. In fact, aluminum, calcium, and silicon were usually removed from the permeant influent and remained in the sample.

For columns permeated with pH 9 leachates, silicon levels increased slightly in the effluents. The increase did not, however, indicate appreciable internal changes in the sample.

The above column effluent analyses would suggest that the principal soil minerals were stable in the presence of the permeating leachates.

3.5 ACID NEUTRALIZING CAPACITY AND CARBONATE MINERALS DISTRIBUTION AT THE MWDF SITE AREA 41

3.5.1 Acid Neutralizing Capacity

3.5.1.1 Introduction

The migration of an acid front (e.g., low pH seepage from the MWDF) is governed by the ground water flow and neutralization capabilities of the geomedia (soils and water) in which the acid is advancing. In geomedia with no neutralization capabilities, the acid front will usually migrate at the same rate as that of ground water flow (assuming no dilution or dispersion). However, if the geomedia has a neutralization capability (e.g., calcium carbonate soils and/or alkaline ground water), neutralization of the acidity will occur causing the acid front to lag behind the advancing ground water front. In this study, the neutralization capacity of the MWDF site soils were evaluated.

Four methods, with varying success, were used to evaluate the acid neutralizing - pH buffering capacity of the MWDF site soils. These included determination of:

- Mass balance acidity retardation factor for MWDF site soil neutralization capacity (calcium carbonate equivalence) and tailing leachate acidity data;
- Acidity retardation factor from column tests;
- Mass balance calculations based upon the characteristics of the leachate permeate and postcolumn test results; and
- Soil titrations using tailing leachates.

A discussion of the methods and results of the above evaluations follows.

3.5.1.2 Mass Balance Acidity Retardation Factor

Mass transport models use a retardation factor (R_d) to calculate the lag of a chemical parameter front behind the associated ground water front originating at the chemical source. Mass transport models consider not only geochemical controls, but dispersion and dilution of the chemical parameter front as well. Therefore, if a retardation factor can be determined for an acid in geomedia, a mass transport model will be an appropriate tool to calculate the time-distance of an acid-front migration within a geomedia (soil). By correlating acidity and pH measurements, predictions of the pH front movement can also be made.

A geomedia's neutralization capacity and the seepage acidity can be used to estimate a retardation factor for acid similar to that discussed in Section 3.3 for other chemical species. For a particular geomedia and chemical parameters, the retardation factor is defined as the ratio of the average linear ground water velocity to the chemical migration velocity. For acidity in seepage, the retardation factor can be determined by dividing the weight of neutralization capacity in a unit weight of geomedia by the weight of acidity in the seepage which can be present in that unit weight of geomedia. The retardation factor, R_d, for acidity as derived in Table 3.23 is given by:

$$R_d = 1 + \left(\frac{\rho}{n_e}\right)\left(\frac{\text{tons } CaCO_3 \text{ neutralization in geomedia (or ground water)}}{\text{mg/}\ell \; CaCO_3 \text{ acidity in seepage}}\right)$$

where

R_d = Retardation factor for acidity,
ρ = Bulk density of the geomedia, and
n_e = Effective porosity of the geomedia.

When $R_d = 1$, no neutralization capacity is present; hence, the acid and ground water front migrate at the same velocity within the aquifer. When $R_d > 1$, neutralization capacity is present in the aquifer and the acid front lags behind the associated ground water front.

The above approach to the calculation of the retardation factor for water acidity does not consider the efficiency or rate of neutralization reactions. When the acid neutralization reaction is slow, the acid front will probably migrate beyond the modeled acid-front location within the aquifer. However, the slow movement of ground water allows more water-sediment contact time. Additionally, complete removal of the acid neutralization capacity present within an aquifer (100 percent reaction efficiency) will occur with time assuming an indefinite source. The retardation factor for acidity behind the acid front is equal to 1.

Table 3.24 presents the results of the above mass balance acidity retardation factor calculations. Compared to the other methods of site soil neutralization capabilities discussed below, these retardation factors are high.

Acidity is the quantitative capacity of a water to neutralize bases. It is a measure of the hydrogen ions present as a result of dissociation or hydrolysis of solutes in a water sample. There are three sources of water acidity, H^+, including (a) strong mineral acids such as sulfuric (H_2SO_4); (b) weak acids such as carbonic (H_2CO_3); and (c) hydrolyzing salts such as iron or aluminum sulfates.

The contribution of hydrogen ion, H^+, to the available acidity (solution titrated to pH 8.3) of pH 3 leachate only represents a small fraction, two percent, of the total available acidity. The hydrolysis of metal ions, i.e., aluminum, iron, and zinc are responsible for nearly all of the available acidity (Table 3-17). The pH of the effluent from the columns permeated with pH 3 leachate was approximately five after ten pore volumes. This increase in pH from three (influent) to five ($H^+ = 10^{-5}$ m) as leachate permeates through columns represents nearly complete, 99 percent, neutralization of hydrogen ion, H^+. However, an appreciable available acidity remains in the column effluent because of the iron and zinc remaining. The available acidity for pH 3 influent permeant is 2,850 milligrams per liter calcium carbonate and the effluent from the glacial till column is 1,100 milligrams per liter calcium carbonate (Table 3-17).

Acidity mass balance calculations to determine acidity retardation for correlation to pH front movement was found not to be an appropriate method when reduced valence states of chemical species are present and may lead to inaccurate chemical species movement predictions. The error lies in the definition and use of the acidity term. The acidity value used in the mass value calculation is termed available acidity. The method of determining available acidity (Appendix D) is by titrating the sample to pH 8.3 with no prior oxidation, i.e., this is not a total acidity value. However, because of the reduced state of the leachates used in this study, this value also does not represent the acidity present in the leachates available for neutralization by the soils, i.e., it is not an accurate indicator of pH front movement. This is because, as the pH of the leachates is increased during the acidity titration, many of the reduced valence state chemical species oxidize and produce acid. Hydrolyzable ions such as iron and manganese contribute more acidity in their fully ozidized valance states than their reduced valance states. This is illustrated by the hydrolysis of ferrous (reduced valance state) iron:

$$Fe^{+2} + 2H_2O \Rightarrow Fe(OH)_2^{\circ} + 2H^+$$

and ferric (oxidized valance state) iron:

$$Fe^{+3} + 3H_2O \Rightarrow Fe(OH)_3^{\circ} + 3H^+$$

Therefore, until a solution is fully oxidized, not all measurable acidity may be present for neutralization. Potential acidity can exist even after the water has passed through a neutralizing geomedia. Slow rates of oxidation, hydrolysis, or dissociation reactions can prevent some sources of potential water acidity from being neutralized as fast as may be indicated by the mass balance neutralization calculation method.

3.5.1.3 Column Test Acidity Retardation Factors

Acidity retardation factors or acidity breakthrough can often be determined from column tests. However, as with the mass balance acidity retardation factors discussed above, this method was not an accurate indicator of pH front movement (by correlation to acidity) within the columns due to the source of acidity present in the potential MWDF leachates. The available acidity retardation factors presented in Tables 3.15 and 3.24 were determined in a manner similar to the other solutes (Appendix F). However, the available acidity breakthrough curves presented in Figures 3-1 through 3-5 show no correlation to column effluent pH.

The measured acidity values simply resulted from the breakthrough of hydrolyzable metals such as iron, zinc, and others. There is an approximate correlation between zinc and iron attenuation with that of available acidity. As the normalized (C/C_o) iron and zinc concentrations increase with increasing pore volumes, the acidity also increases. If the source of the acidity was principally due to strong mineral acids, then this method would have been a more appropriate predictor of pH front movement.

3.5.1.4 Acidity Retardation by Post-Column Test Characterizations

Table 3.25 presents a summary of the postcolumn test acid neutralization capacity determinations and total acidity available during the column tests to react with the soils. In each column, the neutralization capacity decreased after acidic leachates were permeated through them. However, the neutralization capacities decreased to much lower levels than predicted by the total weight of acidity permeated through the columns. This reduction results in anomalous neutralization capacities.

A possible explanation of the anomalous values may be found in the samples selected for testing. The pre and postcolumn test samples used for the neutralization capacity determinations were riffle split fractions of the bulk composite samples. Additionally, the sample used to characterize the postcolumn test material was riffle split from the entire column sample. A possible heterogeneous distribution of carbonate minerals in the bulk composite (as discussed in Section 3.4) and/or column samples may have caused the observed results.

This mass balance technique was not able to predict the neutralization capacity of the postcolumn test samples. It is, therefore, not considered to be an appropriate method to predict the pH front movement through MWDF site soils.

3.5.1.5 Soil Titrations

The time-monitored pH of leachate-site soil reactions should be an appropriate predictor of pH front movement through the MWDF geomedia. Figures 3-11 and 3-12 present the results of soil titrations using the pH 3 and pH 6 leachates, respectively. The column effluent pH results plotted on the column test chemical breakthrough curves (Figures 3-1 through 3-5) also essentially represent titration results for lower leachate to soil ratios.

For the pH 3 leachate permeant column tests (Figures 3-1 through 3-3), a pH of 5 was reached in the seepage at about 5 to 7.7 pore volume displacements through the columns and remained constant throughout the duration of the test. A break in slope on the titration curves (Figure 3-11) also occurs at about pH 5. For the pH 6 leachate permeant column tests (Figures 3-4 through 3-5), a seepage pH of 6 also occurred at about 7.5 and 5 pore volume displacements for the glacial till and stratified drift columns, respectively. Examining the ratios of volume of leachate added per weight of soil for the titration curves and column test results (Table 3.26), there is reasonable agreement between the results of the two tests, except for the stratified drift titrated with pH 6 leachate. As discussed earlier, the differences which occur are probably the result of a heterogeneous distribution of carbonate minerals between the samples, slower reaction rates for the stratified drift in the titration test, or dilution effects from the different soil water volumes present at the start of each test.

Therefore, the pore volume displacement and monitored column test pH results are expected to reasonably predict the pH front movement for the acidic (pH 3 and 6) leachates. Chapter 4.0 addresses the field time simulated by the column tests so that the pH results shown in Figures 3-1 through 3-5 can be directly related to field conditions.

3.5.2 Carbonate Minerals Distribution

3.5.2.1 Introduction

Since the amount of carbonate in the soils is directly related to neutralization capacity, the distribution of carbonate minerals over the MWDF site provides an indication of the site's neutralization capacity. An analytical program was, therefore, developed and implemented to characterize the spatial variability of carbonate minerals and map their distribution in MWDF site Area 41 subsurface soils. The program consisted of relating carbonate effervescence data (semiquantitative) to the results of calcium carbonate equivalent analyses (quantitative). These relationships were evaluated to assess the acid neutralizing potential for subsoil materials beneath and adjacent to MWDF site Area 41. The accuracy of the results was to the level of data available.

3.5.2.2 Methodology

Approximately 650 samples from 27 borings completed by Golder Associates (1981c and 1981d) and Dames and Moore (1981b) at MWDF site Area 41 were initially examined for the carbonate minerals distribution study. The samples from the borings (locations shown in Figure 3-13) represent the full stratigraphic sequence of soil materials to the underlying bedrock.

Soil samples were tested for carbonate effervescence with dilute hydrochloric acid and assigned a numerical rating based on the observed reaction as follows:

- Effervescence Value 0 - No observable reaction.
- Effervescence Value 1 - Very slight reaction.
- Effervescence Value 2 - Slight to moderate reaction.
- Effervescence Value 3 - Strong reaction.

Results of the carbonate effervescence testing for 23 of the tested borings are presented in Appendix H.

Since Borings G41-H9, G41-G13, G41-H18B, and G41-K21A were used in the attenuation study (Figure 2-1), samples from these borings were tested using a rating scale of 0 to 5 in conjunction with the more detailed analyses of these borings. The rating system used for these samples and results of the effervescence tests are presented in Appendix C.

One hundred and five samples were selected for calcium carbonate equivalent analysis based on a review of the carbonate effervescence data, boring logs and sample descriptions, cross sections, and hydrogeologic data. Sample selection criteria included:

- Representation (approximately equal number of samples) of the stratified drift or upper glacial till stratigraphic units.
- Vertical and horizontal distribution within and between borings.
- Sample descriptions representative of the two stratigraphic units.
- Representation (approximately equal number of samples and the full range of effervescence values) for each carbonate effervescence rating group.
- An appropriate number of samples above and below the water table.

Samples were analyzed for percent calcium carbonate equivalent (Sobek, et al., 1978) by reaction with an excess quantity of standardized acid. When the reaction was completed, the remaining acid was titrated with standardized base; the quantity of acid consumed in reaction was calculated and expressed on the basis of calcium carbonate equivalent. Results of the calcium carbonate equivalent analyses are presented in Appendix G.

The calcium carbonate equivalent data were reviewed and compared to the carbonate effervescence results and representative carbonate equivalent ranges developed for each carbonate effervescence rating in the glacial till and stratified drift units. These ranges were established on the basis of "typical" values; extraneous data were not included in the development of the representative ranges. Simple statistical calculations including median, mean, frequency, and standard deviation were also employed in establishing representative calcium carbonate equivalent ranges.

The established carbonate equivalent ranges were extrapolated to the complete set of samples for which carbonate effervescence data were available and ranges of carbonate values were assigned by stratigraphic unit to the borings in plan view and by sample in geologic cross sections.

3.5.2.3 Results and Discussion

Results of the carbonate minerals distribution study are presented in Appendix G. The data show considerable variability ranging from 0.2 to more than 36 percent calcium carbonate equivalent. However, most values are between 0.5 and 8 percent.

Representative ranges of calcium carbonate equivalent were developed for the till and drift units using the carbonate effervescence rating scale of 0 to 3. The established ranges follow:

- Effervescence Rating 0. Calcium carbonate equivalent ranges from 0.2 to 0.8 percent in the glacial till and 0.2 to 0.6 percent in the stratified drift.

- Effervescence Rating 1. Calcium carbonate equivalent ranges from 0.4 to 3.8 percent in the glacial till and 0.3 to 4.3 percent in the stratified drift.

- Effervescence Rating 2. Calcium carbonate equivalent ranges from 2.8 to 8.6 percent in the glacial till and 3.4 to 6.2 percent in the stratified drift.

- Effervescence Rating 3. Calcium carbonate equivalent ranges from 5.5 to 10.3 percent in the glacial till and 6 to 13.1 percent in the stratified drift.

Samples from Borings G41-H9, G41-G13, G41-H18B, and G41-K21A, as discussed previously, were tested using a carbonate effervescence rating scale of 0 to 5. The representative calcium carbonate equivalent values for these samples without differentiating stratigraphic units are:

- Effervescence Value 0. Calcium carbonate equivalent is less than 1.5 percent.
- Effervescence Value 1. Calcium carbonate equivalent ranges from 1.5 to 3 percent.
- Effervescence Value 2. Calcium carbonate equivalent ranges from 3 to 5 percent.
- Effervescence Value 3. Calcium carbonate equivalent ranges from 5 to 9 percent.
- Effervescence Values 4 and 5. Calcium carbonate equivalent is greater than 9 percent.

The apparent variable relationship which exists between the carbonate effervescence results and carbonate mineral content may be due to the mineralogical characteristics of the soils. Results of X-ray diffraction analyses, Table 3.2 presented in Section 3.1, of the composite samples and the two samples with a carbonate effervescence rating of 2 selected from the glacial till (Sample No. 10, Boring G41-E19A) and stratified drift (Sample No. 22, Boring G41-C15) indicate that dolomite, a calcium-magnesium carbonate, is the principal carbonate mineral present. Dolomite typically does not effervesce when treated with cold, dilute hydrochloric acid. Thus, samples containing appreciable amounts of dolomite may effervesce less vigorously when tested, resulting in an underestimation of the calcium carbonate equivalent present.

Plan views of representative stratigraphic carbonate minerals distribution are presented in Figures 3-13 and 3-14 for the glacial till and stratified drift, respectively. Additionally, calcium carbonate equivalent data are plotted on cross sections in Figures 3-15 through 3-19, as well as ranges inferred from carbonate effervescence testing. Close inspection of these data indicates several apparent trends. These include:

- The actual quantities of carbonate minerals present indicate that considerable acid neutralizing potential (roughly 0.4 to 6.6 percent $CaCO_3$) is present in the sediments beneath and adjacent to the MWDF site Area 41.
- Carbonate mineral content appears to be slightly higher in the saturated zone in comparison to the partially saturated zone. However, concentrations of several percent or more carbonates are also frequent above the water table.
- Carbonate mineral content of the glacial till is highest in the vicinity of the MWDF site (typically more than several percent) and decreases to the south and east.
- Carbonate mineral content of the stratified drift unit is lowest in the north (less than several percent) and increases to the south and west of the MWDF site (generally greater than about 3 percent).

4.0 EVALUATION OF ATTENUATION TEST RESULTS

4.1 INTRODUCTION

The laboratory test results set forth in Chapter 3.0 provide the basis for evaluating (a) potential seepage rates from the MWDF and (b) chemical parameter movement in the underlying soil. The process for making such determinations can be very complex involving many variables. Computer simulation is required to define or predict vertical and horizontal distribution of seepage and chemical parameters. Initial analytical calculations can be made, however, to bracket the seepage amounts and chemical parameter distribution.

In this chapter of the report, the analytical assessments are made to evaluate (a) the anticipated time rate of tailing leachate vertical movement through a 0.15 meter thick liner composed of a four percent bentonite/till admixture, (b) the time rate of tailing pond seepage vertical movement through the underlying glacial till and horizontal movement through the stratified drift to the 366 meter (1,200 foot) compliance boundary, and (c) the estimation of migration of various chemical parameters through the liner and underlying stratigraphic units.

To conduct this analysis, the following assumptions were made:

- A single layer for each unit. The liner, glacial till, and stratified drift were assumed to have unrestrained inflow at the top of the layer and outflow at the bottom of the layer. This is a relatively valid assumption for the liner since water seeping through the liner will enter the more permeable glacial till. Field conditions will place different constraints on the glacial till and stratified drift and will, in general, decrease the velocity of seepage compared to that assumed herein.

- Complete saturation in each unit. The laboratory work was done with saturated samples. For this assessment, consistency between laboratory and analytical assessments is required. However, field conditions will show a partially saturated till beneath the MWDF site. Partially saturated permeability is anticipated to be less than the assumed saturated permeability. Thus the analysis discussed is conservative (i.e., has larger seepage quantities and faster chemical species movement than will actually occur).

- Constant Head On Liner. A constant head of approximately 0.2 meters of water on top of the liner is assumed. The water level on the liner during operations should be near zero due to the underdrain system. After operations and reclamation, when pumping in the underdrain ceases, free water will accumulate on the liner. The underdrain is 0.46 meters thick (Golder, 1982a). An assumption of 0.2 meters of water above the liner appears reasonable.

- Similar Soil Material in Laboratory and Field. The compositing of MWDF site soil samples and resulting effort to make these samples representative indicate that this assumption should be reasonably valid. Field soil (liner, till, and drift) permeabilities were assumed to be equal to that determined in this study.

4.2 FLOW RATE DETERMINATIONS

Since the bentonite/till admixture liner material was tested at constant water head (Appendix F), flow rates were determined using a constant head method of assessment. Likewise, water flow rates through the glacial till and the stratified drift used a constant water flow rate method of analysis.

4.2.1 Evaluation of Constant Head Flow Tests

A method for evaluation of constant water head flow rate is discussed in detail by Haji-Djafari and Wright (1982). In this evaluation, a field time scale is calculated based on laboratory data and field conditions. This scale is used to convert laboratory pore volume displacement to field equivalent time, which relates field time required for the concentration of a monitored chemical parameter to reach measured concentrations at the pore volume displacements on Figures 3-1 and 3-6. The method is used to estimate flow rates through the liner in this section and chemical parameter migration in Section 4.3.

The equation for calculating the field time simulated by a constant water head flow rate test is derived as follows:

$$
\begin{aligned}
K &= Q_\ell/(i_\ell \times A_\ell) \\
\bar{Q}_f &= \bar{Q}_\ell \times (i_f/i_\ell) \\
t_\ell &= (1/PV_t) \\
t_f &= t_s \times t_\ell
\end{aligned}
$$

therefore

$$t_f = (L_f/L_\ell) \times (i_\ell/i_f) \times (1/PV_t) \qquad (1)$$

where

K = permeability (L/t),

Q_ℓ = permeant effluent flow rate from the laboratory sample (L^3/t),

A_ℓ = laboratory sample surface area (L^2),

i_ℓ = laboratory hydraulic gradient (L/L),

i_f = field hydraulic gradient (L/L),

$\bar{Q}_f$ = field seepage rate per unit area (L^3/L^2t),

$\bar{Q}_\ell$ = laboratory effluent (flow) rate per unit area (L^3/L^2t),

PV_t = Average pore volume flow ratio per unit time (L^3/L^3t),

t_ℓ = laboratory time (t),

t_f = corresponding field time (t),

t_s = time scale for converting laboratory time to corresponding field time (dimensionless),

L_f = thickness or length of field stratum (L), and

L_ℓ = length of laboratory sample (L).

The parameters specific to this assessment of water flow through the liner and appropriate laboratory tests are:

PARAMETER	VALUE	SOURCE/ DEFINITION
L_f	0.15 meters	Liner Thickness
L_ℓ	0.116 meters	Appendix F, Table F.1
i_ℓ	$\frac{30 \text{ meters}}{0.116 \text{ meters}} = 258$	Sample Gradient
i_f	$\frac{0.20 \text{ (head on liner)} + 0.15 \text{ (liner thickness)}}{0.15 \text{ (liner thickness)}}$	
	$= 2.33$	Field Gradient
PV_t	0.71	Table 3.14

Using the above data and Equation (1), field time is calculated as follows:

$$t_f = (0.15/0.1163) \times (258/2.33) \times (1/0.71) = 201 \text{ weeks}$$

This implies that it will take 201 weeks in the field to pass one pore volume of water through a 0.15 meter thick saturated four percent bentonite/till admixture liner with a hydraulic gradient of 2.33 and permeability identical to the laboratory sample. Therefore, each pore volume on Figures 3-1 and 3-6 represent 201 weeks (3.9 years) of anticipated field time. Thus, approximately 50 years (13 pore volumes x 3.9 years) of field time was simulated for the four percent bentonite/till admixture columns during the laboratory study. Similar calculations can be made for other various liner thicknesses and field hydraulic gradients.

4.2.2 Evaluation of Constant Flow Tests

Similar methods can be used to calculate the field time simulated by constant water flow rate column tests of the glacial till and stratified drift. The equation for calculating the field time simulated when field flow rates are known is derived as follows:

$$t_f = t_s \times t_\ell$$
$$t_f = L_f/V_f = (L_f \times A_f)/Q_f$$
$$t_\ell = L_\ell/V_\ell = (L_\ell \times A_\ell)/Q_\ell = TV/Q_\ell = 1/PV_t$$
$$Q_\ell = PV_t \times PV$$
$$t_s = (L_f \times A_f)/Q_f \times (PV_t \times PV)/TV$$

therefore

$$t_f = (L_f \times A_f \times PV)/(TV \times Q_f) \qquad (2)$$

where

A_f = field surface area (L^2),
V_f = field velocity (L/t),
V_ℓ = laboratory velocity (L/t),
Q_f = field flow rate (L^3/t),
TV = total volume of laboratory sample (L^3),
PV = pore volume of laboratory sample (L^3), and
Other terms defined in derivation of Equation (1).

When the field hydraulic gradient can be determined, the equation for calculating the field time simulated by a constant water flow rate test is derived as follows:

$$t_f = L_f/V_f = L_f/(K \times i_f)$$
$$t_s = L_f/(K \times i_f) \times (PV_t \times PV)/TV$$

therefore

$$t_f = L_f/(K \times i_f) \times (PV/TV) \qquad (3)$$

where terms are defined in the derivation of Equations (1) and (2).

The appropriate parameters for field soil conditions beneath the MWDF are:

- Total bottom area of tailing ponds - 53.45 hectare (Golder, 1982a).
- Representative depth of glacial till from bottom of MWDF to top of stratified drift - approximately 33 meters (Figure 2-4).
- Total steady-state water flow rate from bottom of MWDF at post-reclamation is expected to be in the range of:
  - 647 cubic meters per week, to
  - 2,637 cubic meters per week (Golder, 1982c).
- Horizontal distance (length) to compliance boundary from outside edge of MWDF - 365.8 meters (1,200 feet).
- Approximate hydraulic gradient in the stratified drift 0.006 (Golder, 1982b).

The necessary pore volume and total volume data for the glacial till and stratified drift test columns are presented in Table 3.14. The stratified drift permeability data are presented in Table 3.21.

Using the above data, experimental parameters from glacial till Column I-1, and Equation (2), field time is calculated for two potential steady-state MWDF seepage conditions as follows:

- Low seepage rate -

  $$t_f = (33 \times 5.345 \times 10^5 \times 1.412 \times 10^{-4})/(5.533 \times 10^{-4} \times 647) = 6,957 \text{ weeks}$$

- High seepage rate -

  $$t_f = 4.5 \times 10^6/2,637 = 1,707 \text{ weeks}$$

These calculations indicate that it will take between 1,707 to 6,957 weeks (32.8 to 133.8 years) in the field to pass one pore volume through a 33 meter thick saturated glacial till for the anticipated combined MWDF tailing ponds steady-state (post-reclamation) seepage rates. Time spread reflects predicted range of precipitation infiltration rates (2.0 to 8.6 cm per year) into sealed tailing ponds. Each pore volume on

Figure 3-2 represents between 32.8 and 133.8 years of anticipated field time for saturated till percolation to the drift. Thus, for glacial till permeated with pH 3, 6, or 9 leachate (physical dimensions of the glacial till columns were similar), approximately 600 to 2,400 years of field time was simulated during the laboratory study.

The above calculations assume saturated conditions. As shown in Figure 2-4, approximately 12 to 15 meters of partially saturated glacial till will be present beneath the MWDF. Therefore, these time estimates are considered conservative. Similar calculations can be made for other MWDF seepage rates and glacial till thicknesses.

The field time simulated by each pore volume passed through the stratified drift Column J-1 is calculated using Equation (3) and the above data. The calculation is:

$$\begin{aligned} t_f &= (365.8 \times 2.062 \times 10^{-4})/(7.86\ (\mathrm{m/wk}) \times 0.006 \times 6.111 \times 10^{-4}) \\ &= 2{,}617 \text{ weeks} \end{aligned}$$

This implies that it will take 2,617 weeks (50.3 years) in the field to hydraulically move one pore volume of water through a unit area of the saturated stratified drift from the outside edge of the MWDF to the 366 meter (1,200 foot) compliance boundary. The time scale would be larger if calculated from the center or inside edge of the MWDF to the compliance boundary. Each pore volume on Figure 3-3 conservatively represents approximately 50 years of anticipated field time. For the stratified drift permeated with the pH 3, 6, or 9 leachate (physical dimensions of the stratified drift columns were similar), approximately 630 years of field time was simulated during the laboratory study. Similar calculations can be made for other stratified drift hydraulic gradients and lengths.

4.3 ESTIMATION OF CHEMICAL PARAMETERS TRANSPORT

Based on the representative field soil conditions discussed above, the field time scales for the various soil units are as follows:

SOIL UNIT	FIELD TIME SCALE (Years/Unit Pore Volume)
Four percent bentonite/ till admixture liner	4
Glacial Till	33 - 134
Stratified drift	50
TOTALS	87 to 188

To displace one pore volume of water through the MWDF liner, down through 33 meters of glacial till and horizontally outward 366 meters (1,200 feet) in the stratified drift to the compliance boundary will require approximately 87 to 188 years.

Table 4.1 has been prepared to show the approximate time for chemical parameters with known retardation factors to migrate through the various individual and combined stratigraphic units to a level of half their source concentration. Chemical species with retardation factors of five or above will require about 950 years or more for their concentration at the 366 meter (1,200 foot) compliance boundary to equal half of their source concentration. This calculation assumed fully saturated conditions in all units and the design conditions noted in Section 4.2. Additionally, the calculation ignored the effects of dilution, dispersion, and possible variation in the source concentration or seepage flow rates.

A review of the retardation factors for the chemical parameters on Tables 3.15 through 3.20 indicate that all but the following chemical parameters have values of about five or above:

- Chloride
- Sulfate
- Total Sulfur
- Specific Conductance/TDS
- Manganese (lower pH leachates)
- Zinc (pH 3 leachate)

analysis only estimates the upper limit concentrations of the chemical parameters and is thus conservative. Computer simulation would be required to more accurately predict time variations in seepage concentrations.

The above analysis, along with potential dilution calculations, can be used to identify the important chemical parameters to consider in further evaluations and eliminate those where further analyses are not required. Table 4.2 presents the spiked leachate chemistry, dilution ratio required before the 366 meter (1,200 feet) compliance boundary to achieve U.S. EPA drinking water standards (assumes zero concentration in existing ground water), and attenuation data for the glacial till (the soil unit exhibiting the greatest retardation to chemical transport). From this table, it is evident, for the pH 9 spiked leachate, that if a chemical parameter will be diluted by less than a factor of 9 before reaching the 366 meter (1,200 foot) compliance boundary, then sulfate, which migrates at essentially the same velocity as the seepage water ($R_d=1$), is the most appropriate parameter for use in predicting potential ground water effects. The other chemical parameters which have higher required dilution ratios also have higher retardation factors and will be attenuated appreciably more than sulfate. The selection of the final parameters for use in any study, must, however, also consider the actual source concentration and its variation over time, i.e., will the actual concentration diminish, remain constant, or increase over time in the MWDF leachates.

5.0 CONCLUSIONS

The study performed by D'Appolonia for Exxon Minerals Company to determine the attenuation characteristics of a potential liner and underlying soils of the MWDF site Area 41 for various tailing leachates was a comprehensive study and meets the requirements of the Wisconsin Administrative Code, NR 182.075. Preceding chapters have discussed in detail the study design, laboratory and analytical methods, study results, and pertinent interpretive discussions relative to the Crandon Project MWDF site. Based on the work performed for this study, the following conclusions are evident:

- The soil samples used in the attenuation test are considered representative of the soil types which will exist beneath the MWDF site and also used in its construction. Therefore, the results of this study can be used to evaluate the fate of solutes from MWDF seepage.
- Both the designed (alkaline) and conservative "worst-case" (acidic) tailing leachates pH and chemistry range in the MWDF tailing ponds were used to determine MWDF site soil and liner chemical attenuation characteristics.
- Most of the chemical species determined for the alkaline leachate will only require minor dilution ratios to have concentrations equal to U.S. EPA Drinking Water Standards at the 366 meter (1,200 feet) compliance boundary.
- Chloride, sulfate, total sulfur, and filterable residue (TDS) could migrate at the same velocity as the MWDF water seepage front. Dilution and dispersion will be the major factors limiting their concentration in the MWDF seepage.
- The MWDF site soils have a substantial attenuation capacity for the other chemical species tested. This attenuation capacity generally increases with increasing seepage pH.
- There was agreement between the batch and column attenuation test results of this study. In addition, there was an agreement between duplicate batch or column tests.

- The MWDF site soils have a very large acid neutralization capacity. The distribution of carbonate minerals (principally dolomite) in the MWDF site Area 41 soil is somewhat variable both vertically and horizontally (laterally). However, considering the overall level of acid-neutralizing minerals present, there is a high capacity for acid neutralization for all directions of possible seepage flow from the MWDF. Therefore, acid-front movement through the soils underlying the MWDF will be very slow, on the order of hundreds of years for even the "worst case" scenario MWDF seepage conditions (i.e., pH 3 leachate) evaluated in this study.

- Due to the high acid neutralization capacity of the MWDF site soils, those heavy metals in the MWDF seepage controlled by acid neutralization (i.e., attenuation increased with increasing pH) will be substantially attenuated by the site soils.

- In relation to anticipated MWDF site conditions, the field time simulated in the laboratory column studies for water migration was approximately 50 years for a four percent bentonite/till liner material, 600 to 2,400 years for the underlying glacial till, and 630 years for the stratified drift.

- Based upon the anticipated field conditions, those chemical species with even limited attenuation by the MWDF site soils will require hundreds of years to reach the 366 meter (1,200 foot) compliance boundary at half their source concentration, assuming their source concentration does not diminish and no dilution or dispersion occurs in the ground water. Therefore, attenuation of heavy metals in MWDF seepage by the MWDF site soils will offer substantial protection to the site ground water resources.

- No changes to the permeability of the proposed MWDF bentonite/till admixture liner or soils underlying the MWDF are expected due to potential reactions with MWDF seepage.

In addition to the above conclusions, the results of this study supply the necessary attenuation data for use in any further evaluation of potential hydrological and geochemical effects of the MWDF, and for selecting those parameters which may be of interest.

Respectfully submitted,

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TABLE 3.1

GRAIN-SIZE DISTRIBUTION OF COMPOSITE SAMPLES

SOIL SAMPLE(1)	GRAIN-SIZE DISTRIBUTION(2) (%)							
	COARSE GRAVEL (76.2-19.05 mm)	FINE GRAVEL (19.05-4.75 mm)	COARSE SAND (4.75-2.0 mm)	MEDIUM SAND (2.0-0.425 mm)	FINE SAND (0.425-0.075 mm)	UNDIFFERENTIATED SILT AND CLAY (<0.075 mm)	SILT (0.075-0.002 mm)	CLAY (<0.002 mm)
Glacial Till (Composite No. 1)								
Bulk	11.1	23.8	3.7	15.0	32.3	14.1	10.2	3.9
Minus No. 4 Sieve Material	-	-	5.7	23.0	49.6	21.7	15.7	6.0
Stratified Drift (Composite No. 2)								
Bulk	0.9	6.7	2.5	29.1	51.5	9.3	7.5	1.8
Minus No. 4 Sieve Material	-	-	2.7	31.5	55.7	10.1	8.1	2.0
4% Bentonite/Till Admixture								
Bulk	1.3	21.4	8.7	23.5	24.8	20.3	14.9	5.4
Minus No. 4 Sieve Material	-	-	11.2	30.4	32.1	26.3	19.3	7.0

(1) See Appendix C for composition of composite samples.

(2) ASTM D 422-63(72). See Appendix C for grain-size distribution curves. Many of the samples, especially tills, had gravel inside the samples, which were not visible during the initial inspection of the aggregated samples. This resulted in composites with significantly more gravel than the index tests (Appendix C) would have predicted.

TABLE 3.2

BULK MINERALOGY OF PRE AND POSTCOLUMN TEST COMPOSITE AND OTHER SITE SAMPLES(1)

SOIL SAMPLE(2)	MINERALS PRESENT (%)										
	QUARTZ	FELDSPAR	AMPHIBOLE	DOLOMITE	CALCITE	GYPSUM	MIXED LAYER CLAYS(3)	SMECTITE	CHLORITE	MICA	KAOLINITE
3Glacial Till											
Composite No. 1											
Precolumn Test	55-60	15	5	5	TR(4)	-(5)	TR	-	5	5	5-10
Postcolumn Test--pH 3 Permeant	55-60	10-15	5	<5	TR	5	TR	-	5	5	5
Postcolumn Test--pH 9 Permeant	55-60	15	5	5	TR	-	TR	-	TR	5	5
Boring G41-E19A Sample No. 10	55-60	15	TR	10	TR	-	-	-	5	TR	5
Stratified Drift											
Composite No. 2 (Precolumn Test)	55-60	15	10	5	TR	-	TR	-	5	5	5
Boring G41-C15 Sample No. 22	55-60	15	10	5-10	TR	-	TR	-	5	5	5
4% Bentonite/Till Admixture											
Precolumn Test	45-50	15	5	5	TR	-	5	5	5	5	5
Postcolumn Test pH 3 Permeant	45-50	15	5-10	<5	TR	<5	TR	<5	10	5	5
Postcolumn Test pH 9 Permeant	45-50	10-15	5	5	TR	-	TR	<5	10	5	5

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(1) Semiquantitative X-ray diffraction analyses were performed on randomly oriented powder mounts of the soil samples in accordance with the procedures of Hutchison (1974) and Wong (1977). A Rigaku Geigerflex X-ray diffractometer equipped with a graphite crystal monochromator using Cu Kα radiation was used to obtain X-ray diffraction patterns. X-ray diffraction peak intensities were used to determine relative percentages of mineral phases present. Bulk mineralogy implies no sample pretreatment.

(2) See Appendix C for composition of composite samples.

(3) Irregularly interstratified chlorite and vermiculite.

(4) "TR" indicates trace.

(5) "-" indicates phases not detected.

TABLE 3.3

CLAY MINERALOGY OF PRE AND POSTCOLUMN TEST SAMPLES(1)

SOIL SAMPLE(2)	MINERALS PRESENT IN THE <0.002 mm FRACTION (%)							
	QUARTZ	FELDSPAR	AMPHIBOLE	MIXED LAYER CLAYS(3)	SMECTITE	CHLORITE	MICA	KAOLINITE
Glacial Till								
Composite No. 1								
Precolumn Test	40-45	10-15	5	5	<5	5	10	15
Postcolumn Test--pH 3 Permeant	40-45	15	5	TR(4)	-(5)	10	15	15
Postcolumn Test--pH 9 Permeant	40-45	15	5	TR	-	5	10	15
Stratified Drift								
Composite No. 2 (Precolumn Test)	50-55	15	5	5	TR	5	10	10
4% Bentonite/Till Admixture								
Precolumn Test	45-50	15	5	5	5-10	5	5	10
Postcolumn Test pH 3 Permeant	45-50	15	5	TR	5	10	10	10
Postcolumn Test pH 9 Permeant	45-50	15	5	TR	<5	5	10	10

---

(1) Semiquantitative X-ray diffraction analyses were performed in accordance with the procedures of Wong (1977), using oriented mounts of deferrated (iron removed) and carbonate phases removed clay fractions of the soil sample. Pretreatments of the clays for iron and carbonate removal were in accordance with the procedures of Jackson (1969), while preparation of the oriented clay mounts was in accordance with the procedures of Drever (1973). A Rigaku Geigerflex X-ray diffractometer equipped with a graphite crystal monochromator using Cu Kα radiation was used to obtain X-ray diffraction patterns. X-ray diffraction peak intensities were used to determine relative percentages of the clay mineral phases present in the <0.002 mm soil fraction.

(2) See Appendix C for composition of composite samples.

(3) Irregularly interstratified chlorite and vermiculite.

(4) "TR" indicates trace.

(5) "-" indicates phase not detected.

TABLE 3.4

RESULTS OF CHARACTERIZATION ANALYSES OF COMPOSITE SAMPLES(1)

SOIL SAMPLE(2)	1:1 REACTION pH(3)	NEUTRALIZATION CAPACITY(4) (% $CaCO_3$ Equivalent)	EXCHANGEABLE CATIONS(5)					CATION EXCHANGE CAPACITY(5) (meq/100g)	ANION EXCHANGE CAPACITY(6) (meq/100g)	ORGANIC MATTER(7) (%)
			HYDROGEN (meq/100g)	CALCIUM (meq/100g)	MAGNESIUM (meq/100g)	POTASSIUM (meq/100g)	SODIUM (meq/100g)			
Glacial Till (Composite No. 1)	9.15	2.3	<0.1	4.2	3.0	<0.1	0.2	7.4	1.7	0.31
Stratified Drift (Composite No. 2)	9.80	1.6	<0.1	2.6	1.4	<0.1	0.2	4.2	1.6	0.22
4% Bentonite/Till Admixture	8.75	0.7	<0.1	3.4	0.9	0.1	0.4	4.7	1.5	0.96
High Carbonate Effervescence Glacial Till (Composite No. 3)	-(8)	7.2	-	-	-	-	-	-	-	-

(1) Characterization analyses performed only on sample fraction less than 4.75 millimeters (minus No. 4 sieve material - coarse sand and below).

(2) See Appendix C for composition of composite samples.

(3) pH of a 1:1 soil to distilled water mixture at 25°C (Sobek, et al., 1978).

(4) HCl Treatment - NaOH titration in accordance with Sobek, et al. (1978). Average of duplicate determinations. In addition, the gravel fraction (plus No. 4 sieve) of each composite sample was tested for carbonate effervescence (Sobek, et al., 1978). These results follow:
- Composite No. 1 had a typical carbonate effervescence numeric rating of 2 (estimated neutralization capacity of 3 to 5% $CaCO_3$ equivalent).
- Composite No. 2 had a typical carbonate effervescence numeric rating of 0 (estimated neutralization capacity of <1.5% $CaCO_3$ equivalent).
- Till used in the 4% bentonite/till admixture had a typical carbonate effervescence numeric rating of 1 (estimated neutralization capacity of 1.5 to 3% $CaCO_3$ equivalent).

(5) Ammonium acetate extraction at pH 7.0 in accordance with Black, ed. (1965). Analytical determinations in accordance with the U.S. EPA (1979). No exchangeable acidity is present by definition for 1:1 reaction pH's above 7.0 (Sobek, et al., 1978).

(6) Extractable and adsorbed phosphorus (Mehlich Method) in accordance with Hesse (1971). Analytical determinations in accordance with the APHA (1981).

(7) Potassium dichromate oxidation (Modified Walkley Method) in accordance with Richards, ed. (1954).

(8) "-" indicates not determined.

TABLE 3.5

SUMMARY OF pH 2 LEACHED, SPIKED, TARGET, AND PREDICTED MWDF TAILINGS LEACHATE CHEMISTRY AND U.S. EPA DRINKING WATER STANDARDS

PARAMETER	UNITS	TAILINGS LEACHED AT pH 2(1)	SPIKED TAILINGS LEACHATE(2) (Highest Representative Value)			SPIKED LEACHATE TARGET CONCENTRATION(3)	PREDICTED MWDF SEEPAGE COMPOSITION(4)	U.S. EPA PRIMARY AND SECONDARY DRINKING WATER STANDARDS(5)
			pH 3	pH 6	pH 9			
pH	pH units	2.01	3.0	5.75	9.0	-	9.48	6.5 - 8.5
Eh	mV	+475	+586	+246	+276	-	-	-
Specific Conductance	µmhos/cm @ 25°C	5,280	8,790	7,240	5,690	-	-	-
Filterable Residue	mg/ℓ	3,120	5,710	5,140	3,430	-	2,660	500
Available Acidity	mg/ℓ $CaCO_3$	5,550	4,260	980	0	-	-	-
Hot Acidity	mg/ℓ $CaCO_3$	6,150	4,920	1,990	0	-	-	-
Alkalinity	mg/ℓ $CaCO_3$	0	0	5	40	-	33.2	-
Chloride	mg/ℓ	65	71	310	340	50	12.1	250
Fluoride	mg/ℓ	0.09	0.23	2.3	7.6	2	4.05	1.4 - 2.4
Nitrate	mg/ℓ N	17	18	6.6	2.3	1	1.15	10.0
Sulfate	mg/ℓ	2,800	6,000	3,400	2,300	1,500	1,540	250
Thiosulfate	mg/ℓ	15	94	530	510	500(6)	44	-
Total Sulfur	mg/ℓ SO_4	4,500	9,100	6,600	4,200	-	-	-
Cyanide	mg/ℓ	<0.1	<0.1	0.1	0.2	0.25	0.0474	-
Dissolved Metals:(7)								
Aluminum	mg/ℓ	44	70	0.5	0.5	-	2.03	-
Arsenic	mg/ℓ	4.7	6.8	0.84	0.091	2	0.01	0.05
Barium	mg/ℓ	<0.01	0.2	0.03	0.4	-	0.0102	1.0
Cadmium	mg/ℓ	1.4	2.3	0.83	0.41	1	0.0127	0.01
Calcium	mg/ℓ	450	555	570	660	-	470	-
Chromium	mg/ℓ	1.1	2.6	0.06	0.2	0.5	0.0406	0.05
Copper	mg/ℓ	120	130	4.5	7.7	10	0.0163	1.0
Iron:								
Ferrous	mg/ℓ	-	-	-	-	-	13.5	-
Total	mg/ℓ	1,200	1,456	730	1.6	50(8)	13.66	0.3
Lead	mg/ℓ	1.6	4.0	0.22	0.08	2	0.0650	0.05
Magnesium	mg/ℓ	190	240	225	145	50	8.13	-
Manganese	mg/ℓ	26	49	43	0.9	5	0.0244	0.05
Mercury	mg/ℓ	0.056	0.007	0.019	0.150	0.1	0.000123	0.002
Potassium	mg/ℓ	6.0	62	71	66	30	17.5	-
Selenium	mg/ℓ	0.006	0.07	0.10	0.21	1	0.256	0.01
Silicon	mg/ℓ	190	290	45	4	-	2.51	-
Silver	mg/ℓ	<0.001	0.001	0.033	0.19	0.2	0.00922	0.05
Sodium	mg/ℓ	17	550	650	770	270	551	-
Zinc	mg/ℓ	490	550	200	0.64	20	0.0406	5.0

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(1) Air dried tailings leached at 1:4 tailings to pH 2.0 sulfuric acid solution. See Appendix D for leaching details and leachate analytical methodology.

(2) Concentrations shown are the highest for the most representative range of leachate analyses. Concentrations significantly above the range of analytical results for the various leachates are not shown. Composition ranges for the leachates are presented in Tables 3.6 through 3.8.

(3) Concentration of species added to the tailings leachates (Appendix D).

(4) CH_2M/Hill Analysis No. 98; Computer Run 103.

(5) U.S. EPA (1975), 40 CFR, Part 141 and U.S. EPA (1979), 40 CFR, Part 143.

(6) pH 3 leachate was spiked with 500 milligrams per liter tetrathionate ($S_4O_6^{-2}$) in place of thiosulfate (Appendix D).

(7) Passing a 0.45 µm membrane filter.

(8) No iron added to pH 9 leachate.

TABLE 3.6

RESULTS OF pH 3 LEACHATE ANALYSIS(1)

PARAMETER	UNITS	PHASE I LEACHATE		PHASE II LEACHATE	
		10/26/81	2/16/82	2/16/82	4/12/82
Temperature	°C	23.4	22.2	21.4	24.2
pH	pH units	3.00	2.98	3.07	2.98
Eh	mV	+586	+387	+609	+587
Specific Conductance	μmhos/cm @ 25°C	8,790	8,160	7,550	7,320
Filterable Residue	mg/ℓ	5,710	5,280	4,820	5,140
Available Acidity	mg/ℓ $CaCO_3$	4,260	3,210	2,950	2,850
Hot Acidity	mg/ℓ $CaCO_3$	4,810	4,920	4,750	4,650
Alkalinity	mg/ℓ $CaCO_3$	0	0	0	0
Chloride	mg/ℓ	62	71	67	120
Fluoride	mg/ℓ	0.18	0.23	2.4	0.09
Nitrate	mg/ℓ N	18	14	14	10
Sulfate	mg/ℓ	6,000	5,100	5,700	5,400
Thiosulfate	mg/ℓ	94	50	42	76
Total Sulfur	mg/ℓ SO_4	8,200	8,100	9,100	8,900
Cyanide	mg/ℓ	<0.1	<0.1	<0.1	<0.1
Dissolved Metals:(2)					
Aluminum	mg/ℓ	69	65	70	33
Arsenic	mg/ℓ	6.8	5.1	2.9	3.8
Barium	mg/ℓ	0.2	<0.01	<0.01	<0.01
Cadmium	mg/ℓ	2.3	1.2	2.0	2.2
Calcium	mg/ℓ	425	455	555	500
Chromium	mg/ℓ	2.6	2.6	2.1	1.8
Copper	mg/ℓ	110	130	110	120
Iron	mg/ℓ	1,360	1,456	910	940
Lead	mg/ℓ	2.0	<0.01	4.0	0.04
Magnesium	mg/ℓ	235	240	210	215
Manganese	mg/ℓ	49	30	30	23
Mercury	mg/ℓ	0.0022	<0.005	<0.005	0.007
Potassium	mg/ℓ	15	50	60	62
Selenium	mg/ℓ	0.07	<0.001	0.020	0.005
Silicon	mg/ℓ	170	290	285	130
Silver	mg/ℓ	<0.001	0.001	<0.001	<0.001
Sodium	mg/ℓ	550	550	495	525
Zinc	mg/ℓ	520	550	450	430

(1) Referenced analytical methods presented in Appendix D.

(2) Analysis of samples filtered through an 0.45 μm membrane filter.

TABLE 3.7

RESULTS OF pH 6 LEACHATE ANALYSIS(1)

PARAMETER	UNITS	PHASE I LEACHATE		PHASE II LEACHATE	
		10/26/81	2/16/82	2/16/82	4/12/82
Temperature	°C	23.4	22.4	21.6	24.2
pH	--	5.75	5.22	5.82	5.61
Eh	mV	+246	+336	+475	+487
Specific Conductance	μmhos/cm @ 25°C	7,240	6,750	6,440	5,790
Filterable Residue	mg/ℓ	5,140	4,360	4,140	4,260
Available Acidity	mg/ℓ $CaCO_3$	930	980	840	750
Hot Acidity	mg/ℓ $CaCO_3$	1,990	1,860	1,740	1,340
Alkalinity	mg/ℓ $CaCO_3$	5	5	5	-(2)
Chloride	mg/ℓ	310	280	280	240
Fluoride	mg/ℓ	2.3	2.3	1.3	1.3
Nitrate	mg/ℓ N	6.6	4.9	4.0	4.1
Sulfate	mg/ℓ	3,200	3,000	3,400	3,100
Thiosulfate	mg/ℓ	450	490	490	530
Total Sulfur	mg/ℓ SO_4	6,000	6,400	6,600	6,100
Cyanide	mg/ℓ	0.1	<0.1	<0.1	<0.1
Dissolved Metals:(3)					
Aluminum	mg/ℓ	0.2	0.3	0.5	<0.1
Arsenic	mg/ℓ	0.3	0.02	0.52	0.84
Barium	mg/ℓ	<0.1	0.03	<0.01	<0.01
Cadmium	mg/ℓ	0.10	<0.01	0.83	0.50
Calcium	mg/ℓ	570	505	555	500
Chromium	mg/ℓ	0.002	0.009	0.004	0.06
Copper	mg/ℓ	0.14	<0.01	4.5	0.10
Iron	mg/ℓ	730	610	410	410
Lead	mg/ℓ	<0.01	<0.01	0.22	0.04
Magnesium	mg/ℓ	220	225	195	205
Manganese	mg/ℓ	43	28	27	20
Mercury	mg/ℓ	<0.0005	<0.005	0.019	0.009
Potassium	mg/ℓ	21	62	60	71
Selenium	mg/ℓ	0.01	0.004	0.10	0.033
Silicon	mg/ℓ	9.8	32	45	18
Silver	mg/ℓ	<0.001	0.003	0.033	0.005
Sodium	mg/ℓ	615	600	595	650
Zinc	mg/ℓ	140	140	200	180

(1) Referenced analytical methods presented in Appendix D.

(2) "-" indicates no analysis performed.

(3) Analysis of samples filtered through an 0.45 μm membrane filter.

TABLE 3.8

RESULTS OF pH 9 LEACHATE ANALYSIS(1)

PARAMETER	UNITS	PHASE I LEACHATE		PHASE II LEACHATE	
		10/26/81	2/16/82	2/16/82	4/12/82
Temperature	°C	23.4	22.4	21.6	24.2
pH	--	9.05	8.83	8.62	8.79
Eh	mV	+276	+308	+487	+506
Specific Conductance	µmhos/cm @ 25°C	5,690	4,960	5,360	4,470
Filterable Residue	mg/ℓ	3,190	2,990	3,430	3,210
Available Acidity	mg/ℓ $CaCO_3$	0	0	0	0
Hot Acidity	mg/ℓ $CaCO_3$	0	0	0	0
Alkalinity	mg/ℓ $CaCO_3$	30	20	40	35
Chloride	mg/ℓ	340	320	340	310
Fluoride	mg/ℓ	7.6	6.8	2.3	1.9
Nitrate	mg/ℓ N	0.6	IS(2)	2.2	2.3
Sulfate	mg/ℓ	2,200	2,300	2,000	2,100
Thiosulfate	mg/ℓ	510	500	490	440
Total Sulfur	mg/ℓ SO_4	3,800	3,900	4,200	3,800
Cyanide	mg/ℓ	0.2	<0.1	<0.1	<0.1
Dissolved Metals:(3)					
Aluminum	mg/ℓ	<0.1	0.5	0.4	<0.1
Arsenic	mg/ℓ	0.091	0.275	0.015	0.009
Barium	mg/ℓ	0.4	0.07	<0.01	<0.01
Cadmium	mg/ℓ	0.27	0.17	0.31	0.41
Calcium	mg/ℓ	660	645	575	575
Chromium	mg/ℓ	0.04	0.2	0.12	0.02
Copper	mg/ℓ	5.4	7.7	6.8	4.4
Iron	mg/ℓ	0.4	1.2	0.4	1.6
Lead	mg/ℓ	0.01	0.08	<0.01	<0.01
Magnesium	mg/ℓ	66	86	140	145
Manganese	mg/ℓ	0.70	0.90	3.4	0.73
Mercury	mg/ℓ	0.150	0.078	0.076	0.066
Potassium	mg/ℓ	20	120	65	66
Selenium	mg/ℓ	0.05	0.21	0.15	0.054
Silicon	mg/ℓ	<0.1	16	4	<1
Silver	mg/ℓ	0.12	0.19	0.12	0.001
Sodium	mg/ℓ	680	770	615	675
Zinc	mg/ℓ	0.64	0.27	0.28	0.04

(1) Referenced analytical methods presented in Appendix D.

(2) Insufficient sample for analysis.

(3) Analysis of samples filtered through an 0.45 µm membrane filter.

TABLE 3.9

RESULTS OF WATEQ ANALYSES FOR PREDOMINATE LEACHATE SPECIES

SOLUTE	PREDOMINATE CHEMICAL SPECIES AT EQUILIBRIUM(1)			
	pH 2 LEACHATE	pH 3 LEACHATE	pH 6 LEACHATE	pH 9 LEACHATE
Chloride	Cl^{-1}	Cl^{-1}	Cl^{-1}	Cl^{-1}
Fluoride	AlF^{+2}	AlF^{+2}	F^{-1}	F^{-1}
Nitrate	NO_3^{-1}	NO_3^{-1}	NO_3^{-1}	NO_3^{-1}
Sulfate	SO_4^{-2}	SO_4^{-2}	SO_4^{-2}	SO_4^{-2}
Aluminum	$AlSO_4^{+1}, Al^{+3}, Al(SO_4)_2^{-1}$	$AlSO_4^{+1}, Al(SO_4)_2^{-1}, Al^{+3}$	$AlF_2^{+1}, AlF_3^{\circ}$	BD(2)
Cadmium	Cd^{+2}, $CdSO_4^{\circ}$	Cd^{+2}, $CdSO_4^{\circ}$	Cd^{+2}, $CdSO_4^{\circ}$, $CdCl^{+1}$	Cd^{+2}, $CdCl^{+1}$, $CdSO_4^{\circ}$
Calcium	Ca^{+2}, $CaSO_4^{\circ}$	Ca^{+2}, $CaSO_4^{\circ}$	Ca^{+2}, $CaSO_4^{\circ}$	Ca^{+2}, $CaSO_4^{\circ}$
Chromium	$CrSO_4^{+1}$	$CrSO_4^{+1}$	$CrOH^{+2}, CrSO_4^{+1}$	CrO_4^{-2}
Copper	Cu^{+2}, $CuSO_4^{\circ}$	Cu^{+2}, $CuSO_4^{\circ}$	Cu^{+2}, $CuSO_4^{\circ}$	$Cu(OH)_2^{\circ}$
Iron	Fe^{+2}, $FeSO_4^{\circ}$	Fe^{+2}, $FeSO_4^{\circ}$	Fe^{+2}, $FeSO_4^{\circ}$	$Fe(OH)_4^{-1}$
Lead	Pb^{+2}, $PbSO_4^{\circ}$	$Pb(SO_4)_2^{-2}$, Pb^{+2}, $PbSO_4^{\circ}$	BD	$PbOH^{+1}$, $Pb(OH)_2^{\circ}$
Magnesium	Mg^{+2}, $MgSO_4^{\circ}$	Mg^{+2}, $MgSO_4^{\circ}$	Mg^{+2}, $MgSO_4^{\circ}$	Mg^{+2}, $MgSO_4^{\circ}$
Manganese	Mn^{+2}, $MnSO_4^{\circ}$	Mn^{+2}, $MnSO_4^{\circ}$	Mn^{+2}, $MnSO_4^{\circ}$	Mn^{+2}, $MnSO_4^{\circ}$
Potassium	K^{+1}	K^{+1}	K^{+1}	K^{+1}
Silicon	$H_4SiO_4^{\circ}$	$H_4SiO_4^{\circ}$	$H_4SiO_4^{\circ}$	BD
Silver	BD	BD	BD	$AgCl^{\circ}$ $AgCl_2^{-1}$
Sodium	Na^{+1}	Na^{+1}	Na^{+1}	Na^{+1}
Zinc	Zn^{+2}, $ZnSO_4^{\circ}$	Zn^{+2}, $ZnSO_4^{\circ}$	Zn^{+2}, $ZnSO_4^{\circ}$	$Zn(OH)_2^{\circ}$

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(1) Thermodynamic equilibrium distribution of the solutes as calculated by WATEQ using the chemical analyses of the leachates and measurements of pH and Eh. Other than the solutes noted above, no other solutes were considered in this calculation. The leachate analyses used in these calculations were the pH 2 leachate analysis shown in Table 3.5 and the October 26, 1981 analyses of the pH 3, 6, and 9 leachates shown on Tables 3.6 through 3.8. When more than one species is depicted for a given solute, they are present at near equal molalities; the first species noted is predominate.

(2) "BD" indicates that solute was below analytical detection limits in the leachate.

TABLE 3.10

RESULTS OF WATEQ ANALYSES FOR STATE OF LEACHATE SOLUTION EQUILIBRIUM WITH POSSIBLE SOLUTION CHEMISTRY CONTROLLING MINERAL PHASES

MINERAL NAME/ FORMULA	LOG K(1)	EQUILIBRIUM STATE OF SATURATION(2)			
		pH 2 LEACHATE	pH 3 LEACHATE	pH 6 LEACHATE	pH 9 LEACHATE
Amorphous $Al(OH)_3$	-32.37	-	-	-	BD(3)
Gibbsite, $Al(OH)_3$	-34.06	-	-	0	BD
Diaspore, $AlO(OH)$	-35.20	-	-	0	BD
$AlOHSO_4$	-17.23	0	0	-	BD
Amorphous $Cd(OH)_2$	-13.7	-	-	-	-
Amorphous $CdCO_3$	-11.6	BD	BD	-	0
$CdSO_4$	-0.159	-	-	-	-
Fluorite, CaF_2	-9.05	-	-	-	0
Gypsum, $CaSO_4 \cdot 2H_2O$	-4.59	0	0	0	0
Calcite, $CaCO_3$	-8.48	BD	BD	-	+
Portlandite, $Ca(OH)_2$	-5.23	-	-	-	-
$Cr(OH)_3$	-30.10	-	-	-	-
Cr_2O_3	+7.68	-	-	+	+
CuO	+7.70	-	-	-	+
$Cu(OH)_2$	-19.35	-	-	-	+
Amorphous $Fe(OH)_3$	-38.50	-	0	+	+
Geothite, FeO(OH)	-44.32	0	+	+	+
Siderite, $FeCO_3$	-10.55	BD	BD	0	-
Amorphous $Pb(OH)_2$	+12.91	-	-	BD	-
Cerussite, $PbCO_3$	-12.83	BD	BD	BD	-
Anglesite, $PbSO_4$	-7.75	0	0	BD	-
Magnesite, $MgCO_3$	-4.90	BD	BD	-	-
Dolomite, $CaMg(CO_3)_2$	-16.96	BD	BD	-	+
Brucite, $Mg(OH)_2$	-10.88	-	-	-	-
Manganosite, MnO	+18.06	-	-	-	-
Pyrochroite, $Mn(OH)_2$	+15.31	-	-	-	-
Rhodocrosite, $MnCO_3$	-10.65	BD	BD	-	0
Cerargyrite, AgCl	-3.27	BD	BD	BD	0
Amorphous $Zn(OH)_2$	+10.93	-	-	-	0
Smithsonite, $ZnCO_3$	-10.78	BD	BD	-	0
$ZnSO_4$	+3.14	-	-	-	-

(1) Solubility constant used in calculation of state of mineral equilibria.

(2) Thermodynamic equilibrium state of the leachates with the mineral phases depicted as calculated by WATEQ using measurements of leachate pH and Eh and the calculated equilibrium distribution of chemical species in the leachates. "-" indicates a state of undersaturation with respect to the mineral phase; "0" indicates a state of saturation (within the accuracy of the calculation--range of log ion activity product divided by log solubility constant from -1 to +1) with respect to the mineral phase; and "+" indicates a state of supersaturation with respect to the mineral phase. The leachate analyses used in these calculations were the pH 2 leachate analysis shown in Table 3.5 and the October 26, 1981 analyses of the pH 3, 6, and 9 leachates shown on Tables 3.6 through 3.8.

(3) "BD" indicates one or more of the elements in the mineral phase was below analytical detection limits in the leachate.

TABLE 3.11

SUMMARY OF RETARDATION FACTORS (R_d) DETERMINED BY CONSTANT pH SORPTION BATCH TESTS(1)

PARAMETER	4% BENTONITE/TILL ADMIXTURE		GLACIAL TILL (COMPOSITE NO. 1)			STRATIFIED DRIFT (COMPOSITE NO. 2)		
	pH 3	pH 9	pH 3	pH 6	pH 9	pH 3	pH 6	pH 9
Arsenic	62	1640	23	111	1310	24.0	161	1010
Cadmium	5	681	3.4	113	737	2.2	143	421
Chromium	74	113	129	BD(2)	257	31	BD	168
Copper	7	376	12	32	353	3.5	58	94
Iron	9	1	4.2	11	1	3.5	4.4	1
Lead	129	BD	120	BD	BD	41	BD	BD
Manganese	1	246	1	1	525	1	1	133
Mercury	48	2.5	>145(3)	BD	177	>112	BD	189
Selenium	BD	>81	BD	1	>65	BD	BD	>50
Silver	BD	2.5	BD	1	65	BD	BD	218
Zinc	4	526	2.2	11	273	1	3.5	325
Cyanide	9	21	14	1	23	7.2	1	1

(1) $R_d = 1 + (\rho/n_e) K_r$; where bulk density (ρ) in g/cm^3 and effective porosity (n_e) are given for each soil sample in Table 3.24 and distribution ratios (K_r) are averages of the duplicate determinations presented in Appendix E.

(2) R_d values reported as "BD" represent soluble metal levels which were below the detection limit before the leachate was allowed to react with the soil.

(3) ">" indicates the concentration in the soil-reacted leachate was below the analytical detection limit. The lower the R_d values with ">" signs, the lower the initial concentration of that metal in the leachate; i.e., its concentration was near the detection limit before contact with the soil sample. Therefore, the values reported as greater than are the lower limit, and the detectable concentration of these metals were sorbed or removed from solution. See Appendix E for the initial and final leachate analyses.

TABLE 3.12
SUMMARY OF RETARDATION FACTORS (R_d) DETERMINED BY LEACHATE NEUTRALIZATION/SORPTION BATCH TESTS(1)

PARAMETER	4% BENTONITE/TILL ADMIXTURE	GLACIAL TILL (COMPOSITE NO. 1)		STRATIFIED DRIFT (COMPOSITE NO. 2)	
	pH 3 to 9	pH 3 to 6	pH 3 to 9	pH 3 to 6	pH 3 to 9
Arsenic	264,000	9,250	211,200	12,060	162,890
Cadmium	7,070	3,760	7,550	4,360	4,360
Chromium	14,050	>61,840(2)	27,040	71,550	17,870
Copper	7,910	69,110	7,320	90,470	2,250
Iron	240,000	43	123,400	25	148,100
Lead	>8,360	>6,690	>6,690	>5,160	5,160
Manganese	26,100	1.4	50,370	1.3	14,230
Mercury	1	>145	1	>112	1
Selenium	BD(3)	1	BD	BD	BD
Silver	1	1	1	BD	1
Zinc	850,000	145	456,000	87	524,500
Cyanide	1	1	1	1	1

(1) $R_d = 1 + (\rho/n_e) K_r$; where bulk density (ρ) in g/cm^3 and effective porosity (n_e) are given for each soil sample in Table 3.24 and distribution ratios (K_r) are averages of the duplicate determinations presented in Appendix E. To include the effect of leachate neutralization in the R_d calculation, the pH 3.0 control sample analysis (Table E.2) was used as the initial leachate concentration before contact with the soil.

(2) ">" indicates the concentration in the soil-reacted leachate was below the analytical detection limit. The lower the R_d values with ">" signs, the lower the initial concentration of that metal in the leachate; i.e., its concentration was near the detection limit before contact with the soil sample. Therefore, the values reported as greater than are the lower limit, and the detectable concentration of these metals were sorbed or removed from solution. See Appendix E for the initial and final leachate analyses.

(3) R_d values reported as "BD" represent soluble metal levels which were below the detection limit before the leachate was allowed to react with the soil.

TABLE 3.13

GENERAL SOIL ATTENUATION MECHANISMS AND TRENDS FOR HEAVY METALS

MECHANISM/TREND	SUPPORTING LITERATURE
The primary attenuation mechanism for heavy metal cations below pH 5 are cation exchange-adsorption.	Griffin, et al., 1976a, 1976b, and 1977
Mineral precipitation is a significant attenuation mechanism for heavy metal cations above pH 5.	Griffin, et al., 1976a, 1976b, and 1977
Attenuation of heavy metal cations increases with increasing pH.	Griffin, et al., 1976a, 1976b, and 1977; and Gee, et al., 1980
The attenuation of heavy metal cations decreases with increasing ionic strength.	Griffin, et al., 1976a, 1976b, and 1977
Attenuation of heavy metal cations increases with a decrease in metal complexation (larger ionic charge enhances attenuation).	Bigger, et al., 1981
The primary attenuation mechanism for heavy metal anions (i.e., anionic oxides of arsenic, selenium and chromium VI, and cyanide) below pH 5 is anionic adsorption.	Griffin, et al., 1976a, 1976b, and 1977
Attenuation of heavy metal anions increases with decreasing pH.	Griffin, et al., 1976a, 1976b, and 1977; Alesii and Fuller, 1976; and Fuller, 1977, 1978, and 1981
Attenuation of both heavy metal cations and anions and cyanide increases with increasing amounts of sesquioxides, humus (organic colloids), and clay in the soil.	Bondietti, et al., 1973; Gardiner, 1974; Fuller, 1977 and 1978; Jenne, 1969 and 1977, and Frost and Griffin, 1977

TABLE 3.14

EXPERIMENTAL DESIGN OF COLUMN ATTENUATION STUDY, COLUMN DIMENSION AND PORE VOLUME, AND AVERAGE LEACHATE FLOW RATE DATA

SOIL SAMPLE(1)	COLUMN DESIGNATION	LEACHATE PERMEANT pH	FINAL LENGTH (cm)	TOTAL VOLUME (cm^3)	PORE VOLUME(2) (cm^3)	AVERAGE PORE VOLUME FLOW PER WEEK(3)	TOTAL PORE VOLUMES PASSED THROUGH COLUMN
Glacial Till (Composite No. 1)	I-1	3	13.0	553.3	141.2	1.04	18.2
	I-2	6	12.9	554.6	143.8	0.85	17.3
	I-3	9	12.9	557.4	143.5	1.09	17.1
	I-4	9	12.7	540.6	145.3	0.93	8.5
Stratified Drift (Composite No. 2)	J-1	3	14.1	611.1	206.2	0.74	12.6
	J-2	6	13.6	592.1	187.2	0.70	13.9
	J-3	9	13.9	601.7	195.6	0.73	13.3
	J-4	9	14.0	605.8	200.6	0.64	7.7
4% Bentonite/ Till Admixture	K-1	3	11.6	485.5	138.5	0.71	13.3
	K-2	9	11.6	485.5	138.9	0.71	13.0

(1) See Appendix C for composition of composite samples.

(2) Sample free pore space. Calculation based upon final sample dimensions and measured specific gravity for the 4% bentonite/till admixture of 2.74 g/cm^3. Specific gravities used for the till and drift columns were estimated from existing site data at 2.70 and 2.67 g/cm^3, respectively, as discussed in Appendix F.

(3) Calculation based upon first nine weeks of test, as chemical breakthrough for most of the mobile solutes occurred during this time period.

TABLE 3.15

SUMMARY OF RETARDATION FACTORS (R_d) BY THE SOLUTE FRONT ADVANCEMENT COLUMN TEST FOR MONITORED PARAMETERS(1)

LEACHATE PERMEANT pH	SOIL SAMPLE(2)	CHEMICAL PARAMETER							
		CHLORIDE(3)	SPECIFIC CONDUCTANCE/TDS	SULFATE	TOTAL SULFUR	ARSENIC	IRON	ZINC	AVAILABLE ACIDITY
pH 3(4)	4% Bentonite/Till Admixture	1	1	1.4	1	>11(5)	5.3	5.3	10.4
	Glacial Till	1	1	1	1.1	>18.2	12.4	4.4	>18.2
	Stratified Drift	1	1	1.5	1.6	>15.7	4.5	3.6	14.2
pH 6	Glacial Till	1	1	1	1	>14.4	>14.4	>14.4	7.5
	Stratified Drift	1	1.1	1.3	1.7	>13.9	4.9	9	5.7
pH 9	4% Bentonite/Till Admixture	1	1	1	1	–(6)	–	–	–
	Glacial Till	1	1	1	1	–	–	–	–
	Stratified Drift	1	1	1	1	–	–	–	–

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(1) R_d values calculated as discussed in text using chloride as the tracer solute. Data used for the R_d calculations is presented in Figures 3.1 through 3.10.

(2) Glacial till refers to Composite Sample No. 1 and stratified drift refers to Composite Sample No. 2. See Appendix C for composition of composite samples.

(3) Tracer solute; R_d set equal to 1.

(4) pH 3 R_d's calculated using the maximum chloride initial concentration (C_o) depicted in Figures 3.1 through 3.3.

(5) The "greater than" symbol (>) indicates that the normalized half concentration of this solute did not "breakthrough" during the duration of the column test.

(6) "--" indicates R_d not calculated as initial leachate permeant concentrations (C_o) were too close to analytical detection limits. See text.

TABLE 3.16

COLUMN TEST EFFLUENT CHARACTERISTICS AND APPROXIMATE RETARDATION FACTORS (R_d) FOR THE 4% BENTONITE/TILL ADMIXTURE(1)

PARAMETER	CONCENTRATION UNITS	pH 3 LEACHATE (COLUMN K-1)					pH 9 LEACHATE (COLUMN K-2)				
		PHASE II PERMEANT COMPOSITION		EFFLUENT COMPOSITION		APPROXIMATE R_d(2)	PHASE II PERMEANT COMPOSITION		EFFLUENT COMPOSITION		APPROXIMATE R_d(2)
		2/16/82	4/19/82	2/24/82	4/19/82		2/16/82	4/19/82	2/24/82	4/19/82	
Pore Volumes of Flow	-(3)	-	-	7.6	13.3	-	-	-	7.3	13.0	-
Temperature	°C	21.4	23.0	-	-	-	21.6	23.0	-	-	-
pH	pH units	3.07	3.29	5.04	5.01	-	8.62	6.49	7.03	7.10	-
Eh	mV	+609	+492	+366	+376	-	+487	+376	+260	+267	-
Specific Conductance	μmhos/cm @ 25°C	7,550	8,140	8,360	7,720	1(4)	5,360	5,740	4,940	5,910	1(4)
Filterable Residue	mg/ℓ	4,820	-	5,260	4,990	1(4)	3,430	-	3,200	3,620	1(4)
Available Acidity	mg/ℓ $CaCO_3$	2,950	520	-	910	10.4(4)	0	-	-	-	-
Hot Acidity	mg/ℓ $CaCO_3$	4,750	1,950	810	2,430	-	0	-	-	-	-
Alkalinity	mg/ℓ $CaCO_3$	0	-	-	-	-	40	90	-	-	-
Chloride	mg/ℓ	67	83	140	170	1(4)	340	260	210	660	1(4)
Fluoride	mg/ℓ	2.4	0.17	-	0.17	<11	2.3	0.05	0.41	0.05	>5.6
Nitrate	mg/ℓ N	14	-	2	4.2	>11	2.2	-	<1	<1	>10
Sulfate	mg/ℓ	5,700	6,200	6,400	6,300	1.4(4)	2,000	2,700	6,000	6,900	1(4)
Thiosulfate	mg/ℓ	42	-	130	140	<6.3	490	-	360	490	<5.6
Total Sulfur	mg/ℓ SO_4	9,100	6,900	6,800	7,000	1(4)	4,200	3,400	6,600	8,300	1(4)
Cyanide	mg/ℓ	<0.1	-	-	-	-	<0.1	-	-	-	-
Dissolved Metals:											
Aluminum	mg/ℓ	70	34	1.0	1.0	>11	0.4	-	<0.1	<0.1	BD
Arsenic	mg/ℓ	2.9	1.1	0.014	0.012	>11	0.015	-	0.003	0.003	>10
Barium	mg/ℓ	<0.01	-	0.13	0.08	BD(5)	<0.01	-	0.35	0.06	BD
Cadmium	mg/ℓ	2.0	-	0.03	0.04	>11	0.31	-	-	0.02	>10
Calcium	mg/ℓ	555	525	500	500	<6.3	575	-	525	650	<5.6
Chromium	mg/ℓ	2.1	-	0.05	0.06	>11	0.120	-	0.06	0.01	>10
Copper	mg/ℓ	110	100	0.04	0.02	>11	6.8	1.8	0.01	0.01	>10
Iron	mg/ℓ	910	990	1,400	1,200	5.3(4)	0.4	0.1	1.8	0.9	BD
Lead	mg/ℓ	4.0	-	<0.01	<0.01	>11	<0.01	-	<0.01	<0.01	BD
Magnesium	mg/ℓ	210	235	275	250	<6.3	140	-	110	110	<5.6
Manganese	mg/ℓ	30	-	40	26	<6.3	3.44	-	17	21	<5.6
Mercury	mg/ℓ	<0.005	-	0.004	0.005	BD	0.076	-	<0.001	0.010	>10
Potassium	mg/ℓ	60	-	-	-	-	65	-	-	-	-
Selenium	mg/ℓ	0.020	<0.001	<0.001	-	BD	0.150	-	<0.001	<0.001	>10
Silicon	mg/ℓ	285	130	48	63	>11	4	4	13	8	<5.6
Silver	mg/ℓ	<0.001	-	<0.001	<0.001	BD	0.120	-	<0.001	<0.001	>10
Sodium	mg/ℓ	495	550	575	525	<6.3	615	-	675	700	<5.6
Zinc	mg/ℓ	450	490	420	490	5.3(4)	0.28	0.1	-	0.10	>10

(1) Referenced analytical methods presented in Appendix D.

(2) Retardation factors approximated using chloride as the tracer solute (Figures 3.1 and 3.6) and column effluent concentrations at pore volume sampled. See text.

(3) "-" indicates not applicable or not determined.

(4) Retardation factor as calculated from Figures 3.1 and 3.6 (Table 3.15).

(5) R_d values reported as "BD" represent solute concentrations which were below the detection limit before the leachate had permeated the columns or which were too low to allow the determination of significant differences in influent leachates and seepage effluent concentration once the leachate had permeated the columns.

TABLE 3.17

COLUMN TEST EFFLUENT CHARACTERISTICS AND APPROXIMATE RETARDATION FACTORS (R_d) FOR THE GLACIAL TILL AND STRATIFIED DRIFT COMPOSITE SAMPLES PERMEATED WITH pH 3 LEACHATE(1)

PARAMETER	CONCENTRATION UNITS	PHASE II PERMEANT COMPOSITION		GLACIAL TILL (COLUMN I-1)			STRATIFED DRIFT (COLUMN J-1)		
				EFFLUENT COMPOSITION		APPROXIMATE R_d(2)	EFFLUENT COMPOSITION		APPROXIMATE R_d(2)
		2/16/82	4/12/82	2/24/82	4/19/82		2/24/82	4/19/82	
Pore Volumes of Flow	-(3)	-	-	8.3	18.2	-	6.6	12.6	-
Temperature	°C	21.4	24.2	-	-	-	-	-	-
pH	pH units	3.07	2.98	5.11	5.27	-	5.14	5.36	-
Eh	mV	+609	+587	+331	+376	-	+298	+307	-
Specific Conductance	µmhos/cm @ 25°C	7,550	7,320	7,520	7,260	1(4)	7,530	7,430	1(4)
Filterable Residue	mg/ℓ	4,820	5,140	4,620	4,590	1(4)	4,870	4,760	1(4)
Available Acidity	mg/ℓ $CaCO_3$	2,950	2,850	-	1,100	>18.2(4)	-	1,440	14.2(4)
Hot Acidity	mg/ℓ $CaCO_3$	4,750	4,650	620	1,400	>18.2	860	1,710	>15.7
Alkalinity	mg/ℓ $CaCO_3$	0	0	-	-	-	-	-	-
Chloride	mg/ℓ	67	120	120	170	1(4)	210	260	1(4)
Fluoride	mg/ℓ	2.4	0.09	1.04	0.84	>8.3	0.14	1.42	>8.2
Nitrate	mg/ℓ N	14	10	2.7	3.0	>18.2	2.6	1.7	>15.7
Sulfate	mg/ℓ	5,700	5,400	6,800	7,700	1(4)	6,900	7,400	1.5(4)
Thiosulfate	mg/ℓ	42	76	92	100	<8.3	67	110	<8.2
Total Sulfur	mg/ℓ SO_4	9,100	8,900	8,400	8,600	1.1(4)	8,000	8,500	1.6(4)
Cyanide	mg/ℓ	<0.1	<0.1	-	-	-	-	-	-
Dissolved Metals:									
Aluminum	mg/ℓ	70	33	<0.1	1.0	>18.2	<0.1	<0.1	>15.7
Arsenic	mg/ℓ	2.9	3.8	0.044	0.260	>18.2(4)	0.007	0.006	>15.7(4)
Barium	mg/ℓ	<0.01	<0.01	0.07	0.04	BD(5)	0.06	0.05	BD
Cadmium	mg/ℓ	2.0	2.2	0.03	0.4	>18.2	0.03	0.07	>15.7
Calcium	mg/ℓ	555	500	500	475	<8.3	475	500	<8.2
Chromium	mg/ℓ	2.1	1.8	0.03	0.06	>18.2	0.04	0.04	>15.7
Copper	mg/ℓ	110	120	0.04	0.03	>18.2	0.03	0.02	>15.7
Iron	mg/ℓ	910	940	700	830	12.4(4)	960	860	4.5(4)
Lead	mg/ℓ	4.0	0.04	<0.01	<0.01	>18.2	<0.01	<0.01	>15.7
Magnesium	mg/ℓ	210	215	400	325	<8.3	400	325	<8.2
Manganese	mg/ℓ	30	23	30	25	<8.3	22	22	<8.2
Mercury	mg/ℓ	<0.005	0.007	0.009	0.013	BD	0.016	0.010	BD
Potassium	mg/ℓ	60	62	-	-	-	-	-	-
Selenium	mg/ℓ	0.020	0.005	0.001	0.004	BD	<0.001	0.011	BD
Silicon	mg/ℓ	285	130	45	53	>18.2	30	41	>15.7
Silver	mg/ℓ	<0.001	<0.001	<0.001	<0.001	BD	<0.001	<0.001	BD
Sodium	mg/ℓ	495	525	575	550	<8.3	550	550	<8.2
Zinc	mg/ℓ	450	430	240	400	4.4(4)	370	420	3.6(4)

(1) Referenced analytical methods presented in Appendix D. See Appendix C for composition of composite samples.

(2) Retardation factors approximated using chloride as the tracer solute (Figures 3.2 and 3.3) and column effluent concentrations at pore volume sampled. See text.

(3) "-" indicates not applicable or not determined.

(4) Retardation factor as calculated from Figures 3.2 and 3.3 (Table 3.15).

(5) R_d values reported as "BD" represent solute concentrations which were below the detection limit before the leachate had permeated the columns or which were too low to allow the determination of significant differences in influent leachates and seepage effluent concentration once the leachate had permeated the columns.

TABLE 3.18

COLUMN TEST EFFLUENT CHARACTERISTICS AND APPROXIMATE RETARDATION FACTORS (R_d) FOR THE GLACIAL TILL AND STRATIFIED DRIFT COMPOSITE SAMPLES PERMEATED WITH pH 6 LEACHATE(1)

PARAMETER	CONCENTRATION UNITS	PHASE II PERMEANT COMPOSITION		GLACIAL TILL (COLUMN I-2)			STRATIFED DRIFT (COLUMN J-2)		
				EFFLUENT COMPOSITION		APPROXIMATE R_d(2)	EFFLUENT COMPOSITION		APPROXIMATE R_d(2)
		2/16/82	4/12/82	2/24/82	4/19/82		2/24/82	4/19/82	
Pore Volumes of Flow	-(3)	-	-	8.9	17.3	-	8.4	13.9	-
Temperature	°C	21.6	24.2	-	-	-	-	-	-
pH	pH units	5.82	5.61	6.02	5.97	-	6.13	6.17	-
Eh	mV	+475	+487	+276	+214	-	+220	+221	-
Specific Conductance	µmhos/cm @ 25°C	6,440	5,790	6,450	6,710	1(4)	6,620	6,610	1.1(4)
Filterable Residue	mg/ℓ	4,140	4,260	4,900	4,280	1(4)	4,210	4,230	1.1(4)
Available Acidity	mg/ℓ $CaCO_3$	840	750	-	610	7.5(4)	-	770	5.7(4)
Hot Acidity	mg/ℓ $CaCO_3$	1,740	1,340	680	870	>7.4	730	1,310	>8.4
Alkalinity	mg/ℓ $CaCO_3$	5	-	-	-	-	-	-	-
Chloride	mg/ℓ	280	240	240	380	1(4)	260	400	1(4)
Fluoride	mg/ℓ	1.3	1.3	0.32	0.26	>14.4	0.58	0.05	>13.9
Nitrate	mg/ℓ N	4.0	4.1	3.5	4.8	<7.4	4.5	4.8	<8.4
Sulfate	mg/ℓ	3,400	3,100	6,200	6,600	1(4)	6,800	7,100	1.3(4)
Thiosulfate	mg/ℓ	490	530	270	410	<7.4	440	480	<8.4
Total Sulfur	mg/ℓ SO_4	6,600	6,100	7,200	7,900	1(4)	7,100	7,500	1.7(4)
Cyanide	mg/ℓ	<0.1	<0.1	-	-	-	-	-	-
Dissolved Metals:									
Aluminum	mg/ℓ	0.5	<0.1	<0.1	<0.1	BD(5)	<0.1	<0.1	BD
Arsenic	mg/ℓ	0.52	0.84	0.002	0.002	>14.4(4)	0.004	0.002	>13.9(4)
Barium	mg/ℓ	<0.01	<0.01	<0.01	0.07	BD	0.07	0.06	BD
Cadmium	mg/ℓ	0.83	0.50	<0.01	0.02	>14.4	0.02	0.02	>13.9
Calcium	mg/ℓ	555	500	550	525	<7.4	500	525	<8.4
Chromium	mg/ℓ	0.004	0.06	0.04	0.04	BD	0.03	0.02	BD
Copper	mg/ℓ	4.5	0.10	0.01	0.01	>14.4	0.02	0.02	>13.9
Iron	mg/ℓ	410	410	180	190	>14.4(4)	570	360	4.9(4)
Lead	mg/ℓ	0.22	0.04	<0.01	<0.01	>14.4	<0.01	<0.01	>13.9
Magnesium	mg/ℓ	195	205	275	250	<7.4	250	225	<8.4
Manganese	mg/ℓ	27	20	27	25	<7.4	23	21	<8.4
Mercury	mg/ℓ	0.019	0.009	0.009	0.010	BD	0.014	0.001	BD
Potassium	mg/ℓ	60	71	-	-	-	-	-	-
Selenium	mg/ℓ	0.10	0.033	<0.001	<0.001	>14.4	<0.001	<0.001	>13.9
Silicon	mg/ℓ	45	18	21	20	>7.4	20	18	<8.4
Silver	mg/ℓ	0.033	0.005	<0.001	<0.001	>14.4	<0.001	<0.001	>13.9
Sodium	mg/ℓ	595	650	650	625	<7.4	650	675	<8.4
Zinc	mg/ℓ	200	180	0.25	50	>14.4(4)	46	110	9(4)

(1) Referenced analytical methods presented in Appendix D. See Appendix C for composition of composite samples.

(2) Retardation factors approximated using chloride as the tracer solute (Figures 3.4 and 3.5) and column effluent concentrations at pore volume sampled. See text.

(3) "-" indicates not applicable or not determined.

(4) Retardation factor as calculated from Figures 3.4 and 3.5 (Table 3.15).

(5) R_d values reported as "BD" represent solute concentrations which were below the detection limit before the leachate had permeated the columns or which were too low to allow the determination of significant differences in influent leachates and seepage effluent concentration once the leachate had permeated the columns.

TABLE 3.19

COLUMN TEST EFFLUENT CHARACTERISTICS AND APPROXIMATE RETARDATION FACTORS (R_d) FOR THE GLACIAL TILL AND STRATIFIED DRIFT COMPOSITE SAMPLES PERMEATED WITH pH 9 LEACHATE(1)

PARAMETER	CONCENTRATION UNITS	PHASE II PERMEANT COMPOSITION		GLACIAL TILL (COLUMN I-3)			STRATIFED DRIFT (COLUMN J-3)		
				EFFLUENT COMPOSITION		APPROXIMATE R_d(2)	EFFLUENT COMPOSITION		APPROXIMATE R_d(2)
		2/16/82	4/12/82	2/24/82	4/19/82		2/24/82	4/19/82	
Pore Volumes of Flow	-(3)	-	-	8.3	17.1	-	7.0	13.3	-
Temperature	°C	21.6	24.2	-	-	-	-	-	-
pH	pH units	8.62	8.79	6.97	6.83		7.31	7.17	-
Eh	mV	+487	+506	+201	+231	-	+155	+191	-
Specific Conductance	µmhos/cm @ 25°C	5,360	4,470	5,140	5,940	1(4)	6,240	6,240	1(4)
Filterable Residue	mg/ℓ	3,430	3,210	3,310	3,780	1(4)	3,970	3,890	1(4)
Available Acidity	mg/ℓ $CaCO_3$	0	0	-	-	-	-	-	-
Hot Acidity	mg/ℓ $CaCO_3$	0	0	-	-	-	-	-	-
Alkalinity	mg/ℓ $CaCO_3$	40	35	-	-	-	-	-	-
Chloride	mg/ℓ	340	310	48	210	1(4)	190	210	1(4)
Fluoride	mg/ℓ	2.3	1.9	0.36	0.73	>14.3	0.34	1.80	>7.0
Nitrate	mg/ℓ N	2.2	2.3	1.1	0.9	6.9	-	-	-
Sulfate	mg/ℓ	2,000	2,100	4,800	6,200	1(4)	6,400	6,200	1(4)
Thiosulfate	mg/ℓ	490	440	480	570	<6.9	520	390	<7.0
Total Sulfur	mg/ℓ SO_4	4,200	3,800	6,100	6,800	1(4)	7,000	7,300	1(4)
Cyanide	mg/ℓ	<0.1	<0.1	-	-	-	-	-	-
Dissolved Metals:									
Aluminum	mg/ℓ	0.4	<0.1	<0.1	<0.1	BD(5)	<0.1	<0.1	BD
Arsenic	mg/ℓ	0.015	.009	0.004	0.007	BD	0.008	0.005	BD
Barium	mg/ℓ	<0.01	<0.01	0.08	0.02	BD	0.12	0.09	BD
Cadmium	mg/ℓ	0.31	0.41	<0.01	<0.01	>14.3	<0.01	<0.01	>13.3
Calcium	mg/ℓ	575	575	575	625	<6.9	575	600	<7.0
Chromium	mg/ℓ	0.12	0.02	0.03	0.02	BD	0.02	0.07	BD
Copper	mg/ℓ	6.8	4.4	0.02	0.01	>14.3	0.02	0.01	>13.3
Iron	mg/ℓ	0.4	1.6	1.9	3.0	BD	4.8	4.7	BD
Lead	mg/ℓ	<0.01	<0.01	<0.01	<0.01	BD	<0.01	<0.01	BD
Magnesium	mg/ℓ	140	145	125	155	<6.9	77	150	<7.0
Manganese	mg/ℓ	3.4	0.73	7.5	6.5	<6.9	7.8	4.7	<7.0
Mercury	mg/ℓ	0.076	0.066	0.009	0.012	>14.3	0.006	0.005	>13.3
Potassium	mg/ℓ	65	66	-	-	-	-	-	-
Selenium	mg/ℓ	0.15	0.054	0.002	0.007	>14.3	0.001	0.001	>13.3
Silicon	mg/ℓ	4	<1	26	22	<6.9	24	23	<7.0
Silver	mg/ℓ	0.12	0.001	<0.001	<0.001	>14.3	<0.001	-	>7.0
Sodium	mg/ℓ	615	675	700	625	<6.9	700	650	<7.0
Zinc	mg/ℓ	0.28	0.04	0.10	0.17	BD	0.12	0.58	BD

(1) Referenced analytical methods presented in Appendix D. See Appendix C for composition of composite samples.

(2) Retardation factors approximated using chloride as the tracer solute (Figures 3.7 and 3.9) and column effluent concentrations at pore volume sampled. See text.

(3) "-" indicates not applicable or not determined.

(4) Retardation factor as calculated from Figures 3.7 and 3.9 (Table 3.15).

(5) R_d values reported as "BD" represent solute concentrations which were below the detection limit before the leachate had permeated the columns or which were too low to allow the determination of significant differences in influent leachates and seepage effluent concentration once the leachate had permeated the columns.

TABLE 3.20

COMPARISON OF RETARDATION FACTORS (R_d) DETERMINED BY CONSTANT pH SORPTION BATCH AND pH CONTROLLED PERMEATE COLUMN TESTS(1)

PARAMETER	4% BENTONITE/ TILL ADMIXTURE				GLACIAL TILL(2) (COMPOSITE NO. 1)						STRATIFIED DRIFT(2) (COMPOSITE NO. 2)					
	pH 3		pH 9		pH 3		pH 6		pH 9		pH 3		pH 6		pH 9	
	BATCH	COLUMN	BATCH	COLUMN	BATCH	COLUMN	BATCH	COLUMN	BATCH	COLUMN	BATCH	COLUMN	BATCH	COLUMN	BATCH	COLUMN
Arsenic	62	>11	1,640	>10	23	>18.2	111	>14.4	1,310	BD(3)	24.0	>15.7	161	>13.9	1,010	BD
Cadmium	5	>11	681	>10	3.4	>18.2	113	>14.4	737	>14.3	2.2	>15.7	143	>13.9	421	>13.3
Chromium	74	>11	113	>10	129	>18.2	BD	BD	257	BD	31	>15.7	BD	BD	168	BD
Copper	7	>11	376	>10	12	>18.2	32	>14.4	353	>14.3	3.5	>15.7	58	>13.9	94	>13.3
Iron	9	5.3	1	BD	4.2	12.4	11	>14.4	1	BD	3.5	4.5	4.4	4.9	1	BD
Lead	129	>11	BD	BD	120	>18.2	BD	>14.4	BD	BD	41	>15.7	BD	>13.9	BD	BD
Manganese	1	<6.3	246	<5.6	1	<8.3	1	<7.4	525	<6.9	1	<8.2	1	<8.4	133	<7.0
Mercury	48	BD	2.5	>10	>145	BD	BD	BD	177	>14.3	>112	BD	BD	BD	189	>13.3
Selenium	BD	BD	>81	>10	BD	BD	1	>14.4	>65	>14.3	BD	BD	BD	>13.9	>50	>13.3
Silver	BD	BD	2.5	>10	BD	BD	1	>14.4	65	>14.3	BD	BD	BD	>13.9	218	>7.0
Zinc	4	5.3	526	>10	2.2	4.4	11	>14.4	273	BD	1	3.6	3.5	9	325	BD
Cyanide	9	-(4)	21	-	14	-	1	-	23	-	7.2	-	1	-	1	-

(1)See Table 3.11 and Tables 3.16 through 3.19 for source of R_d data.

(2)See Appendix C for composition of composite samples.

(3)R_d values reported as "BD" represent solute concentrations which were below the detection limit or which were too low to allow the determination of significant differences in the initial and final leachate concentrations once the leachate had reacted with the sediment sample.

(4)"-" indicates not determined.

TABLE 3.21

COMPARISON OF INITIAL AND FINAL LABORATORY COLUMN TEST PERMEABILITIES WITH FIELD MEASURED PERMEABILITIES

SOIL SAMPLE(1)	COLUMN DESIGNATION	LEACHATE PERMEANT pH	LABORATORY PERMEABILITY @ 20°(2) (m/sec)		FIELD MEASURED PERMEABILITY(3) (m/sec)		LABORATORY LINER PERMEABILITY TESTS(4) (m/sec)
			INITIAL WITH SITE GROUND WATER	FINAL WITH WASTE LEACHATES	VERTICAL	HORIZONTAL	
Glacial Till (Composite No. 1)	I-1	3	5.5×10^{-8}	1.4×10^{-7}	9.4×10^{-7}	2.8×10^{-6}	3.0×10^{-8}
	I-2	6	3.8×10^{-8}	3.4×10^{-7}			
	I-3	9	5.7×10^{-8}	5.6×10^{-7}			
	I-4	9	3.6×10^{-7}	5.7×10^{-7}			
Stratified Drift (Composite No. 2)	J-1	3	1.8×10^{-5}	1.3×10^{-5}	1.3×10^{-5}	1.3×10^{-4}	-(5)
	J-2	6	1.5×10^{-5}	1.2×10^{-5}			
	J-3	9	1.3×10^{-5}	1.3×10^{-5}			
	J-4	9	2.1×10^{-5}	2.1×10^{-5}			
4% Bentonite/Till Admixture	K-1	3	1.0×10^{-10}	1.5×10^{-10}(6)	-	-	6.9×10^{-10}
	K-2	9	1.0×10^{-10}	1.5×10^{-10}(7)			

---

(1) See Appendix C for composition of composite samples.

(2) Permeability calculations based upon final column sample dimensions (Table 3.14). See Appendix F for method of determination.

(3) Golder recommended values from pumping tests (Golder, 1982b).

(4) Permeability determined in a triaxial apparatus for a TP-22 glacial till sample and a four percent bentonite/till admixture; samples assumed fully saturated (Golder, 1981a).

(5) "-" indicates not determined.

(6) Determined at 83.1 percent saturation based upon final moisture content measurements.

(7) Determined at 83.4 percent saturation based upon final moisture content measurements.

TABLE 3.22

COMPARISON OF PRE AND POSTCOLUMN TEST SOIL CHARACTERISTICS

SOIL SAMPLE(1)	COLUMN DESIGNATION	1:1 REACTION pH(2)	NEUTRALIZATION CAPACITY(3) (% $CaCO_3$ EQUIVALENT)
Glacial Till (Composite No. 1)			
Precolumn Test	-	9.15	2.3
Postcolumn Test:			
pH 3 Permeant	I-1	6.86	0.6
pH 6 Permeant	I-2	6.79	0.4
pH 9 Permeant	I-3	7.57	1.2
pH 9 Permeant	I-4	7.62	0.8
Stratified Drift (Composite No. 2)			
Precolumn Test	-	9.80	1.6
Postcolumn Test:			
pH 3 Permeant	J-1	6.60	0.6
pH 6 Permeant	J-2	6.84	0.6
pH 9 Permeant	J-3	7.51	0.8
pH 9 Permeant	J-4	7.57	1.0
4% Bentonite/Till Admixture			
Precolumn Test	-	8.75	0.7
Postcolumn Test:			
pH 3 Permeant	K-1	6.53	0.4
pH 9 Permeant(4)	K-2	7.21	0.8

---

(1) See Appendix C for composition of composite samples.

(2) pH of a 1:1 soil to distilled water mixture at 25°C (Sobek, et al., 1978).

(3) HCl treatment - NaOH titration in accordance with Sobek, et al. (1978).

(4) pH decreased to 6.5 to 7.0 during column test (Table D.5 of Appendix D).

TABLE 3.23

DERIVATION OF THE RETARDATION FACTOR (R_d) FOR ACIDITY MIGRATION IN SATURATED GEOMEDIA

The retardation factor (R_d) for acidity migration in a geomedia can be written as:

$$R_d = 1 + \frac{\text{tons CaCO}_3\text{ neutralization}}{\text{tons CaCO}_3\text{ acidity}} \qquad \text{(a)}$$

when $R_d = 1$, the geomedia processes no neutralization capacity, hence the acid front migrates at the same velocity as groundwater.

Because acidity present in groundwater is usually expressed as a weight per volume of water and the neutralization capacity of the geomedia is expressed as a weight per weight of geomedia, a conversion must be made so that acidity is converted to the same units as the neutralization capacity. Therefore, when the neutralization capacity of the geomedia is expressed as tons of calcium carbonate equivalent per 1,000 tons of geomedia, the acidity present must also be provided as tons per 1,000 tons of geomedia. When water acidity is given as milligrams per liter as calcium carbonate equivalent required to neutralize, the tons of acid in groundwater present within 1,000 tons of geomedia is found by:

$$\frac{1{,}000\text{ tons geomedia}}{\rho\ (\text{kg/m}^3)} \times \frac{1{,}000\text{ kg}}{1\text{ ton}} \times n_e \times \frac{1{,}000\ \ell}{1\text{ m}^3} \times \frac{10^{-9}\text{ tons}}{1\text{ mg}}$$

$$\times \frac{\text{mg CaCO}_3\text{ acidity}}{1\ \ell\text{ water}} = \begin{array}{l}\text{tons CaCO}_3\text{ equivalent}\\ \text{required to neutralize}\\ \text{acidity present}\end{array} \qquad \text{(b)}^{(1)}$$

where: ρ = bulk density (expressed as kg/m^3)
n_e = effective porosity (expressed as ratio)

Incorporating this conversion and separating the bulk density and effective porosity terms yields:

$$R_d = 1 + \left(\frac{\rho}{n_e}\right)\left(\frac{\text{tons CaCO}_3\text{ neutralization}}{1{,}000\text{ tons} \times 1{,}000\text{ kg/ton} \times 1{,}000\ \ell/\text{m}^3 \times 10^{-9}\text{ tons/mg} \times \text{mg}/\ell\text{ CaCO}_3\text{ acidity}}\right) \qquad \text{(c)}$$

simplifying:

$$R_d = 1 + \left(\frac{\rho}{n_e}\right)\left(\frac{\text{tons CaCO}_3\text{ neutralization}}{\text{mg}/\ell\text{ CaCO}_3\text{ acidity}}\right) \qquad \text{(d)}$$

---

(1) If it is desired to add groundwater alkalinity to the neutralization capacity of the geomedia, the tons of calcium carbonate equivalent neutralization in the groundwater present in 1,000 tons of geomedia is found using Equation (b), where the groundwater alkalinity expressed in milligrams per liter as calcium carbonate equivalent is substituted for the acidity value. The tons of groundwater calcium carbonate equivalent neutralization is then added to the tons of geomedia calcium carbonate equivalent neutralization and this value is used in Equation (d).

TABLE 3.24

SUMMARY OF ACIDITY RETARDATION FACTORS

				pH 3 LEACHATE			pH 6 LEACHATE		
SOIL SAMPLE(1)	BULK DENSITY(2) (kg/m^3)	EFFECTIVE POROSITY(2)	NEUTRALIZATION CAPACITY(3) (tons $CaCO_3$ equivalent per 1,000 tons)	AVAILABLE ACIDITY(4) (mg/ℓ $CaCO_3$)	MASS BALANCE ACIDITY RETARDATION FACTOR(5)	COLUMN TEST ACIDITY RETARDATION FACTOR(6)	AVAILABLE ACIDITY(4) (mg/ℓ $CaCO_3$)	MASS BALANCE ACIDITY RETARDATION FACTOR(5)	COLUMN TEST ACIDITY RETARDATION FACTOR(6)
Glacial Till (Composite No. 1)	2,000	0.25	23	3,210	58	>18.2	980	189	7.5
Stratified Drift (Composite No. 2)	1,850	0.30	16	3,210	32	14.2	980	102	5.7
High Carbonate Effervescence Till (Composite No. 3)	2,000	0.25	72	3,210	180	-(7)	980	589	-
4% Bentonite/ Till Admixture	2,000	0.20	7	3,210	23	10.4	980	72	-

(1) See Appendix C for composition of composite samples.

(2) Average value as estimated from existing site data (Golder, 1981b).

(3) HCl treatment - NaOH titration in accordance with Sobek, et al. (1978). Average of duplicate determinations.

(4) Available implies no oxidation of leachate during acidity titration to pH 8.3 (see Appendix D).

(5) See Table 3.23 for method of acidity retardation factor calculation.

(6) Lag of acidity half concentration in comparison to chloride half concentration breakthrough in column test.

(7) "-" indicates sample not tested.

TABLE 3.25

SUMMARY OF POSTCOLUMN TEST ACID NEUTRALIZATION CAPACITY AND COLUMN AVAILABLE ACIDITY

SOIL SAMPLE[1]	COLUMN DESIGNATION	PRECOLUMN TEST NEUTRALIZATION CAPACITY[2] (% $CaCO_3$ EQUIVALENT)	POSTCOLUMN TEST NEUTRALIZATION CAPACITY[2] (% $CaCO_3$ EQUIVALENT)	APPROXIMATE COLUMN DRY WEIGHT[3] (g)	WEIGHT OF CALCIUM CARBONATE EQUIVALENT LOST (g)	TOTAL WEIGHT OF AVAILABLE ACIDITY PASSED THROUGH THE COLUMN[4] (g $CaCO_3$)	TOTAL WEIGHT OF HYDROGEN (pH) PASSED THROUGH THE COLUMN[5] (g $CaCO_3$)
Glacial Till (Composite No. 1) Permeated with pH 3 leachate	I-1	2.3	0.6	1,112	18.9	8.25	0.128
Glacial Till (Composite No. 1) Permeated with pH 6 leachate	I-2	2.3	0.4	1,109	21.1	2.44	0.00013
Stratified Drift (Composite No. 2) Permeated with pH 3 leachate	J-1	1.6	0.6	1,131	11.3	8.34	0.130
Stratified Drift (Composite No. 2) Permeated with pH 6 leachate	J-2	1.6	0.6	1,095	11.0	2.55	0.00013
4% Bentonite/Till Admixture Permeated with pH 3 leachate	K-1	0.7	0.4	952	2.86	5.91	0.092

---

(1) See Appendix C for composition of composite samples.

(2) HCl treatment - NaOH titration in accordance with Sobek, et al. (1978).

(3) Based upon column dry density (Appendix F) and column volume (Table 3.14).

(4) Based upon total seepage volume from column (Table 3.14) and representative available acidity source concentrations (Figures 3-1 through 3-5).

(5) Based upon total seepage volume from column (Table 3.14) and leachate permeant pH.

TABLE 3.26

SUMMARY OF LEACHATE ADDED TO SOIL RATIOS FOR THE COLUMN AND TITRATION TESTS

SOIL SAMPLE(1)	LEACHATE TITRANT pH	ADDED LEACHATE/SOIL RATIO TO REACH pH 5		ADDED LEACHATE/SOIL RATIO TO REACH pH 6	
		COLUMN TEST(2)	TITRATION TEST(3)	COLUMN TEST(2)	TITRATION TEST(3)
Glacial Till (Composite No. 1)	3	0.86	0.70	0.13	0.12
Stratified Drift (Composite No. 2)	3	0.91	0.60	0.40	0.12
4% Bentonite/Till Admixture	3	1.24	0.84	0.66	0.16
Glacial Till (Composite No. 1)	6	-(4)	-	0.97	0.70
Stratified Drift (Composite No. 2)	6	-	-	0.86	2.1

(1) See Appendix C for composition of composite samples.

(2) Calculated using data from Figures 3-1 through 3-5 and Table 3.14 (milliliters of leachate per gram of soil).

(3) Calculated using data from Figure 3-11 or 3-12 (milliliters of leachate per gram of soil).

(4) "-" indicates cannot be determined.

TABLE 4.1

APPROXIMATE MIGRATION TIME FOR CHEMICAL PARAMETERS AS RELATED TO SOIL ATTENUATION

CHEMICAL PARAMETERS RETARDATION FACTOR (R_d)	YEARS TO REACH $C/C_o = 0.5$(1)			
	BASE OF MWDF LINER	BASE OF GLACIAL TILL	COMPLIANCE BOUNDARY IN STRATIFIED DRIFT(2)	TOP OF LINER TO COMPLIANCE BOUNDARY(2)
1	4	134	50	188
5	20	669	250	940
10	39	1,338	500	1,880
25	98	3,345	1,250	4,700
50	195	6,690	2,500	9,400
100	390	13,380	5,000	18,800

(1) Approximate years to reach half concentration of source for probable MWDF site soil conditions, as presented in Sections 4.2 and 4.3. Calculation assumes fully saturated conditions and a constant source concentration above each soil unit; i.e., soil units are not connected. Calculation ignores dilution, dispersion, and variation in source concentrations. Calculation ignores dilution, dispersion, and variation in source concentration. Therefore, time values shown are considered to be more conservative than expected for the design conditions of the probable MWDF site operations.

(2) 366 meters (1,200 feet).

TABLE 4.2

LEACHATE CHEMISTRY, REQUIRED DILUTION BEFORE THE 366 METER COMPLIANCE BOUNDARY, AND ATTENTUATION CHARACTERISTICS OF THE GLACIAL TILL

PARAMETER	pH 3.0 SPIKED TAILINGS LEACHATE				pH 6.0 SPIKED TAILINGS LEACHATE				pH 9.0 SPIKED TAILINGS LEACHATE				U.S. EPA PRIMARY AND SECONDARY DRINKING WATER STANDARDS(5) (mg/ℓ)
	C(1) (mg/ℓ)	C/DW(2)	R_d		C(1) (mg/ℓ)	C/DW(2)	R_d		C(1) (mg/ℓ)	C/DW(2)	R_d		
			BATCH(3)	COLUMN(4)			BATCH(3)	COLUMN(4)			BATCH(3)	COLUMN(4)	
Filterable Residue	5,710	11.4	–(6)	1	5,140	10.3	–	1	3,430	6.9	–	1	500
Chloride	71	0.28	–	1	310	1.24	–	1	340	1.4	–	1	250
Fluoride	0.23	0.16	–	>8.3	2.3	1.6	–	>14.4	7.6	5.4	–	>14.3	1.4-7.4
Nitrate-Nitrogen	18	1.8	–	>18.2	6.6	0.7	–	<7.4	2.3	0.2	–	6.9	10.0
Sulfate	6,000	24	–	1	3,400	13.6	–	1	2,300	9.2	–	1	250
Arsenic	6.8	136	23	>18.2	0.84	16.8	111	>14.4	0.091	1.8	1,310	BD	0.05
Barium	0.2	0.2	–	BD(7)	0.03	0.03	–	BD	0.4	0.4	–	BD	1.0
Cadmium	2.3	230	3.4	>18.2	0.83	83	113	>14.4	0.41	41	737	>14.3	0.01
Chromium	2.6	52	129	>18.2	0.06	1.2	BD	BD	0.2	4.0	257	BD	0.05
Copper	130	130	12	>18.2	4.5	4.5	32	>14.4	7.7	7.7	353	>14.3	1.0
Iron	1,456	4,853	4.2	12.4	730	2,433	11	>14.4	1.6	5.3	1	BD	0.3
Lead	4.0	80	120	>18.2	0.22	4.4	BD	>14.4	0.08	1.6	BD	BD	0.05
Manganese	49	980	1	<8.3	43	860	1	<7.4	3.4	68	525	<6.9	0.05
Mercury	0.007	3.5	>145	BD	0.019	9.5	BD	BD	0.150	75	177	>14.3	0.002
Selenium	0.07	7	BD	BD	0.10	10	1	>14.4	0.21	21	>65	>14.3	0.01
Silver	0.001	0.02	BD	BD	0.033	0.66	1	>14.4	0.19	3.8	65	>14.3	0.05
Zinc	550	110	2.2	4.4	200	40	11	>14.4	0.64	0.13	273	BD	5.0

(1) Highest representative leachate concentration (Table 3.5).

(2) Highest representative leachate concentration (C) divided by the U.S. EPA Drinking Water Standard (DW); dilution ratio required to reach drinking water standard.

(3) Retardation factors determined by constant pH sorption batch test using the glacial till composite Sample No. 1 (Table 3.11).

(4) Retardation factors determined from column attenuation test results (Tables 3.15 and 3.17 through 3.19).

(5) U.S. EPA (1975), 40 CFR, Part 141 and U.S. EPA (1979), 40 CFR, Part 143.

(6) "–" indicates R_d not determined.

(7) R_d values reported as "BD" represent soluble metal concentrations which were below the detection limit before the leachate was allowed to react with the glacial till or which were to low to allow the determination of significant changes in concentration as a result of the interaction of the leachate with the glacial till.

DRAWN BY	RGN	4-27-82
CHECKED BY	MCF	11/29/82
APPROVED BY	MJT	11.29.82
DRAWING NUMBER	RM81-444-A20	

SURVEY LOCATIONS

G41-H9	117,300 N	2,284,700 E
G41-G13	115,260 N	2,284,725 E
G41-H18b	111,400 N	2,285,100 E
G41-K21a	109,400 N	2,286,200 E

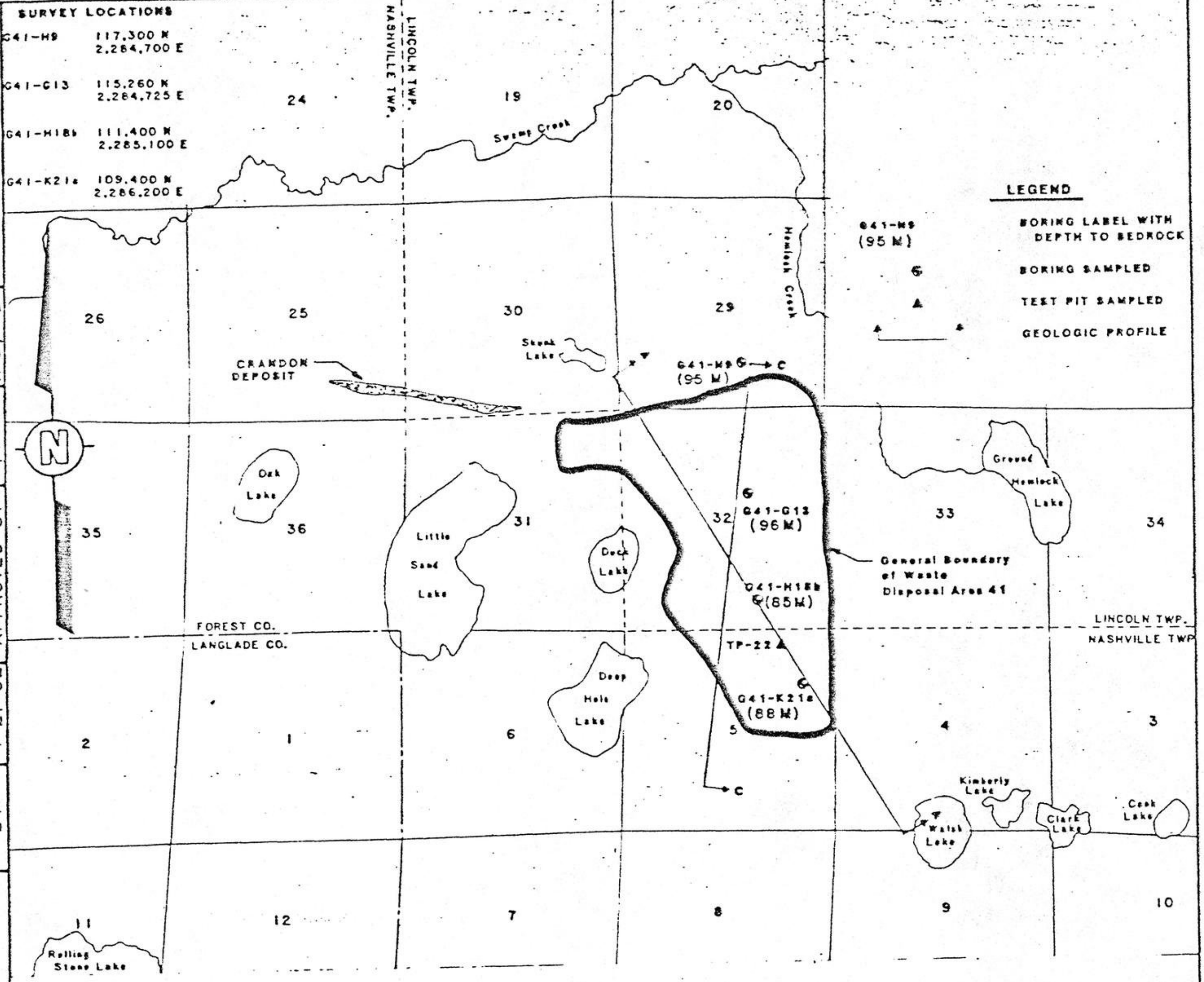


FIGURE 2-1

SOIL SAMPLING & GEOLOGIC PROFILE LOCATIONS RELATIVE TO WASTE DISPOSAL AREA 41

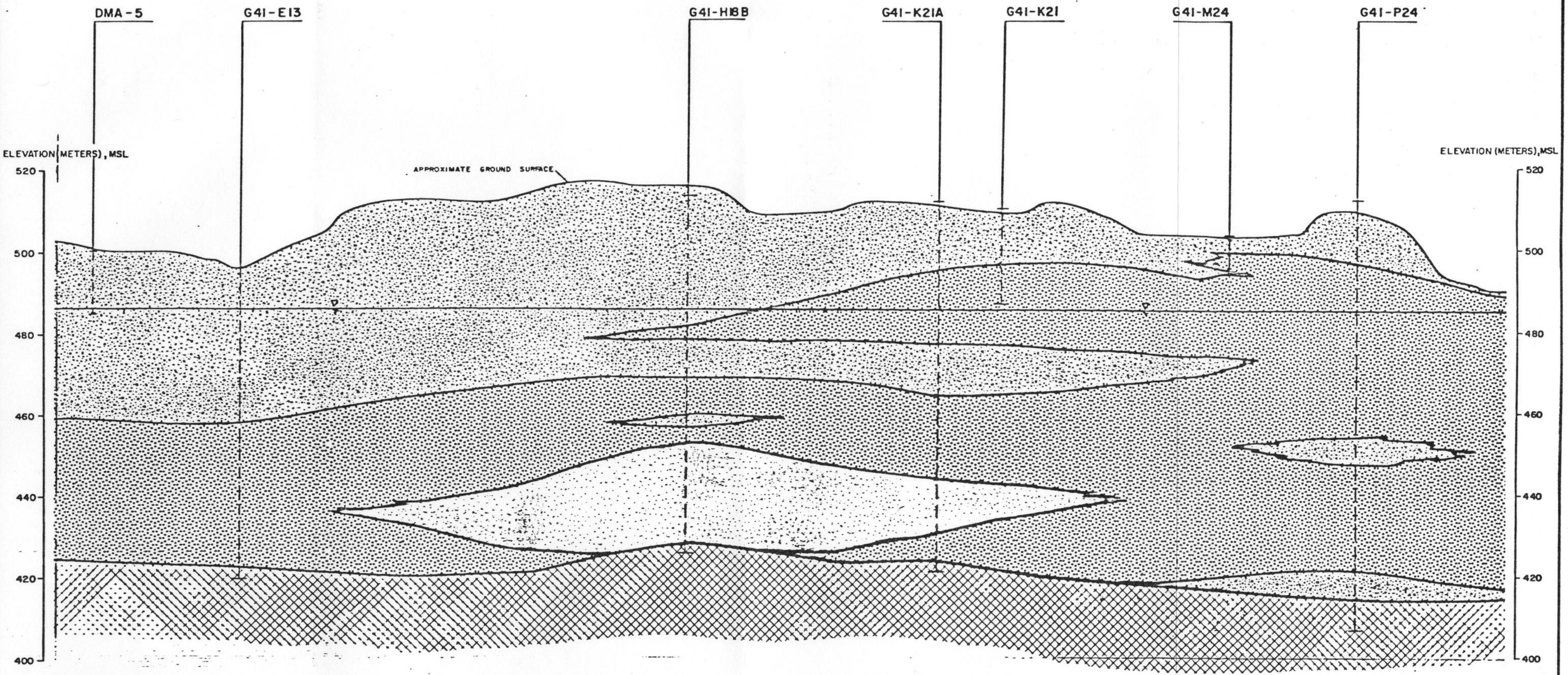
PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

REFERENCES:
EXXON MINERALS COMPANY

3B	DRAWN BY	RGN 4-27-82	CHECKED BY	11/29/82
			APPROVED BY	11.29.82
DRAWING NUMBER	RM81-444-B15			



0 50 100 200 300

HORIZONTAL SCALE IN METERS
VERTICAL EXAGERATION : 10 x

NOTES

1. PROFILE SECTION LOCATIONS SHOWN ON BORING AND PROFILE SECTION LOCATION PLAN, FIGURE 2-1.
2. GROUNDWATER LEVEL PROFILE FROM GROUNDWATER POTENTIOMETRIC CONTOURS, GOLDER ASSOCIATES, DRAWING NO. 050-1-81111.
3. BEDROCK PROFILE FROM BEDROCK CONTOURS, GOLDER ASSOCIATES, DRAWING NO. 050-1-80920.
4. THIS PROFILE IS FOR ILLUSTRATIVE PURPOSES ONLY. THE DISTRIBUTION OF THE GLACIAL MATERIALS HAS BEEN INFERRED FROM THE DATA FROM THE TEST BORINGS SHOWN ON THIS SECTION, TEST BORINGS FROM THE GENERAL SITE AREA, AND TRENDS IMPLIED FROM THE GLACIAL HISTORY AND BORING DATA. THIS ACTUAL DISTRIBUTION OF MATERIALS MAY VARY FROM THAT SHOWN.
5. SAMPLE COMPOSITE SYMBOLS MAY BE PICTURED IN WRONG GEOLOGIC HORIZON DUE TO SURFACE BORING LOCATION NOT EXACTLY CORRELATING WITH GEOLOGIC SECTION DEPICTED; COMPOSITE SAMPLE DEPTHS ARE TRUE REPRESENTATIONS.

REFERENCE:
GOLDER ASSOCIATES, DRAWING NO. 050-1-80911

LEGEND

GEOLOGICAL DEPOSIT SYMBOLS

- ▩ WETLAND AND MARSH
- ☐ LACUSTRINE SEDIMENTS AND FINE GRAINED STRATIFIED DRIFT
- ▒ COARSE GRAINED STRATIFIED DRIFT
- ░ TILL
- ▨ BEDROCK
- INTERPRETED STRATA BOUNDARIES
- STRATA BOUNDARIES UNKNOWN

COMPOSITE SAMPLE NO. 1, LOW CARBONATE GLACIAL TILL
COMPOSITE SAMPLE NO. 2, STRATIFIED DRAFT
COMPOSITE SAMPLE NO. 3, HIGH CARBONATE GLACIAL TILL

G41-H18B
GROUND SURFACE AT BORING LOCATION
BOREHOLE ON LINE OF SECTION
BOTTOM OF BOREHOLE

DMA-5
GROUND SURFACE AT BORING LOCATION
BOREHOLE OFF LINE OF SECTION
BOTTOM OF BOREHOLE

GROUNDWATER LEVEL

FIGURE 2-2

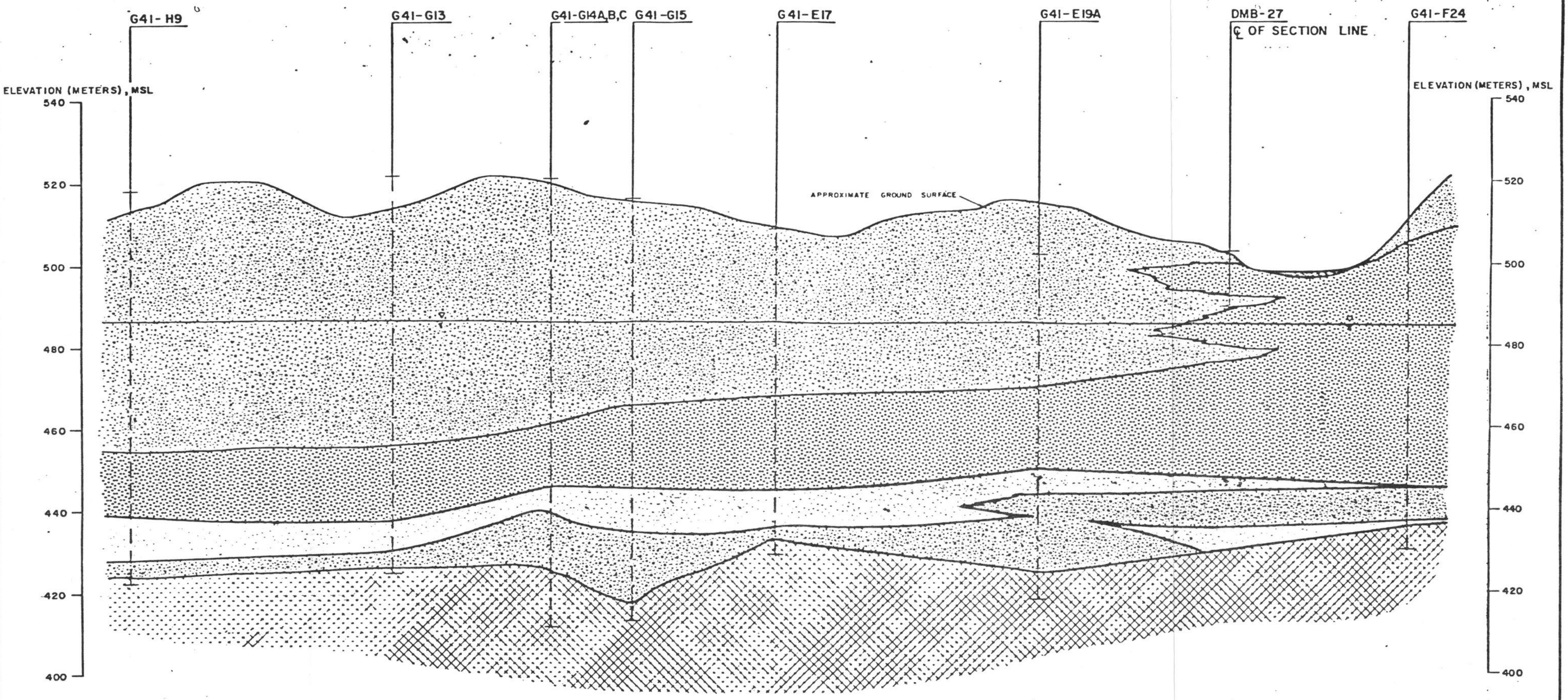
GEOLOGIC PROFILES
SECTION A-A
WITH COMPOSITE SAMPLE LOCATIONS

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

4B	DRAWN BY	RGN	CHECKED BY	LR	11/29/82	DRAWING NUMBER	RM81-444-B16
		4-27-82	APPROVED BY	MJT	11-29-82		



NOTES

1. SEE FIGURE 2-2 FOR GEOLOGIC LEGEND AND GENERAL NOTES.
2. SAMPLE COMPOSITE SYMBOLS MAY BE PICTURED IN WRONG GEOLOGIC HORIZON DUE TO SURFACE BORING LOCATION NOT EXACTLY CORRELATING WITH GEOLOGIC SECTION DEPICTED; COMPOSITE SAMPLE DEPTHS ARE TRUE REPRESENTATIONS

LEGEND

COMPOSITE SAMPLE NO. 1, LOW CARBONATE GLACIAL TILL
COMPOSITE SAMPLE NO. 2, STRATIFIED DRIFT
COMPOSITE SAMPLE NO. 3, HIGH CARBONATE GLACIAL TILL

FIGURE 2-3

GEOLOGIC PROFILES
SECTION C-C
WITH COMPOSITE SAMPLE LOCATIONS

PREPARED FOR

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D'APPOLONIA

REFERENCE:
GOLDER ASSOCIATES, DRAWING NO. 050-1-80913

DRAWN BY	ACS	CHECKED BY		11/29/82	DRAWING NUMBER	RM81-444-A21
	7-19-82	APPROVED BY	MJT	11.29.82		

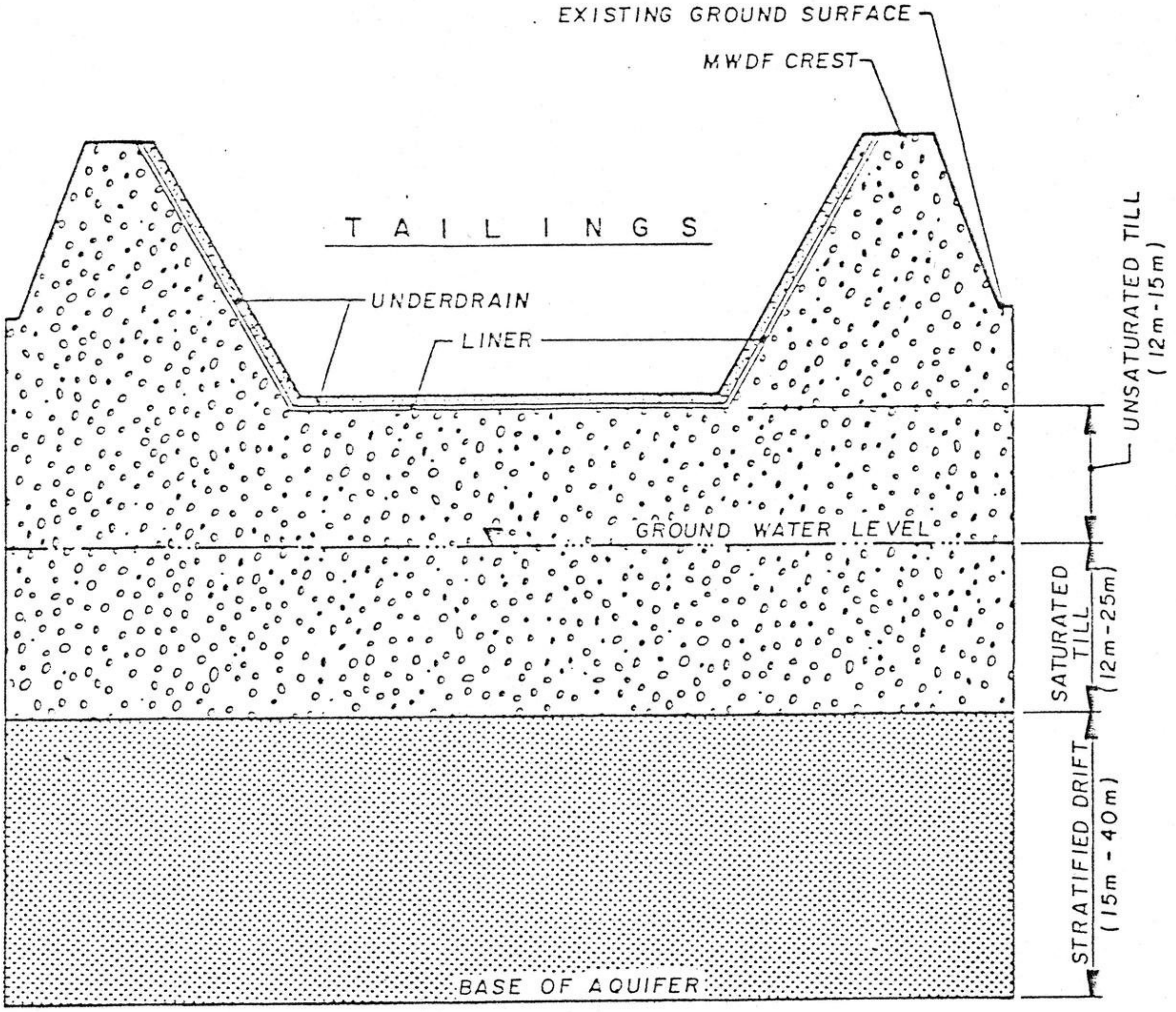


FIGURE 2-4

GENERALIZED VERTICAL CROSS SECTION OF MWDF TAILING POND AND UNDERLYING SOILS

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

(NOT TO SCALE)

DRAWN BY RGN 4-29-82
CHECKED BY 11/29/82
APPROVED BY 11-29-82
DRAWING NUMBER RM81-444-B25

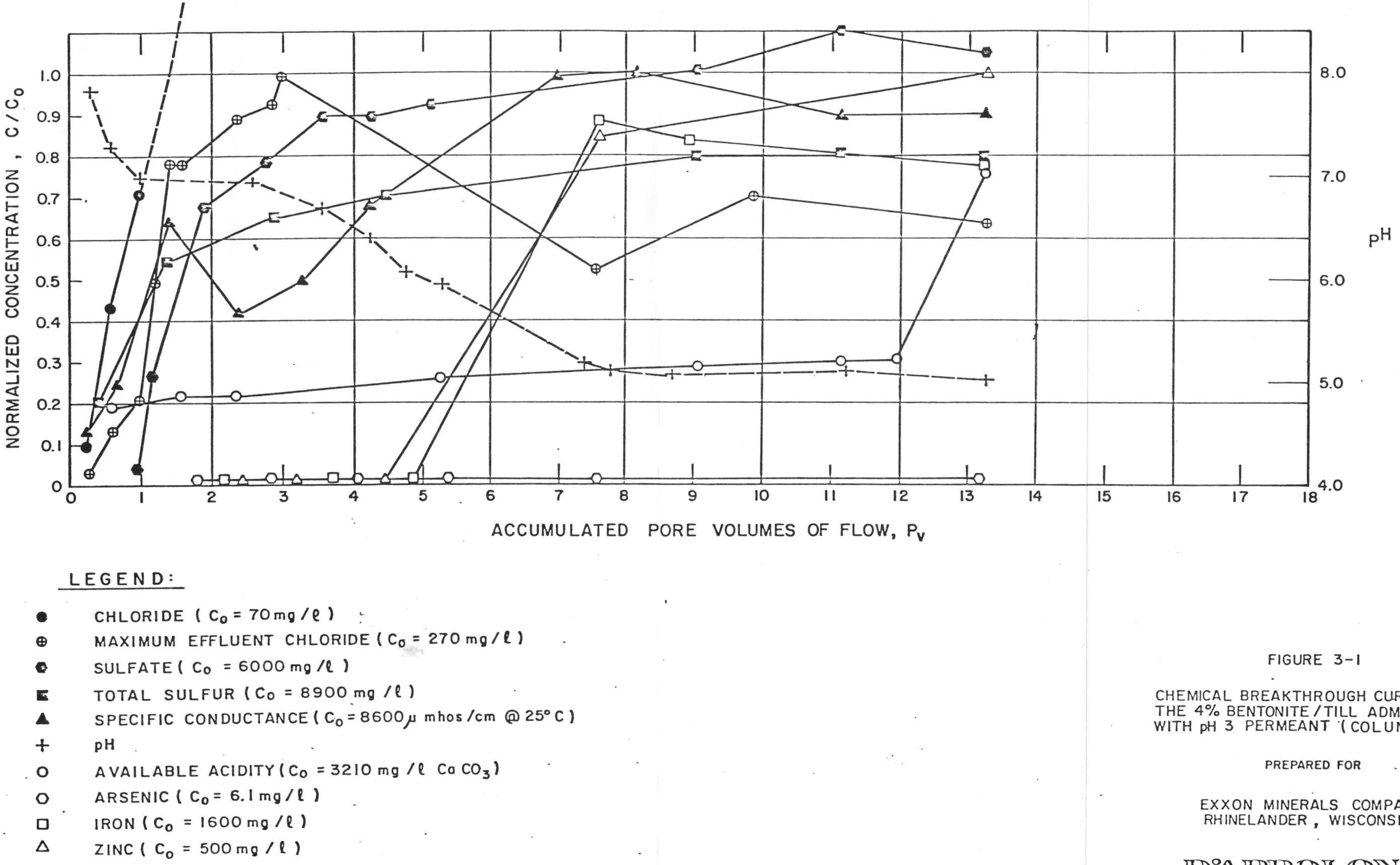


FIGURE 3-1

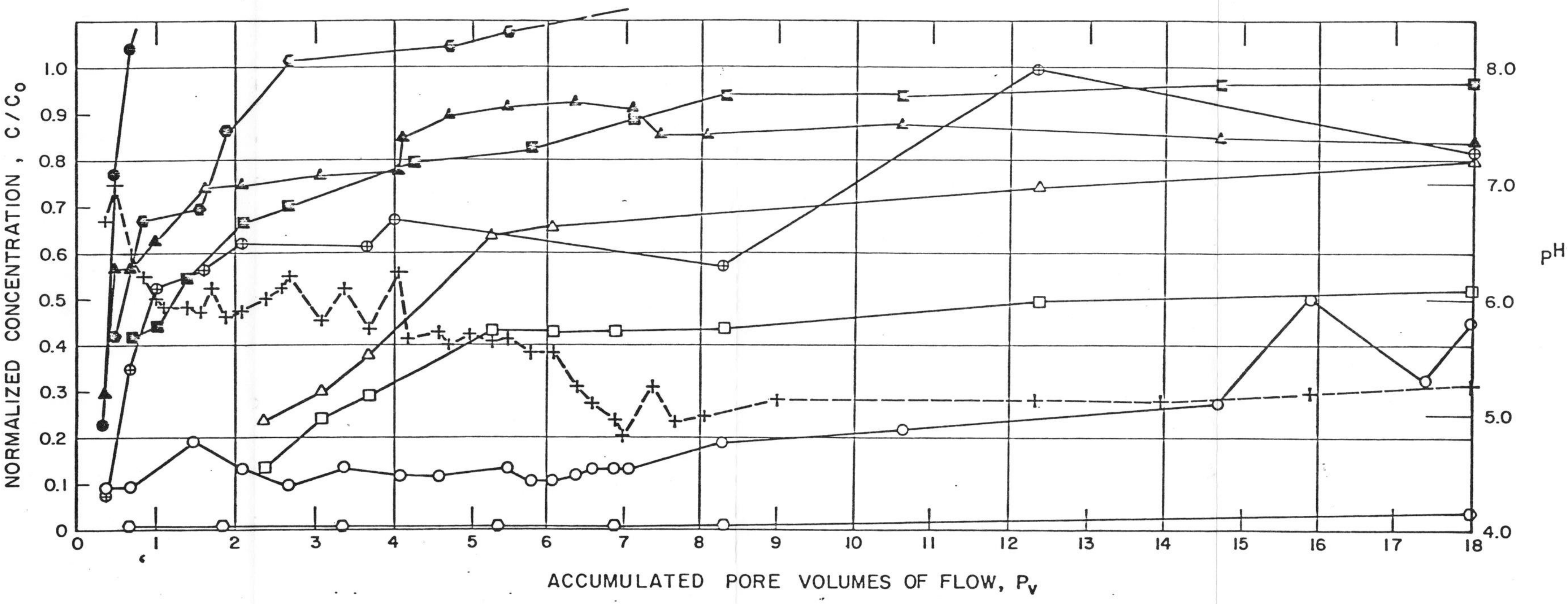
CHEMICAL BREAKTHROUGH CURVE FOR THE 4% BENTONITE / TILL ADMIXTURE WITH pH 3 PERMEANT (COLUMN K-1)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER , WISCONSIN

D'APPOLONIA

DRAWN BY RGN 4-28-82 | CHECKED BY 11/29/82 | APPROVED BY 11/29/82 | DRAWING NUMBER RM81-444-B17



LEGEND:

- ● CHLORIDE (C_o = 70 mg / ℓ)
- ⊕ MAXIMUM EFFLUENT CHLORIDE (C_o = 210 mg / ℓ)
- ◐ SULFATE (C_o = 6000 mg / ℓ)
- ◧ TOTAL SULFUR (C_o = 8900 mg / ℓ)
- ▲ SPECIFIC CONDUCTANCE (C_o = 8600 μ mhos / cm @ 25° C)
- + pH
- ○ AVAILABLE ACIDITY (C_o = 3210 mg / ℓ $CaCO_3$)
- ⬡ ARSENIC (C_o = 6.1 mg / ℓ)
- □ IRON (C_o = 1600 mg / ℓ)
- △ ZINC (C_o = 500 mg / ℓ)

FIGURE 3-2

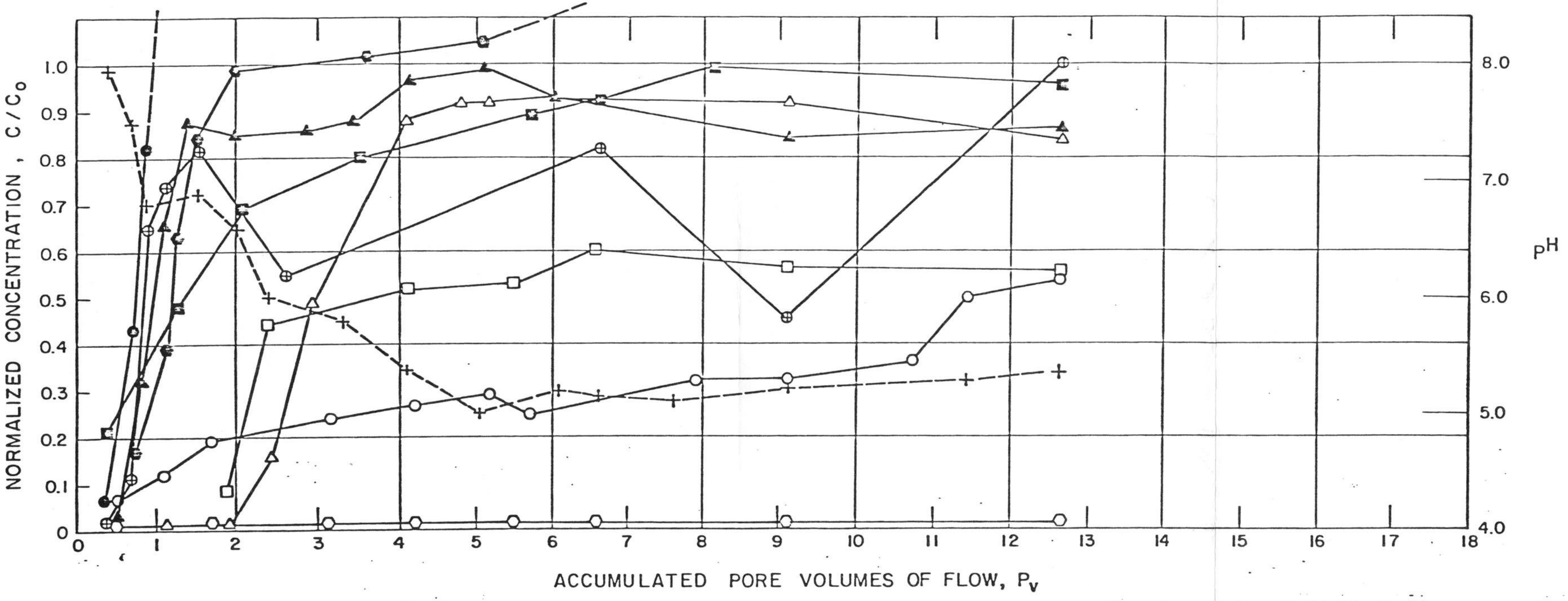
CHEMICAL BREAKTHROUGH CURVE FOR
THE GLACIAL TILL
WITH pH 3 PERMEANT (COLUMN I-1)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER , WISCONSIN

D'APPOLONIA

DRAWN BY RGN 4-28-82 | CHECKED BY | APPROVED BY M J T 11-29-82 | DRAWING NUMBER RM81-444-B2



LEGEND:

- ● CHLORIDE (C_0 = 70 mg / ℓ)
- ⊕ MAXIMUM EFFLUENT CHLORIDE (C_0 = 260 mg / ℓ)
- ● SULFATE (C_0 = 6000 mg / ℓ)
- ■ TOTAL SULFUR (C_0 = 8900 mg / ℓ)
- ▲ SPECIFIC CONDUCTANCE (C_0 = 8600 μ mhos / cm @ 25° C)
- + pH
- ○ AVAILABLE ACIDITY (C_0 = 3210 mg / ℓ $CaCO_3$)
- ○ ARSENIC (C_0 = 6.1 mg / ℓ)
- □ IRON (C_0 = 1600 mg / ℓ)
- △ ZINC (C_0 = 500 mg / ℓ)

FIGURE 3-3

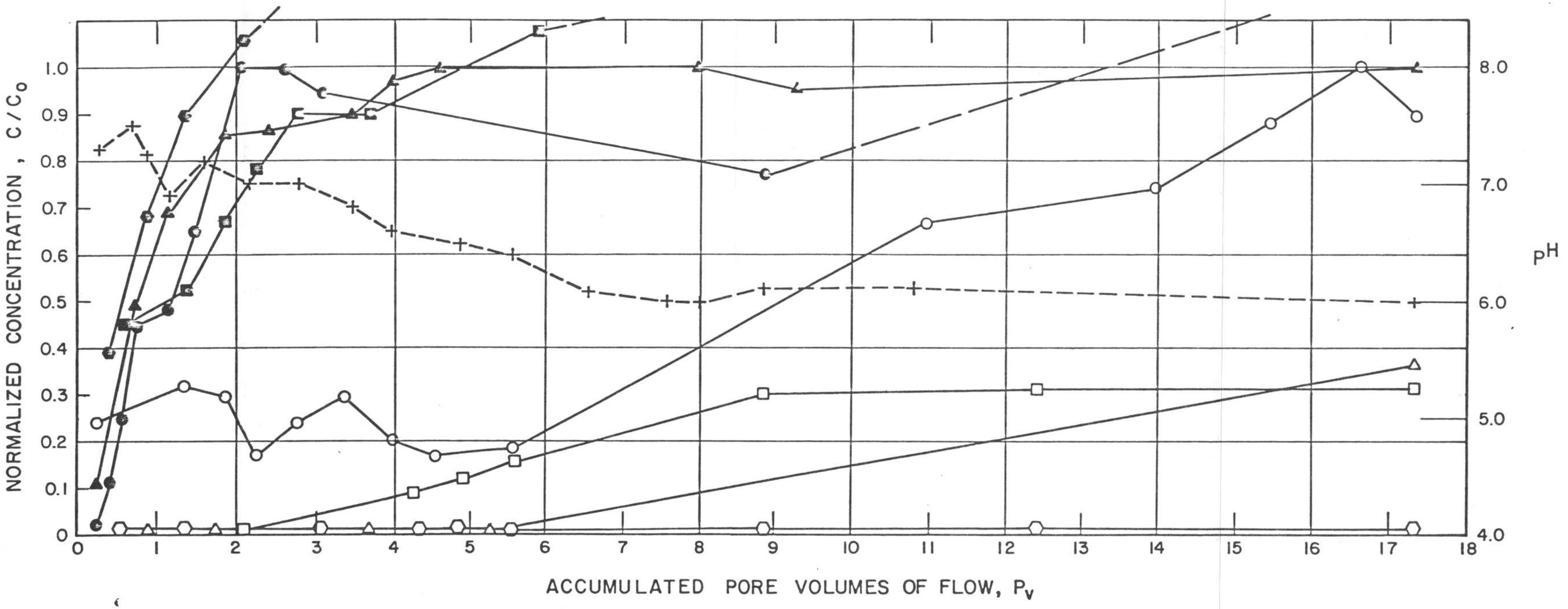
CHEMICAL BREAKTHROUGH CURVE FOR
THE STRATIFIED DRIFT
WITH pH 3 PERMEANT (COLUMN J-1)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

DRAWN BY RGN 4-28-82 | CHECKED BY 11/29/82 | APPROVED BY MJT 11-29-82 | DRAWING NUMBER RM81-444-B18



LEGEND:

- ● CHLORIDE (C_0 = 310 mg / ℓ)
- ⬢ SULFATE (C_0 = 3100 mg / ℓ)
- ■ TOTAL SULFUR (C_0 = 6400 mg / ℓ)
- ▲ SPECIFIC CONDUCTANCE (C_0 = 6750 μ mhos / cm @ 25° C)
- \+ pH
- ○ AVAILABLE ACIDITY (C_0 = 980 mg / ℓ $CaCO_3$)
- ⬡ ARSENIC (C_0 = 0.2 mg / ℓ)
- □ IRON (C_0 = 610 mg / ℓ)
- △ ZINC (C_0 = 140 mg / ℓ)

FIGURE 3-4

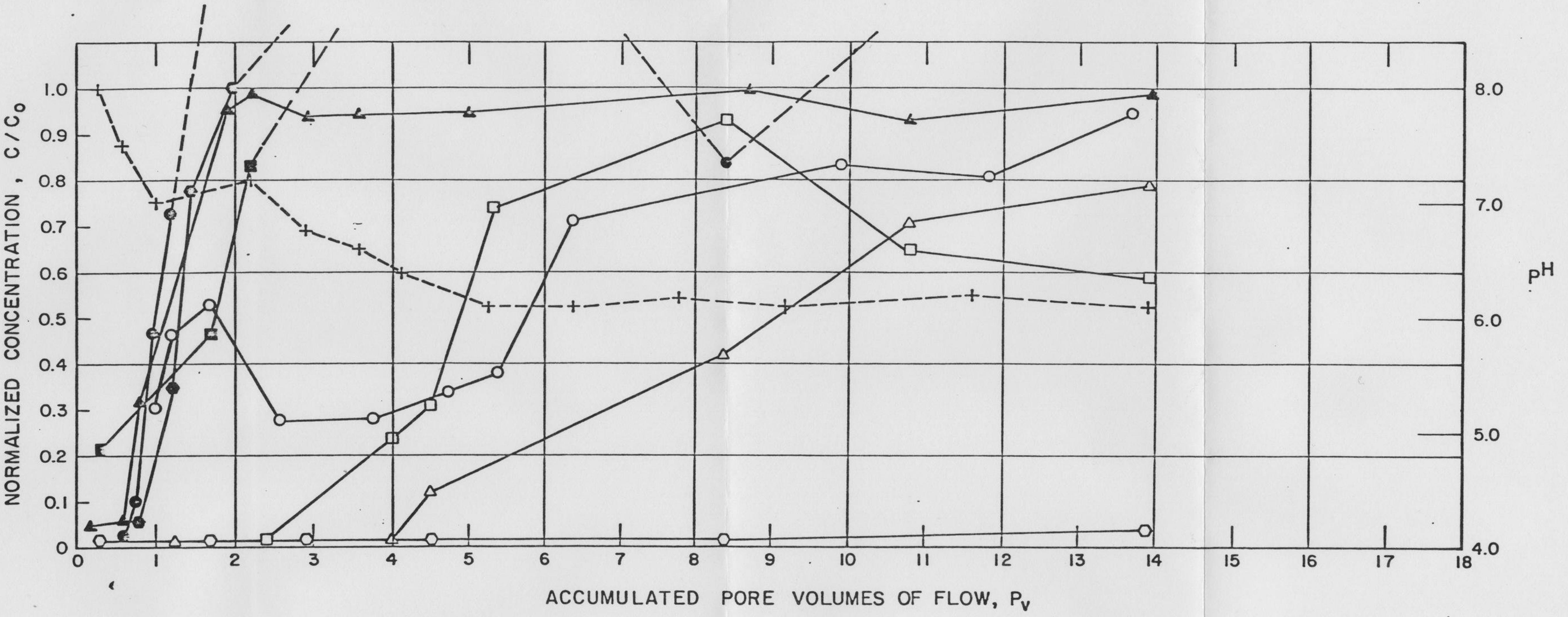
CHEMICAL BREAKTHROUGH CURVE FOR THE GLACIAL TILL WITH pH 6 PERMEANT (COLUMN I-2)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER , WISCONSIN

D'APPOLONIA

DRAWN BY	RGN	CHECKED BY	FJN	11/29/82	DRAWING NUMBER	RM81-444-B22
	4-28-82	APPROVED BY	MST	11-29-82		



LEGEND:

- ● CHLORIDE (C_0 = 310 mg / l)
- ⬣ SULFATE (C_0 = 3100 mg / l)
- ■ TOTAL SULFUR (C_0 = 6400 mg / l)
- ▲ SPECIFIC CONDUCTANCE (C_0 = 6750 μ mhos / cm @ 25° C)
- + pH
- ○ AVAILABLE ACIDITY (C_0 = 980 mg / l $CaCO_3$)
- ⬡ ARSENIC (C_0 = 0.2 mg / l)
- □ IRON (C_0 = 610 mg / l)
- △ ZINC (C_0 = 140 mg / l)

FIGURE 3-5

CHEMICAL BREAKTHROUGH CURVE FOR
THE STRATIFIED DRIFT
WITH pH 6 PERMEANT (COLUMN J-2)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER , WISCONSIN

D'APPOLONIA

DRAWN BY	RGN 4-29-82	CHECKED BY	RCW	11/29/82	DRAWING NUMBER	RM81-444-B26
		APPROVED BY	MJT	11-29-82		

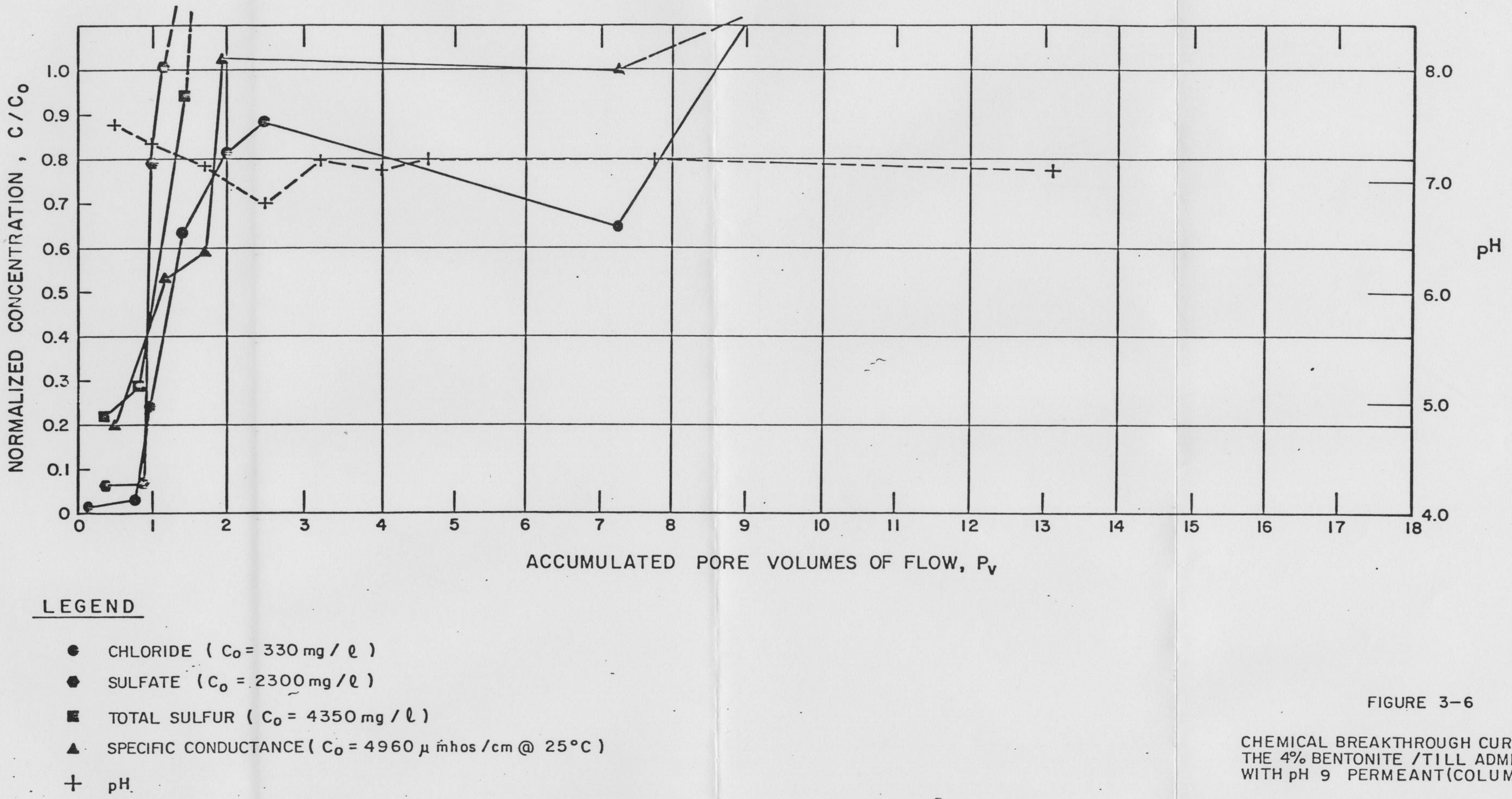


FIGURE 3-6

CHEMICAL BREAKTHROUGH CURVE FOR
THE 4% BENTONITE / TILL ADMIXTURE
WITH pH 9 PERMEANT (COLUMN K-2)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER , WISCONSIN

D'APPOLONIA

19 1253 HERCULENE, A&B SMITH CO., PGH., PA

DRAWN BY RGN 4-28-82 CHECKED BY 11/29/82 APPROVED BY MJT 11/29/82 DRAWING NUMBER RM81-444-B19

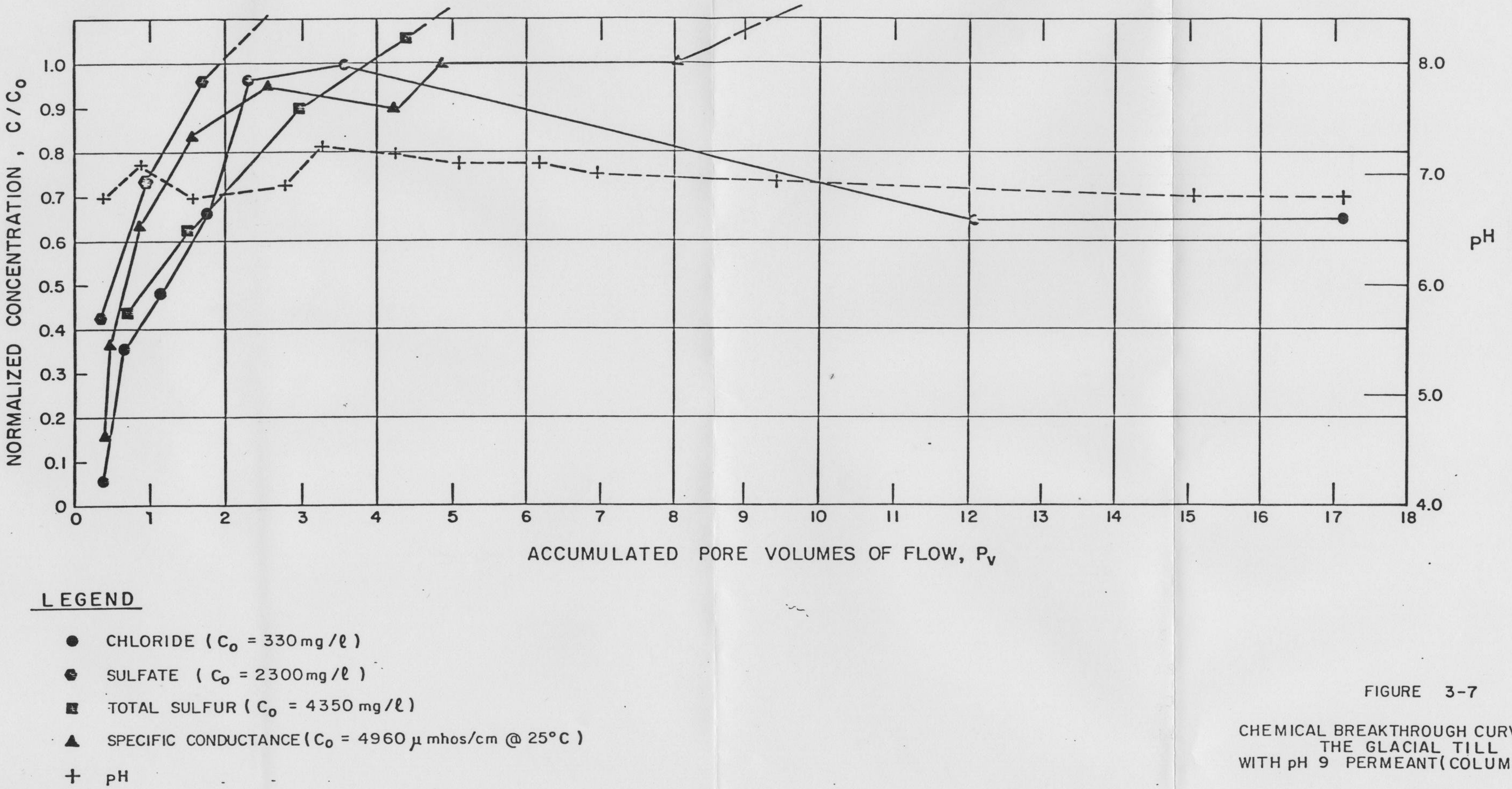


FIGURE 3-7

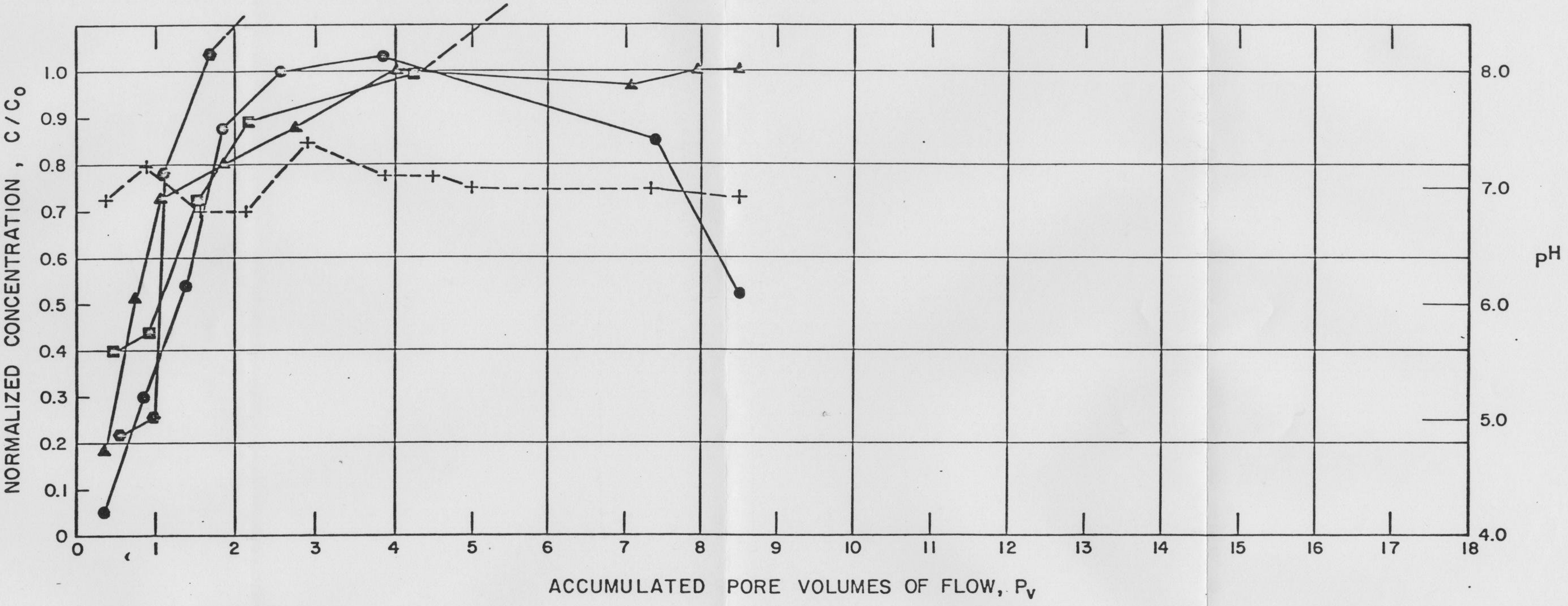
CHEMICAL BREAKTHROUGH CURVE FOR THE GLACIAL TILL WITH pH 9 PERMEANT (COLUMN I-3)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

DRAWN BY RGN 4-28-82
CHECKED BY 11/29/82
APPROVED BY 11-29-82
DRAWING NUMBER RM81-444-B20



LEGEND

- ● CHLORIDE (C_o = 330 mg / ℓ)
- ◐ SULFATE (C_o = 2300 mg / ℓ)
- ⊏ TOTAL SULFUR (C_o = 4350 mg / ℓ)
- ▲ SPECIFIC CONDUCTANCE (C_o = 4960 μ mhos / cm @ 25° C)
- + pH

FIGURE 3-8

CHEMICAL BREAKTHROUGH CURVE FOR
THE GLACIAL TILL
WITH pH 9 PERMEANT (COLUMN I-4)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

DRAWN BY	RGN	CHECKED BY		11/29/82	DRAWING NUMBER	RM81-444-B23
	4-28-82	APPROVED BY	MJT	11.29.82		

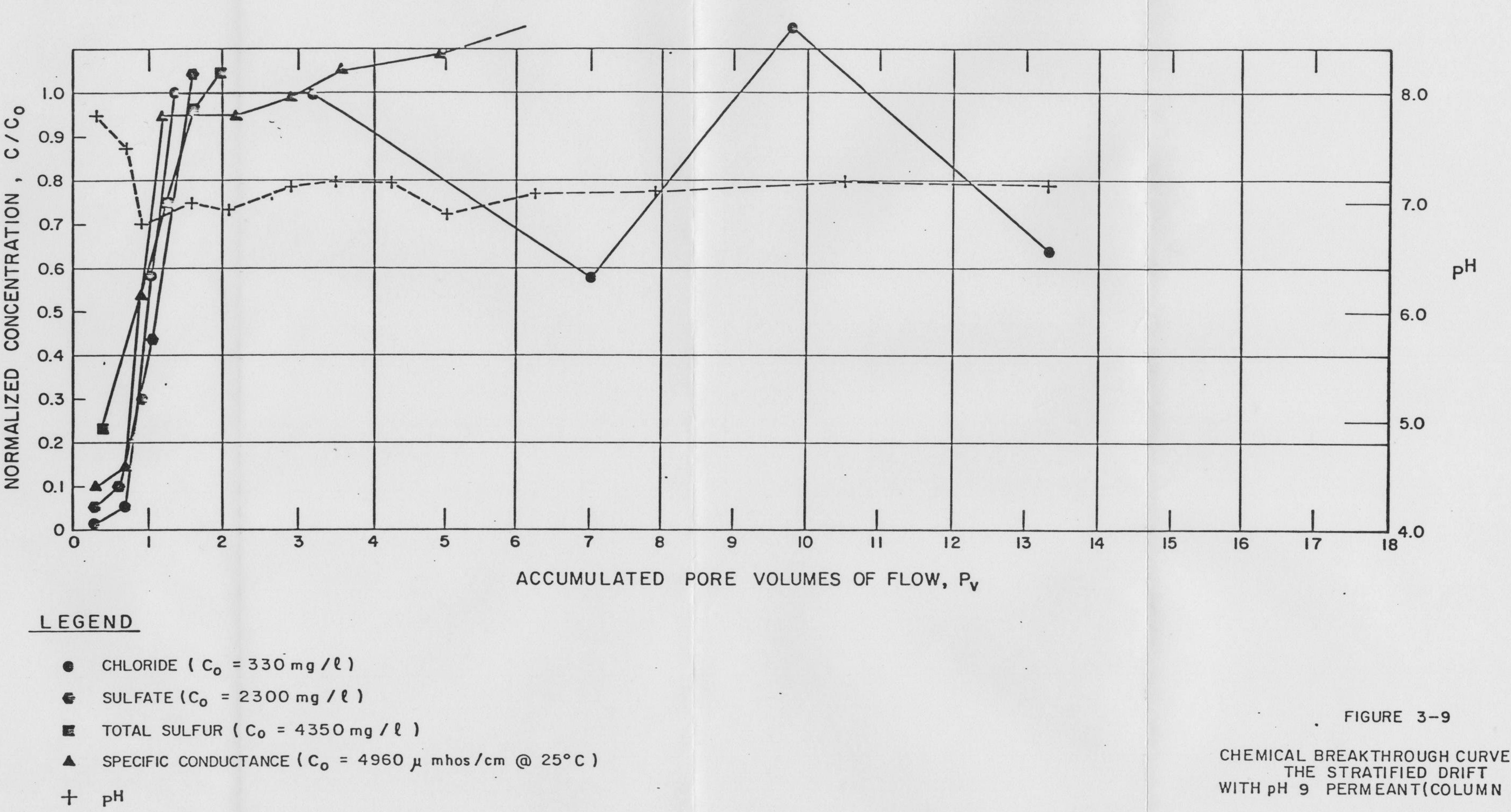


FIGURE 3-9

CHEMICAL BREAKTHROUGH CURVE FOR
THE STRATIFIED DRIFT
WITH pH 9 PERMEANT (COLUMN J-3)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

DRAWN BY RGN 4-28-82
CHECKED BY 11/29/82
APPROVED BY 11-29-82
DRAWING NUMBER RM81-444-B24

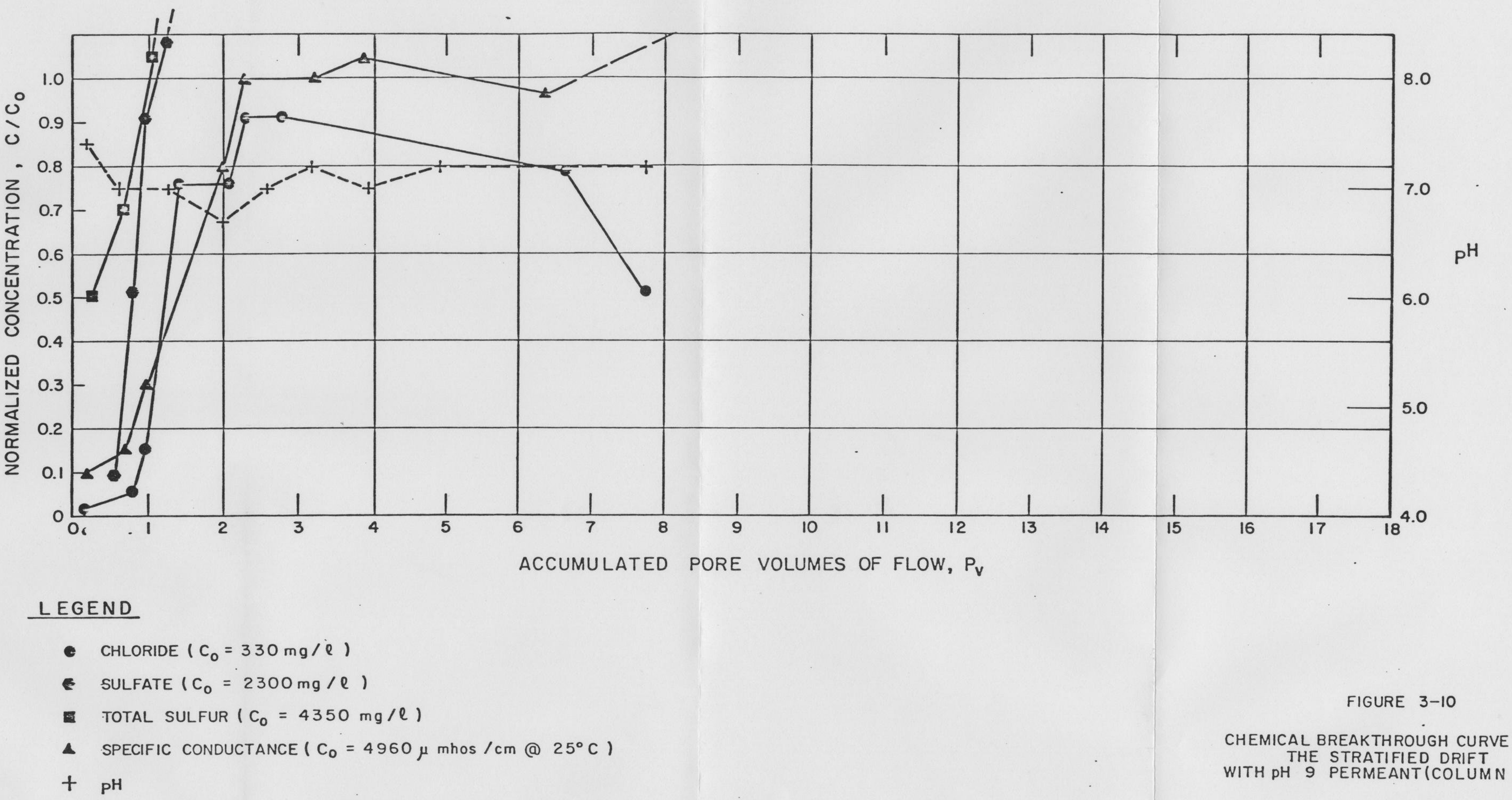


FIGURE 3-10

CHEMICAL BREAKTHROUGH CURVE FOR
THE STRATIFIED DRIFT
WITH pH 9 PERMEANT (COLUMN J-4)

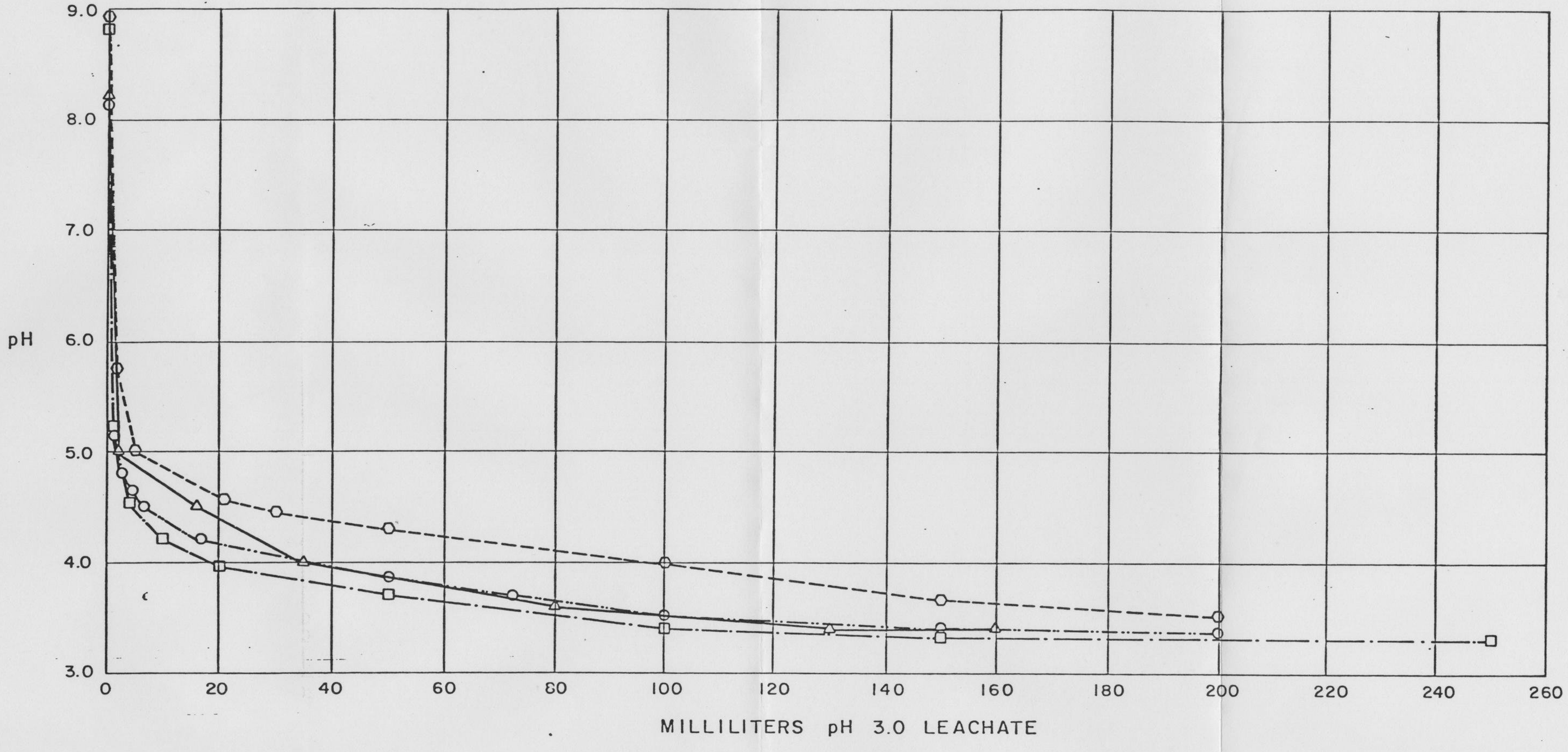
PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER , WISCONSIN

D'APPOLONIA

19 1253 HERCULENE. A&B SMITH CO., PGH., PA

DRAWN BY ACS 5-3-82
CHECKED BY 11/10/82
APPROVED BY MST 11-29-82
DRAWING NUMBER RM81-444-B27



LEGEND:

- ○ GLACIAL TILL (COMPOSITE SAMPLE No. 1)
- ☐ STRATIFIED DRIFT (COMPOSITE SAMPLE No. 2)
- ⬡ HIGH $CaCO_3$ GLACIAL TILL (COMPOSITE No. 3)
- △ 4 % BENTONITE/ TILL ADMIXTURE

NOTE: SOIL MIXTURES AT START OF TITRATIONS WERE 2.5 MILLILITER OF DISTILLED WATER TO 2.5 GRAMS OF SOIL

FIGURE 3-11

TITRATION CURVES FOR pH 3.0 SYNTHETIC TAILINGS LEACHATE AND COMPOSITE SAMPLES

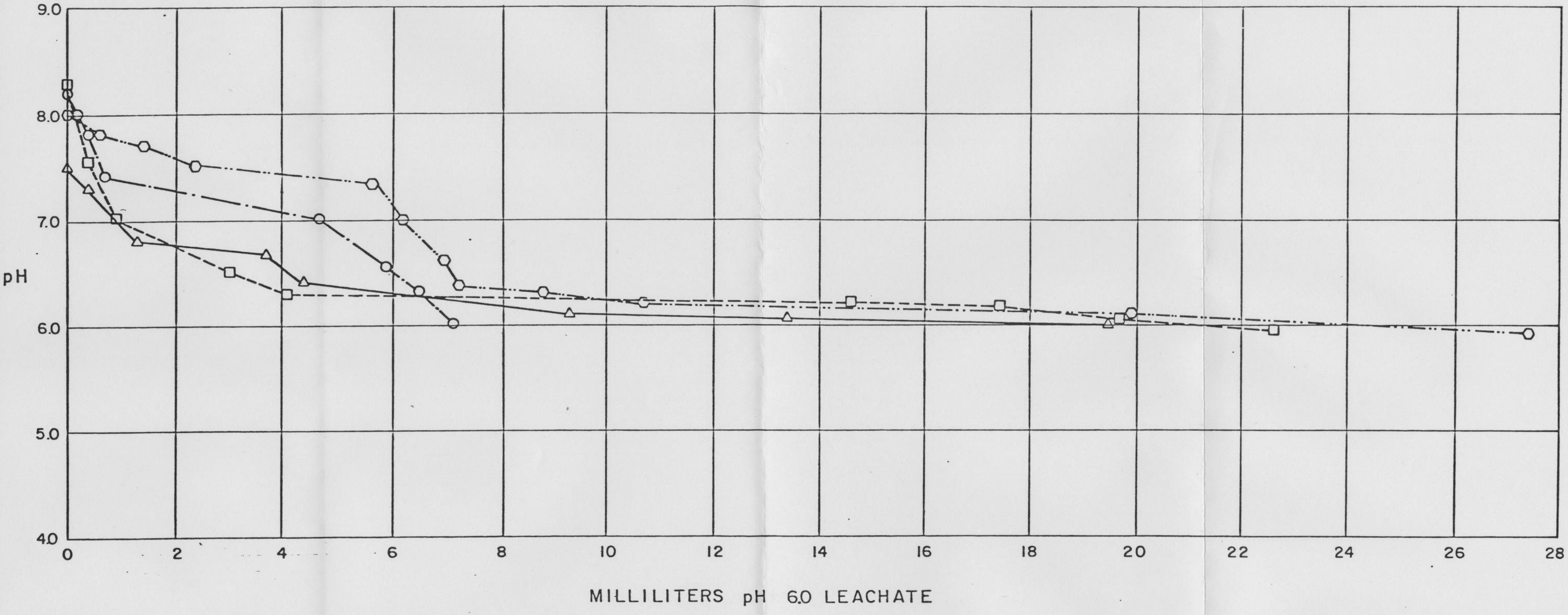
PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

19 1253 HERCULENE. A&B SMITH CO., PGH., PA

DRAWN BY	ACS 5-3-82	CHECKED BY	A LW	11/29/82	DRAWING NUMBER	RM81-444-
		APPROVED BY	MST	11-29-82		



LEGEND:

- O GLACIAL TILL (COMPOSITE SAMPLE No.1)
- □ STRATIFIED DRIFT (COMPOSITE SAMPLE No. 2)
- O HIGH $CaCO_3$ GLACIAL TILL (COMPOSITE SAMPLE No. 3)
- △ 4 % BENTONITE / TILL ADMIXTURE

NOTE: SOIL MIXTURES AT START OF TITRATION WERE 10 MILLILITERS OF DISTILLED WATER TO 10 GRAMS OF SOIL

FIGURE 3-12

TITRATION CURVES FOR pH 6.0
SYNTHETIC TAILINGS LEACHATE
AND COMPOSITE SAMPLES

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

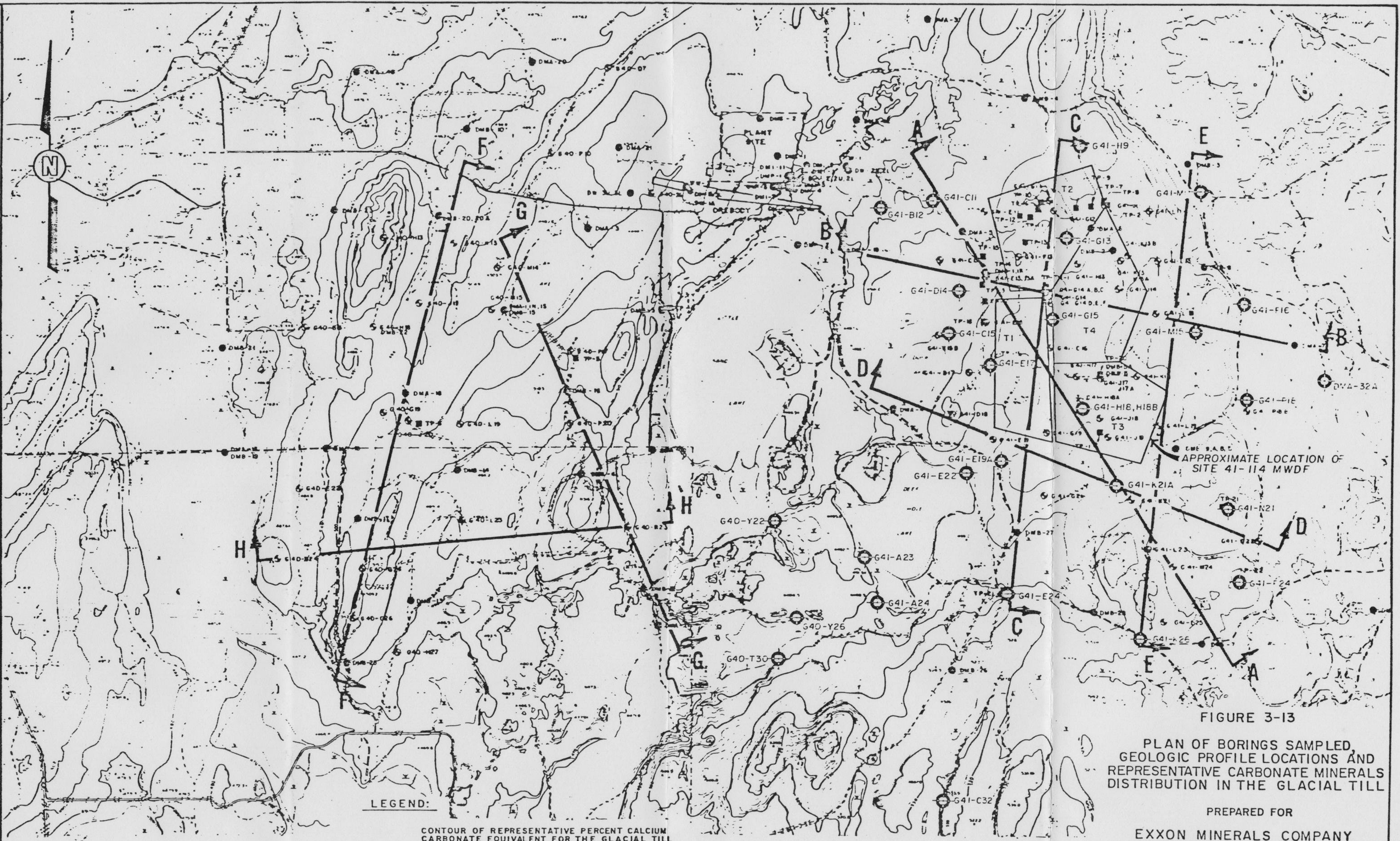
DRAWING NUMBER RMB1-444-B32

CHECKED BY 11/27/82

APPROVED BY 11/29/82

DRAWN BY

B11 100% BS BR BS



LEGEND:

CONTOUR OF REPRESENTATIVE PERCENT CALCIUM CARBONATE EQUIVALENT FOR THE GLACIAL TILL

⊕ BORING SAMPLED IN CARBONATE MINERALS DISTRIBUTION TESTING PROGRAM

— REPRESENTATIVE PERCENT CALCIUM CARBONATE EQUIVALENT FOR GLACIAL TILL

SCALE

500 0 500 1000 METERS

REFERENCE:

GOLDER ASSOCIATES, DRAWING NO. 050-1-81327

FIGURE 3-13

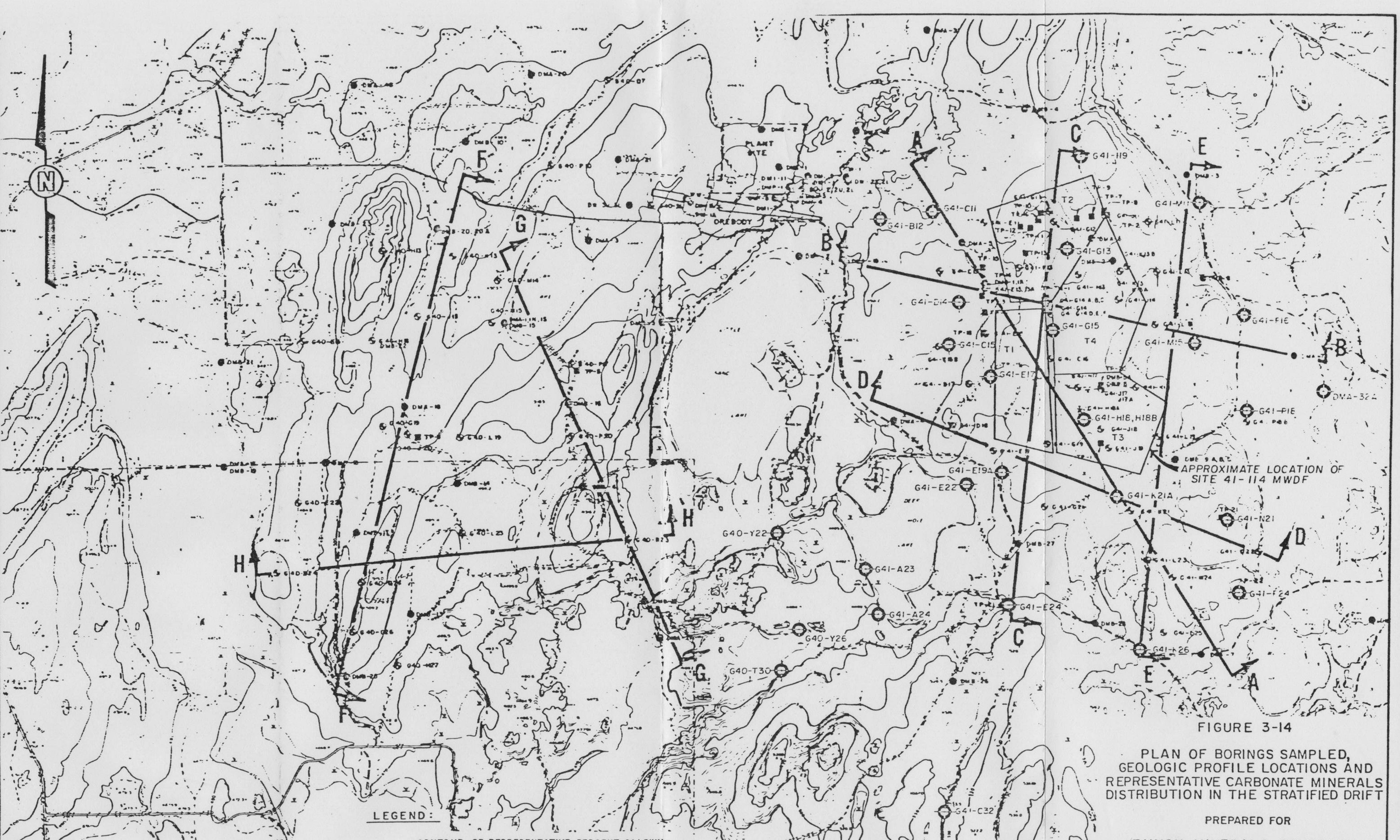
PLAN OF BORINGS SAMPLED, GEOLOGIC PROFILE LOCATIONS AND REPRESENTATIVE CARBONATE MINERALS DISTRIBUTION IN THE GLACIAL TILL

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

B12	100%	B5	DRAWN BY		CHECKED BY	FLN	11/29/82	DRAWING NUMBER RM 81-444-B3
	BR	B6			APPROVED BY	MJT	11.29.82	



LEGEND:

CONTOUR OF REPRESENTATIVE PERCENT CALCIUM CARBONATE EQUIVALENT FOR THE STRATIFIED DRIFT

BORING SAMPLED IN CARBONATE MINERALS DISTRIBUTION TESTING PROGRAM

REPRESENTATIVE PERCENT CALCIUM CARBONATE EQUIVALENT FOR STRATIFIED DRIFT

SCALE

500 0 500 1000 METERS

REFERENCE:

GOLDER ASSOCIATES, DRAWING NO. 050-1-81327

FIGURE 3-14

PLAN OF BORINGS SAMPLED, GEOLOGIC PROFILE LOCATIONS AND REPRESENTATIVE CARBONATE MINERALS DISTRIBUTION IN THE STRATIFIED DRIFT

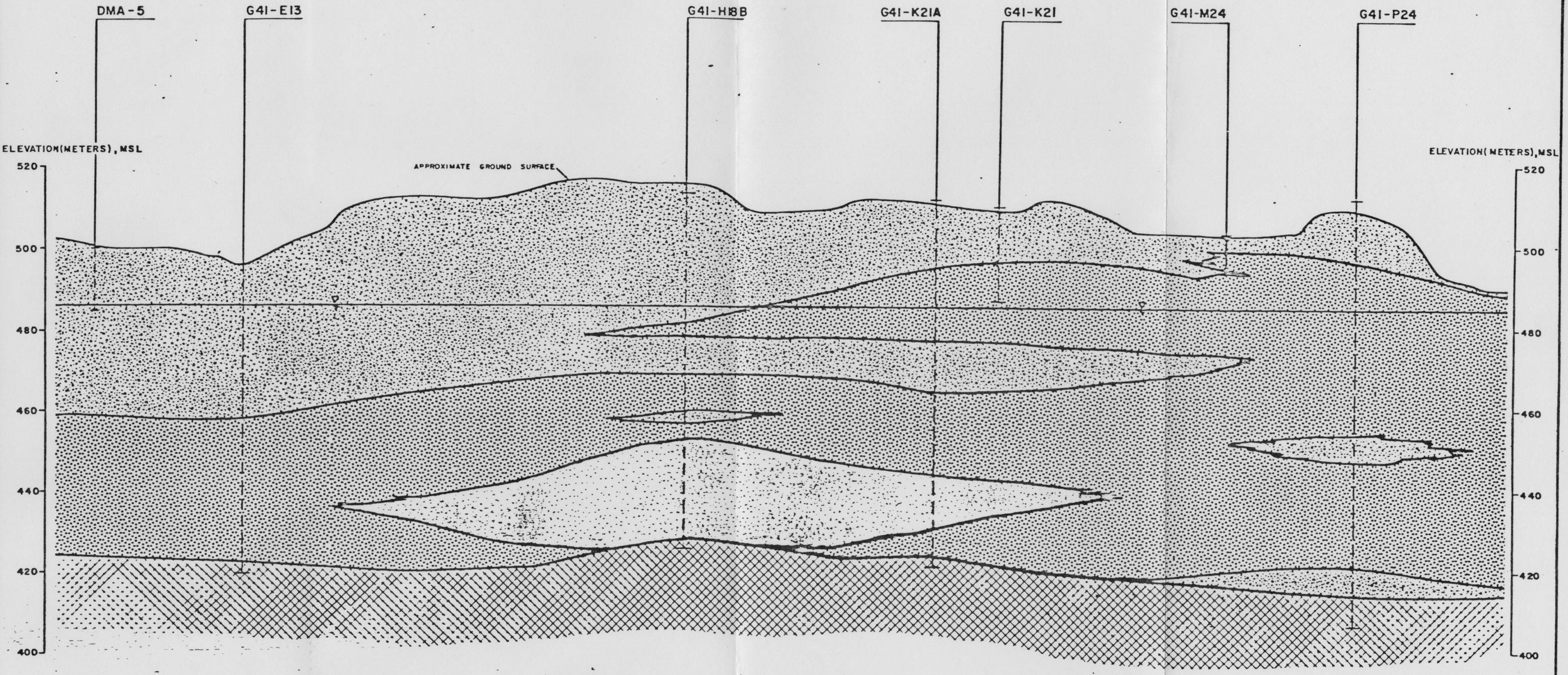
PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

19 1253 HERCULENE. A&B SMITH CO., PGH., PA

DRAWN BY	ACS/DAM	CHECKED BY	Rcw	11/29/82	DRAWING NUMBER RM81-444-B34
68	7-22-82	APPROVED BY	MJT	11.29.82	



0 50 100 200 300

HORIZONTAL SCALE IN METERS
VERTICAL EXAGGERATION : 10 x

NOTES

1. PROFILE SECTION LOCATIONS SHOWN ON BORING AND PROFILE SECTION LOCATION PLAN, FIGURE 3-13.
2. GROUNDWATER LEVEL PROFILE FROM GROUNDWATER POTENTIOMETRIC CONTOURS, GOLDER ASSOCIATES, DRAWING NO. 050-1-8111.
3. BEDROCK PROFILE FROM BEDROCK CONTOURS, GOLDER ASSOCIATES, DWG. NO. 050-1-80920.
4. THIS PROFILE IS FOR ILLUSTRATIVE PURPOSES ONLY. THE DISTRIBUTION OF THE GLACIAL MATERIALS HAS BEEN INFERRED FROM THE DATA FROM THE TEST BORINGS SHOWN ON THIS SECTION, TEST BORINGS FROM THE GENERAL SITE AREA, AND TRENDS IMPLIED FROM THE GLACIAL HISTORY AND BORING DATA. THIS ACTUAL DISTRIBUTION OF MATERIALS MAY VARY FROM THAT SHOWN.

LEGEND

GEOLOGICAL DEPOSIT SYMBOLS

▨ WETLAND AND MARSH
▨ LACUSTRINE SEDIMENTS AND FINE GRAINED STRATIFIED DRIFT
▨ COARSE GRAINED STRATIFIED DRIFT
▨ TILL
▨ BEDROCK
INTERPRETED STRATA BOUNDARIES
STRATA BOUNDARIES UNKNOWN
PERCENT CALCIUM CARBONATE EQUIVALENT
PERCENT CALCIUM CARBONATE EQUIVALENT INFERRED FROM EFFERVESCENCE RESULTS.

G41-H18B
GROUND SURFACE AT BORING LOCATION
BOREHOLE ON LINE OF SECTION
BOTTOM OF BOREHOLE

DMA-5
GROUND SURFACE AT BORING LOCATION
BOREHOLE OFF LINE OF SECTION
BOTTOM OF BOREHOLE

GROUNDWATER LEVEL

FIGURE 3-15

GEOLOGIC PROFILE OF MWDF AREA 41 SECTION A-A WITH APPROXIMATE PERCENT CARBONATE MINERALS PRESENT

PREPARED FOR

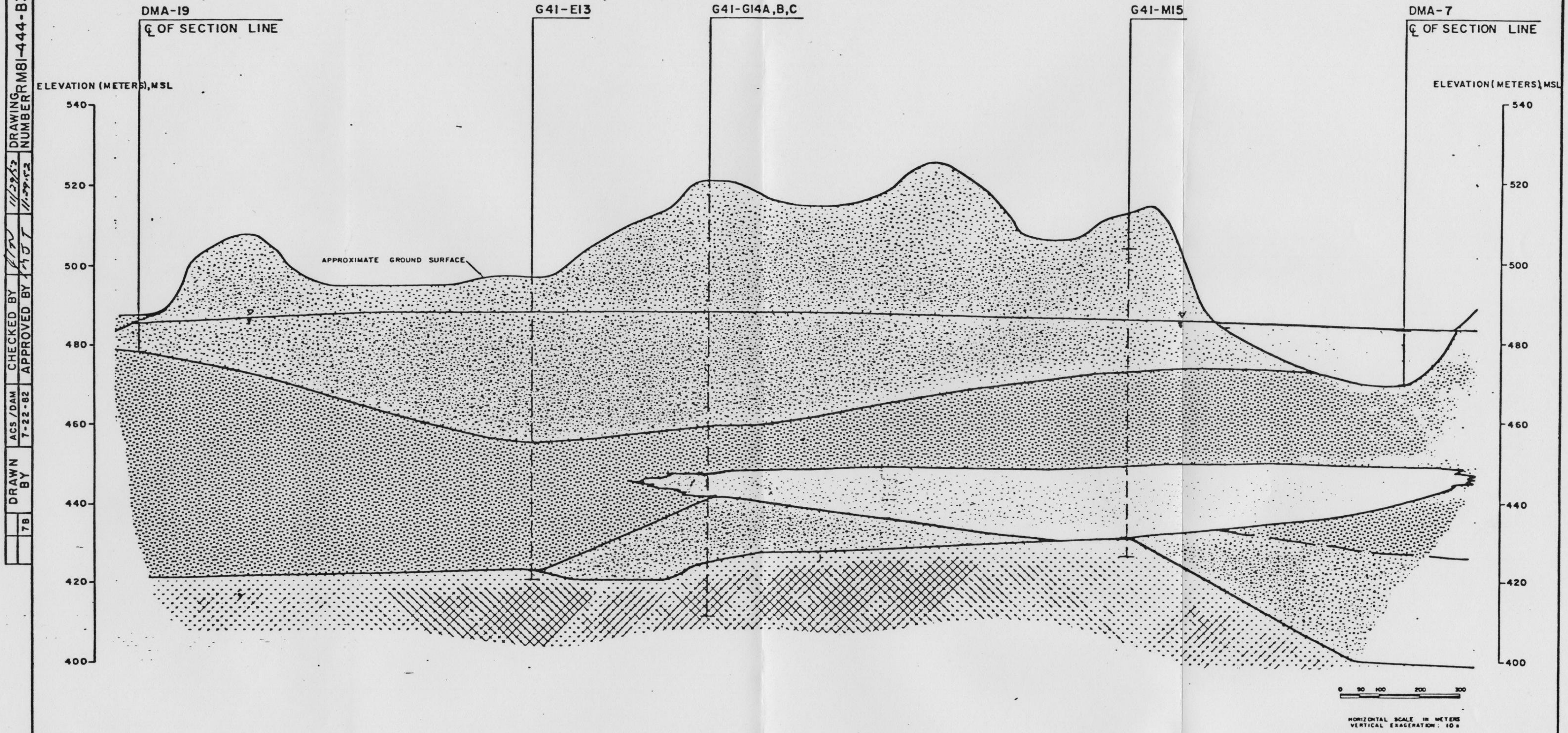
EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

REFERENCE:
GOLDER ASSOCIATES, DRAWING NO. 050-1-80911

19 1253 HERCULENE. A&B SMITH CO., PGH., PA

	DRAWN BY	ACS /DAM	CHECKED BY		11/29/82	DRAWING NUMBER	RM81-444-B35
7B		7-22-82	APPROVED BY		11-29-82		



NOTE:

1. SEE FIGURE 3-15 FOR GEOLOGIC LEGEND AND GENERAL NOTES.

LEGEND:

PERCENT CALCIUM CARBONATE EQUIVALENT.

PERCENT CALCIUM CARBONATE EQUIVALENT INFERRED FROM EFFERVESCENCE RESULTS.

FIGURE 3-16

GEOLOGIC PROFILE OF MWDF AREA 41
SECTION B-B
WITH APPROXIMATE PERCENT
CARBONATE MINERALS PRESENT

PREPARED FOR

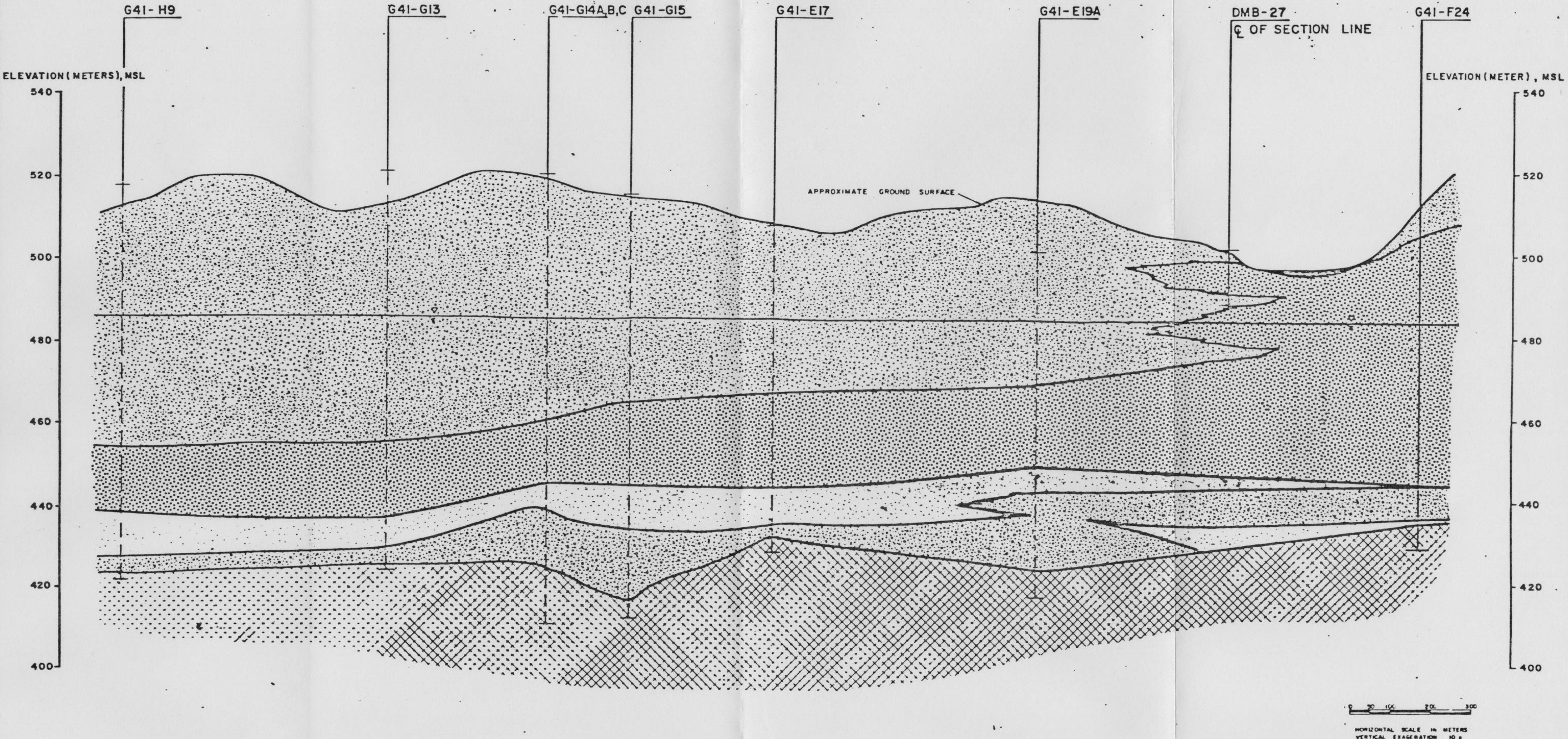
EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

REFERENCE:
GOLDER ASSOCIATES, DRAWING NO. 050-1-80912

19 1253 HERCULENE. A&B SMITH CO., PGH., PA

B8	DRAWN BY	G.J.Graham 7-22-82	CHECKED BY APPROVED BY	11/29/82 MJT 11-29-82	DRAWING NUMBER RM81-444-B36



NOTE:

1. SEE FIGURE 3-15 FOR GEOLOGIC LEGEND AND GENERAL NOTES.

LEGEND:

PERCENT CALCIUM CARBONATE EQUIVALENT.

PERCENT CALCIUM CARBONATE EQUIVALENT INFERRED FROM EFFERVESCENCE RESULTS.

FIGURE 3-17

GEOLOGIC PROFILE OF MWDF AREA 41 SECTION C-C WITH APPROXIMATE PERCENT CARBONATE MINERALS PRESENT

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

REFERENCE:
GOLDER ASSOCIATES, DRAWING NO. 050-1-80913

19 1253 HERCULENE. A&B SMITH CO., PGH., PA

DRAWING NUMBER RM81-444-B37

CHECKED BY 11/29/82

APPROVED BY MJT 11-29-82

DRAWN BY JJL 7-22-82

9B

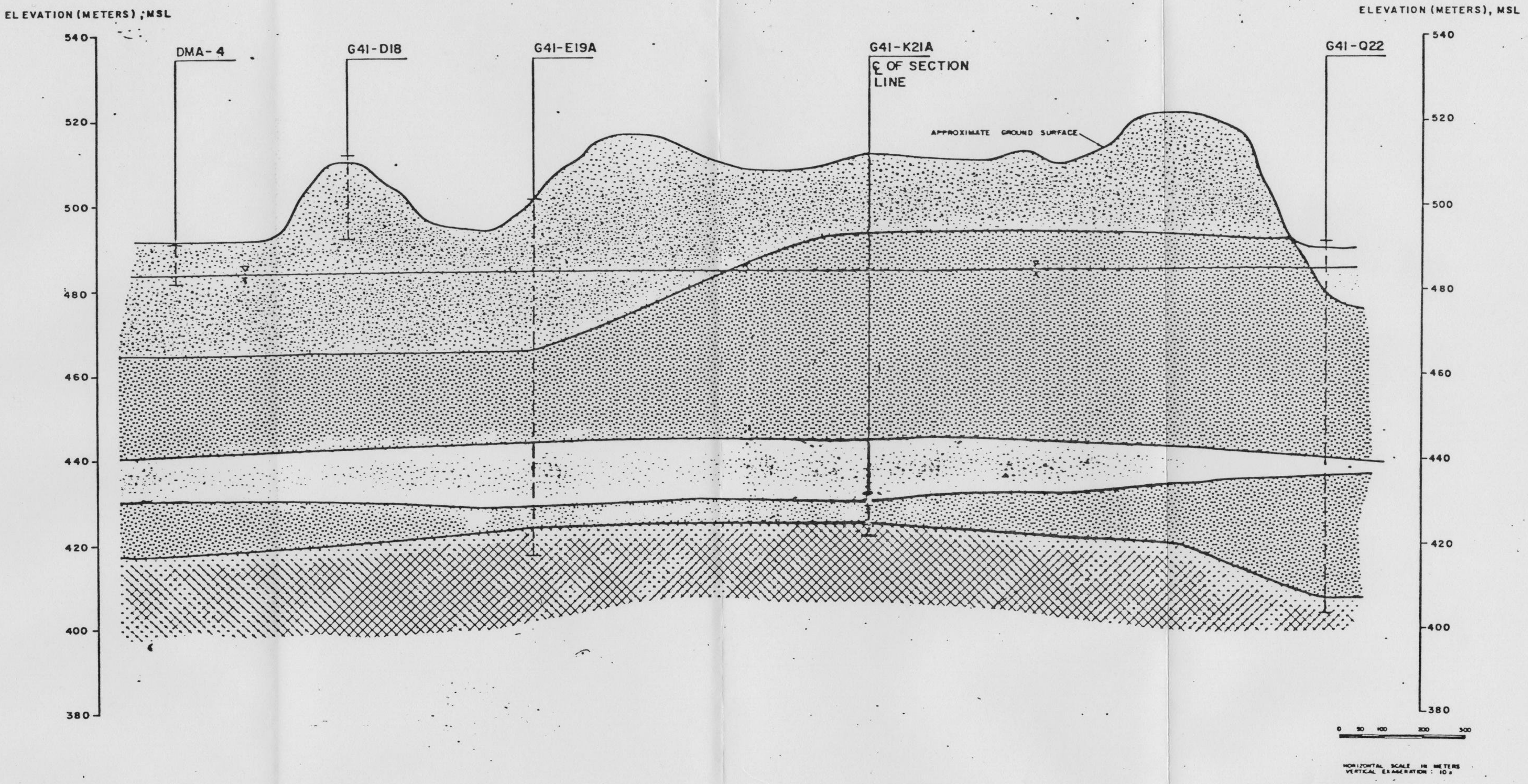


FIGURE 3-18

GEOLOGIC PROFILE OF MWDF AREA 41
SECTION D–D
WITH APPROXIMATE PERCENT
CARBONATE MINERALS PRESENT

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

NOTE:

1. SEE FIGURE 3-15 FOR GEOLOGIC LEGEND AND GENERAL NOTES.

LEGEND:

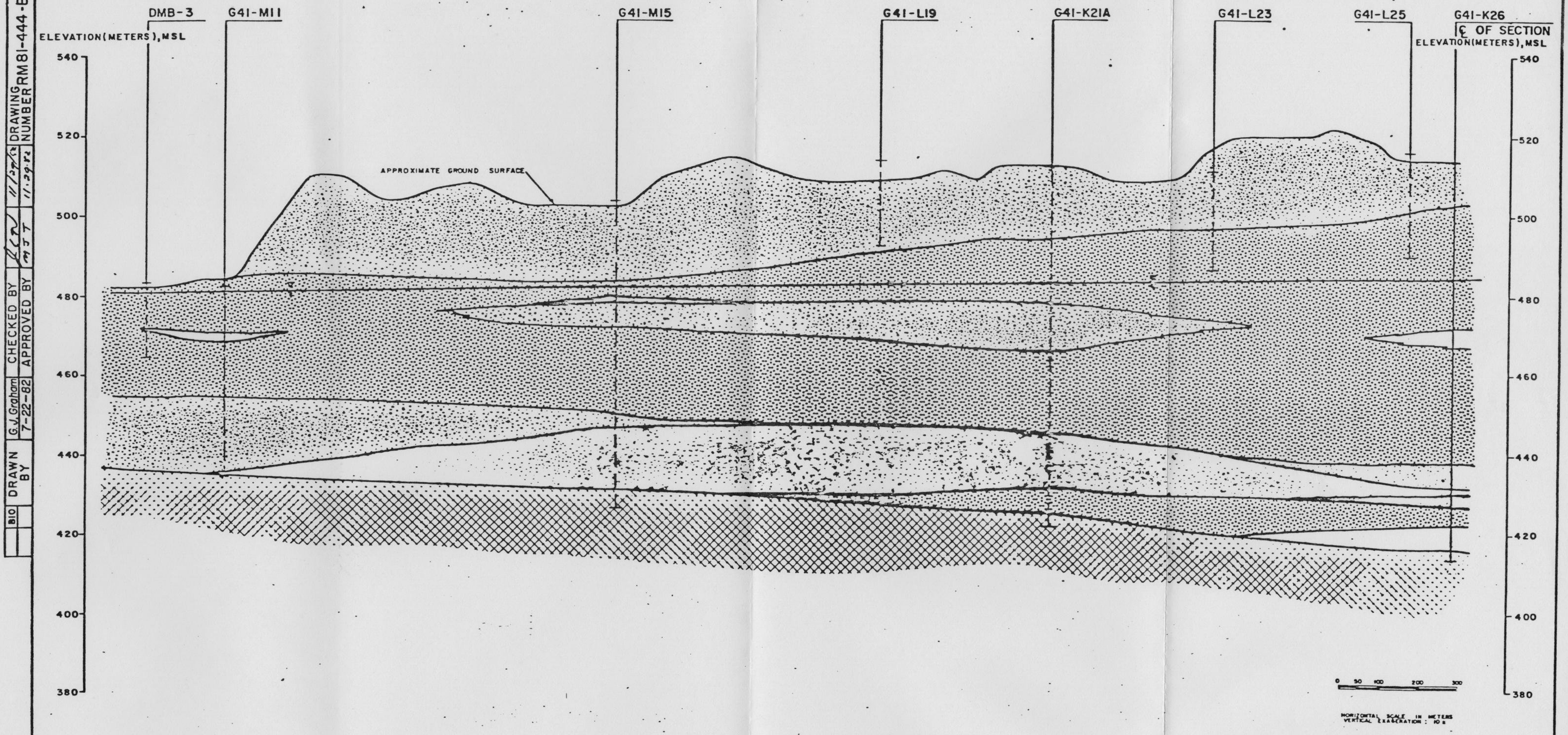
PERCENT CALCIUM CARBONATE EQUIVALENT.

PERCENT CALCIUM CARBONATE EQUIVALENT INFERRED FROM EFFERVESCENCE RESULTS

REFERENCE:
GOLDER ASSOCIATES, DRAWING NO. 050-1-80915

19 1253 HERCULENE, A&B SMITH CO., PGH., PA

BIO	DRAWN BY	G.J. Graham	CHECKED BY	LCN	11/29/82	DRAWING NUMBER RM81-444-B38
		7-22-82	APPROVED BY	MJT	11.29.82	



NOTE:

1. SEE FIGURE 3-15 FOR GEOLOGIC LEGEND AND GENERAL NOTES.

LEGEND:

PERCENT CALCIUM CARBONATE EQUIVALENT.

PERCENT CALCIUM CARBONATE EQUIVALENT INFERRED FROM EFFERVESCENCE RESULTS

FIGURE 3-19

GEOLOGIC PROFILE OF MWDF AREA 41
SECTION E-E
WITH APPROXIMATE PERCENT
CARBONATE MINERALS PRESENT

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

REFERENCE:
GOLDER ASSOCIATES, DRAWING NO. 050-1-80916

19 1253 HERCULENE. A&B SMITH CO., PGH., PA

APPENDIX A
QUALITY CONTROL PROGRAM

APPENDIX A
QUALITY CONTROL PROGRAM

D'Appolonia's Quality Assurance/Quality Control (QA/QC) program was formally established in 1973 to comply with the regulations of the U.S. Nuclear Regulatory Commission and covers all areas of work within the organization. The purpose of the program is to establish policies facilitating the implementation of regulatory requirements, satisfy client needs, and provide internal control and review which assures that work performed by D'Appolonia is of the highest professional standards.

The QA/QC program is implemented by project staff and by a full-time independent Quality Assurance Group of scientists and engineers. Project staff and the Quality Assurance Group, by virtue of their education and experience, are qualified to control, review, and independently verify all phases of project work.

The Quality Control (QC) program for this project is based on the D'Appolonia Quality Assurance Manual and meets or exceeds the QC standards set by Exxon. Specific requirements, standards, and control measures are provided by various chapters of the D'Appolonia Quality Assurance Manual and detailed procedures prepared for the project and applicable contract documents. Where appropriate, QC procedures are in accordance with ASTM, EPA, or other recognized reference standards. The Quality Control Program provides for a systematic means for checking, documentation, testing, and data reduction resulting in a consistent high level of quality. Specific QC procedures for sample handling, laboratory testing, calculations, and computer modeling are described in the following paragraphs.

Samples from Exxon were cataloged and inspected immediately upon receipt as a routine portion of D'Appolonia's QC program. Samples were inspected by laboratory technicians and a professional staff member for signs of container damage, leakage, contamination, sample identification, and material quantities. Samples were stored in their original air-tight containers and shipping cartons to prevent excess exposure to light and heat, on loss of moisture.

Laboratory testing procedures, outlined in various chapters of D'Appolonia's Quality Assurance Manual conform to standardized ASTM, EPA, or other reference techniques, where applicable. Testing procedures routinely include duplicate and/or standard samples for quality control. A detailed description of referenced testing procedures is contained in Appendix D.

D'Appolonia laboratories maintain standard data collection forms for each test performed. In addition to recording raw test data, documentation including testing date, responsible individuals, and equipment used is maintained. On completion of data collection, the data is independently checked for completeness and reviewed by the laboratory director. All laboratory data sheets are permanently stored in the central project files.

Laboratory testing equipment is periodically calibrated at intervals specified by the Quality Assurance staff using standard calibration techniques. Equipment not meeting the necessary tolerance is either repaired or replaced prior to use. An equipment calibration file is maintained on all laboratory and field equipment requiring calibration.

D'Appolonia routinely employes an independent checking procedure on all calculations, drawings, data reductions, tables, and specifications with checking performed by a technically competent individual. Checkprints are generated on which the checker indicates approval or disapproval with methodology and numerical accuracy. Discrepancies between originals and checkprints are resolved following a review by the originator and agreement between the checker and originator. Original calculations are revised, reviewed by the checker, and originals and checkprints signed and dated by both the originator and checker. Drawings, tables, laboratory data, and field data are also verified using this procedure. Originals and checkprints are permanently retained in central project files.

Analytical computer programs are verified prior to use by comparing computation results of known conditions with the same computation run on the computer program. In addition, programs are checked for conceptual accuracy by a competent individual and each revision is verified and documented. Input data to the program are also independently checked.

D'Appolonia's QA/QC program is designed to comply with pertinent regulatory requirements, satisfy client's needs, and assure that work produced is of the highest professional standards. The QA/QC procedures conform to standard reference practices where applicable, or are developed state-of-the-art techniques which have been carefully verified and documented.

APPENDIX B
LITERATURE REVIEWED

APPENDIX B
LITERATURE REVIEWED

D'Appolonia performed a literature review of documents and drawings supplied by Exxon. The purpose of the literature review was to assess the availability of existing data and their relevancy to the ground water/soil attenuation study. This appendix references the documents and drawings reviewed in this study. Relevant information to this study are incorporated in the text.

REFERENCE LIST
FOR LITERATURE REVIEW

DOCUMENT NUMBER	DATE	DESCRIPTION
1A	4/81	Dames and Moore, "Geology Study and Study Methods," Crandon Project Environmental Baseline Study, Dames and Moore, Park Ridge, Illinois.
1B	4/81	Dames and Moore, Appendix to "Geology Study and Study Methods," containing Particle Size Analyses, Boring Logs, Clay Mineral Analyses, and Modified Mercalli Intensity Scale of 1931.
2	10/80	Golder Associates, "Interim Report for Waste Facility Siting, Crandon Project (Draft 2)," Golder Associates, Atlanta, Georgia.
3A	10/81	Golder Associates, "Geotechnical Review, Crandon Project Waste Disposal System, Project Report 2, Volume 1, Analyses and Interpretation" Golder Associates, Atlanta, Georgia.
3B	10/81	Golder Associates, "Geotechnical Review, Crandon Project Waste Disposal System, Project Report 2, Volume 2, Laboratory Test Data, Test Pit Logs and G40 Series Boring Logs," Golder Associates, Atlanta, Georgia.
3C	10/81	Golder Associates, "Geotechnical Review, Crandon Project Waste Disposal System, Project Report 2, Volume 3, G41 Series Boring Logs," Golder Associates, Atlanta, Georgia.
3D	4/82	Golder Associates, "Geotechnical Review, Crandon Project Waste Disposal System, Addendum No. 1, Grain Size Curves and Boring Logs," Golder Associates, Atlanta, Georgia.
4	12/80	Golder Associates, "Pond Seepage Rate Estimate, Interim Report, Waste Facility Siting, Crandon Project," Golder Associates, Atlanta, Georgia.
5	4/81	Golder Associates, "Parametric Seepage Rate Estimates, Crandon Waste Disposal System, Report 3.2.1," Golder Associates, Atlanta, Georgia.

DOCUMENT NUMBER	DATE	DESCRIPTION
6	9/81	Golder Associates, "Pump Test and Analyses, Crandon Project Waste Disposal System, Report No. 4," Golder Associates, Atlanta, Georgia.
7	2/81	Golder Associates, "Tailings Material Properties, Crandon Project Waste Disposal Facilities," Golder Associates, Atlanta, Georgia.
8	4/81	Golder Associates, "General Properties of Common Liners, Crandon Project Waste Disposal Facilities, Report No. 6.1.1," Golder Associates, Atlanta, Georgia
9	1/81	Golder Associates, "Ground-Water Base Map, Crandon Project Waste Disposal System, Report No. 7," Golder Associates, Atlanta, Georgia.
10	4/81	Golder Associates, "Basic Waste Disposal Alternatives, Crandon Project, Report 8.1.1," Golder Associates, Atlanta, Georgia.
11	5/81	Golder Associates, "Simple Mass Transport Model, Version 2.0, Report 9.1," Golder Associates, Atlanta, Georgia.
12	1/81	Dames and Moore, "Hydrodynamics and Associated Chemical Species Transport Calculations Performed in Analysis of the Exxon/Crandon Infiltration Test Site," Dames and Moore, Golden, Colorado.
13	3/81	Dames and Moore, "Attenuation Characteristics of Soils in the Prospecting Program Infiltration Site for Exxon Minerals Company," Dames and Moore.
14	8/81	Exxon Minerals Company, "Crandon Project, Soil Boring Summary Sheet," Exxon Minerals Company.
15	4/77	Gerhardt, Roger A., "Leachate Attenuation in the Unsaturated Zone Beneath Three Sanitary Landfills in Wisconsin," University of Wisconsin Extension and Geological and Natural History Survey, Information Circular No. 35.
16	6/80	Zaporozec, Alexander, "Drought and Ground-Water Levels in Northern Wisconsin," University of Wisconsin Extension and Geological and Natural History Survey, Geoscience Wisconsin, Volume 5, June 5, 1980.

DOCUMENT NUMBER	DATE	DESCRIPTION
17	6/80	Zaporozec, Alexander, "Data for Selected Wells in Northern Wisconsin," University of Wisconsin Extension and Geological and Natural History Survey, Companion Volume to Geoscience Wisconsin, Volume 5, 1980, Miscellaneous Paper 80-1.
18	8/81	Golder Associates, "Thickened Tailings Disposal, Crandon Project Waste Disposal System, Report 5.2," Golder Associates, Atlanta, Georgia.
19	7/81	Golder Associates, "Underdrain Review, Crandon Project Waste Disposal System Report 3.5," Golder Associates, Atlanta, Georgia.
20	1/82	Dames and Moore, "Ground Water Study and Study Methods," Dames and Moore, Park Ridge, Illinois.
21	2/82	Dames and Moore, "Surface Water Study and Study Methods," Dames and Moore, Park Ridge, Illinois.
22	12/81	Golder Associates, "Bedrock Data Map, Crandon Project," Golder Associates, Atlanta, Georgia.
23	9/81	Golder Associates, "Bedrock Contour Map, Crandon Project," Golder Associates, Atlanta, Georgia.
24	10/81	Golder Associates, "Site 40 Glacial Stratigraphy Block Diagram, Crandon Project," Golder Associates, Atlanta, Georgia
25	10/81	Golder Associates, "Site 41 Glacial Stratigraphy Block Diagram, Crandon Project," Golder Associates, Atlanta, Georgia.
26	4/82	Golder Associates, "Alternative Studies, Crandon Project, Waste Disposal System, Report 8," Golder Associates, Atlanta, Georgia.
27	5/82	Golder Associates, "Geohydrologic Characterization, Crandon Project, Waste Disposal System," Golder Associates, Atlanta, Georgia.
28	4/82	CH_2M/Hill, "Predicted Seepage from Tailings, Results of Analysis No. 98," CH_2M/Hill.

DOCUMENT NUMBER	DATE	DESCRIPTION
29	9/81	Golder Associates, "Summary of Laboratory Test to Characterize Bulk Properties of Materials and Mixtures," Golder Associates, Atlanta, Georgia.
30	4/82	Golder Associates, "Miscellaneous Details and Analysis, Crandon Project, Waste Disposal System, Report No. 11," Golder Associates, Atlanta, Georgia.

APPENDIX C

INDEX TESTING AND SAMPLE COMPOSITING

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APPENDIX C
INDEX TESTING AND SAMPLE COMPOSITING

C.1 INTRODUCTION

As discussed in Chapter 3.0, 121 soil samples from four borings within the area of the proposed MWDF were collected by Golder Associates (Golder) in May and June 1981 from use in this attenuation study. The four borings were sampled by split spoon technique, every ten feet (three meters), or at any major stratigraphic change, whichever was more frequent. The borings were advanced using a bentonite drilling fluid. Samples were scrapped clean of the bentonite at time of collection and visual inspection and comparision to control samples (no contact with the gray clay-based drilling fluid) showed no contamination of the collected samples. The soil samples were collected in air-tight quart jars, placed in air-tight plastic bags, and stored in cardboard boxes to prevent exposure to light and kept from excessive heat and cold. Sample collection procedures and boring logs are presented in Golder's (1981a and 1981b) Geotechnical Review of the Waste Disposal System.

This study was designed to assess the potential leachate solute attenuation characteristics of the two major stratigraphic units; the upper glacial till and underlying stratified drift. Therefore, composite samples for laboratory attenuation studies were created from some of the 121 soil samples in accordance with the criteria set forth in this appendix.

C.2 INDEX TESTING AND RESULTS

Index tests (pH, neutralization potential, and grain size distribution) were performed on the soil samples from the two major stratigraphic units of interest to examine the typical range of variability of major characteristics in representive samples. In addition, this testing aided in the development of the compositing plan. Table C.1 presents the sampling location and lithologic description of the 121 soil samples. The samples were examined for color, rock content, degree of possible drilling mud contamination, degree of aggregation, and carbonate effervescence. Samples were selected for index testing after the above examinations and review of the boring logs and geologic cross-sections of the MWDF site area. Thirty samples were selected for index testing according to the following criteria:

- Minimal or no contamination by drilling mud had occurred (no visible contamination was evident in any sample).
- Physical appearance (e.g., color, rock content, grain size distribution) was representative of the stratigraphic unit.
- Vertical distribution within each borehole and horizontal distribution between boreholes was attained.
- A near equal distribution of samples was obtained from the two major stratigraphic units.
- The samples chosen for index testing had a wide range of carbonate effervescence results for later correlation to neutralization capacity determinations.
- Samples representing stratigraphic units other than those of interest to the project were excluded (e.g., glacial till beneath the major stratified drift unit).

Samples chosen for index testing and their results are presented in Table C.2. Reaction pH's were relatively uniform and strongly alkaline (9.55 to 10.70). The neutralization capacity of the samples was high and variable (0.2 to 12.0 percent calcium carbonate equivalent), with no correlation to stratigraphic unit, or sample depth. Results of the grain size distribution determinations indicate the glacial till has a larger variability of grain size than the stratified drift. The glacial till generally has both more gravel and silt and clay than the stratified drift. The typical sand content for the glacial till and stratified drift was 65 to 75 percent and 85 to 95 percent, respectively.

In addition to the above index tests, the three most aggregated glacial till samples were used to determine bulk density and moisture content for later use in the compacting effort of sample columns as discussed in Appendix F. No stratified drift sample was sufficiently aggregated to allow a bulk density determination. Results of these determinations are also presented in Table C.2.

C.3 SAMPLE COMPOSITING

As discussed in Chapter 3.0, the goal of sample compositing was to generate samples with which the range of site attenuation characteristics could be determined, yet the basis of the compositing plan was to be formulated from a conservative approach. Therefore, the following sample composite types were selected for attenuation studies:

- "Fine-grained" glacial till with low neutralization capacity.
- "Coarse-grained" stratified drift with low neutralization capacity.
- Glacial till with high neutralization capacity.

In order to allow the above three composite samples to be generated, each of the 121 soil samples were grouped into one of the following four categories:

- Category 1--"Fine-grained" glacial till with low neutralization capacity.
- Category 2--"Coarse-grained" stratified drift with low neutralization capacity.
- Category 3--Glacial till with high neutralization capacity.
- Category 4--None of the above.

This grouping of the samples was accomplished by visual inspection, grain-size feel of the samples, and carbonate effervescence test. The "fine-grained" samples were defined as having the feel of clays present in the sample. This grouping into fine-grained samples did not consider the amount of other coarse-grained materials present in the sample, only that clays were present. Conversely, the "coarse-grained" samples were defined as having the feel of an absence of clays in the sample. This grouping did not consider the amount of silts and fine sand material in the sample, only that clays were absent in large quantities. The neutralization capacity of the samples were estimated from a correlation of the thirty neutralization capacity and carbonate effervescence results presented in Tables C.1 and C.2, respectively. This correlation resulted in the following neutralization capacity estimates:

CARBONATE EFFERVESCENCE NUMERICAL RATING	ESTIMATED NEUTRALIZATION CAPACITY IN PERCENT CALCIUM CARBONATE EQUIVALENT
0	<1.5
1	1.5-3
2	3-5
3	5-9
4	>9
5	>9

Category grouping results for each sample are presented in Table C.1.

Priorities developed for generating the composite samples are listed below in descending order of importance:

- Proper neutralization capacity category.
- Proper grain-size category.
- Good vertical distribution within each borehole and spacial distribution over the MWDF site.
- Position of sample above and below the water table (Table C.1). Glacial till samples from above the water table were preferred, as most vertical migration of MWDF leachate will occur in this zone. Stratified drift samples from beneath the water table were preferred as most lateral migration of MWDF leachate will occur in this zone.

- Sample mass available to generate the required mass for attenuation testing of each composite sample.

Based upon the above criteria, the selected individual samples and their contributing mass indicated in Table C.3 were used to generate the composite samples. As can be observed from Tables C.1 and C.3, in some instances, samples not having the proper grain size were used and/or needed to generate sufficient composite sample mass or add balance to the composite by meeting one of the other established compositing criteria. However, in no instance was the neutralization capacity criteria violated.

Each individual sample selected for a composite sample was disaggregated using a Nasco-Asplin soil disaggregator (does not grind samples below their inherent grain size), riffle split (ASTM D 421-58[72]) and an equal air-dry weight fraction (if available) from all samples was used to generate the composite samples. Each composite sample was then thoroughly mixed by shaking and several sequences of passing it through the riffle splitter and recompositing it.

Once the composite samples were generated, the coarse and fine gravel fractions (plus No. 4 sieve material) of each composite were separated out and weighted for grain-size distribution. Except for being separately characterized for its carbonate effervescence (Table 3.4), the gravel fraction of each sample was not used in any other characterization or attenuation test. The gravel fraction was removed from each bulk composite sample as it could not be present in the column attenuation test (would not allow proper compaction of the columns), and it was desired to perform characterization tests upon identical (riffle split fractions) samples as those used in the batch attenuation studies.

C.4 COMPOSITE SAMPLE CHARACTERIZATIONS

Composite sample characterizations and results are presented in Chapter 3.0. However, the laboratory grain-size distribution curves are presented in this appendix as Attachment I.

APPENDIX C
REFERENCES

American Society for Testing Materials (ASTM), 1981, Annual Book of Standards, Part 19, Designations D 421-58(72), D 422-63(72), D 2216-71(80) and D 2487-69(75), ASTM, Philadelphia, Pennsylvania.

Golder Associates, 1981a, "Analyses are Interpretation," Geotechnical Review, Crandon Project, Waste Disposal System, Project Report 2, Volume 1, Golder Associates, Atlanta, Georgia.

Golder Associates, 1981b, "G41 Series Boring Logs," Geotechnical Review, Crandon Project, Waste Disposal System, Project Report 2, Volume 3, Golder Associates, Atlanta, Georgia.

Sobek, A. A., W. A. Schuller, J. R. Freeman, and R. W. Smith, 1978, "Field and Laboratory Methods Applicable to Overburdens and Minesoils," EPA-600/2-78-054, U.S. Environmental Protection Agency (U.S. EPA), Cincinnati, Ohio, 203 pp.

APPENDIX C
TABLES

TABLE C.1

SAMPLE SUMMARY, LITHOLOGIC CHARACTERIZATION, USCS CLASSIFICATION, AND COMPOSITING CATEGORY

BORING	SAMPLE INTERVAL (feet above Mean Sea Level)	SAMPLE NO.(1)	LITHOLOGIC DESCRIPTION(2)	SOIL TYPE(2) (Unified Soil Classification System)	CARBONATE EFFERVESCENCE(3) (Fizz Test - 10% HCl)	COMPOSITING CATEGORY(4)
G41-H9	1692.0-1690.0	2	Glacial Till	SM	1	4
	1681.0-1679.5	3	Glacial Till	SM	1	4
	1672.0-1670.5	4	Glacial Till	SP-SM	2	3
	1662.0-1661.0	5	Glacial Till	SP-SM	2	3
	1652.0-1651.3	6	Glacial Till	SP-SM	3	3
	1642.0-1640.7	7	Glacial Till	SM	4	3
	1632.0-1630.2	8	Glacial Till	SM	2	3
	1622.0-1621.0	9	Glacial Till	SM	2	3
	1612.0-1611.0	10	Stratified Drift	GP	2	4
▼(5)	1602.0-1600.0	11	Stratified Drift	SP-SM	0	2
	1591.0-1589.0	12	Stratified Drift	SP-SM	1	2
	1582.0-1580.0	13	Glacial Till	SM	2	3
	1572.0-1571.7	14	Glacial Till	SM	3	3
	1562.0-1560.5	15	Glacial Till	SM	2	3
	1552.0-1550.7	16	Glacial Till	SM	2	3
	1541.0-1540.3	17	Glacial Till	SM	3	3
	1531.0-1530.4	18	Glacial Till	SM	0	1
	1522.0-1521.0	19	Glacial Till	SM	2	3
	1511.0-1510.0	20	Glacial Till	SM	1	4
	1502.0-1501.2	21	Glacial Till	SP-SM	2	3
	1491.5-1490.6	22	Glacial Till	SM	0	1
	1482.0-NA(6)	23	Stratified Drift	SP	1	2
	1472.0-1470.5	24	Stratified Drift	SP	0	2
	1462.0-1460.5	25	Stratified Drift	SP	1	2
	1452.0-1450.5	26	Stratified Drift	SP-SM	1	2
	1442.0-1440.5	27	Stratified Drift	SP-SM	1	-
	1432.0-1430.5	28	Stratified Drift	SM-ML	0	4
	1422.0-1420.5	29	Stratified Drift	SM-ML	1	4
	1412.0-1410.5	30	Stratified Drift	SM-ML	0	4
	1402.0-1400.5	31	Glacial Till	SM	1	4

See footnotes at end of table.

TABLE C.1
(Continued)

BORING	SAMPLE INTERVAL (feet above Mean Sea Level)	SAMPLE NO.(1)	LITHOLOGIC DESCRIPTION(2)	SOIL TYPE(2) (Unified Soil Classification System)	CARBONATE EFFERVESCENCE(3) (Fizz Test - 10% HCl)	COMPOSITING CATEGORY(4)
	1704.6-1702.6	32	Glacial Till	SM	1	1
	1699.6-1698.5	33	Glacial Till	SM	1	4
	1689.6-1688.2	34	Glacial Till	SM	3	3
	1679.6-1677.6	35	Glacial Till	SM	3	3
	1666.6-1664.6	36	Glacial Till	SM	3	3
	1659.6-1658.1	37	Glacial Till	SM	3	3
	1649.6-1647.7	38	Stratified Drift	GP	0	2
	1635.6-1633.3	39	Stratified Drift	GP	1	2
	1629.6-1628.8	40	Glacial Till	SP	1	4
	1619.6-1617.6	41	Glacial Till	SP	2	3
	1609.6-1608.3	42	Glacial Till	SP	1	4
▽	1599.6-1597.8	43	Glacial Till	SP	1	4
	1589.6-NA	44	Glacial Till	SM	1	1
	1579.6-1577.6	45	Glacial Till	SM	0	1
	1569.6-1568.1	46	Glacial Till	SM	1	1
G41-G13	1559.6-1558.1	47	Glacial Till	SM	1	1
	1549.6-1548.6	48	Glacial Till	SP	1	4
	1539.6-1538.7	49	Glacial Till	SM	3	3
	1528.6-1527.8	50	Glacial Till	SM	0	4
	1519.6-1518.8	51	Glacial Till	SM	2	3
	1499.6-1498.9	53	Glacial Till	SM	3	3
	1489.6-1488.9	54	Glacial Till	SM	1	1
	1477.6-1476.8	55	Stratified Drift	SM	2	4
	1469.6-1468.6	56	Stratified Drift	SP	1	2
	1459.6-1457.9	57	Stratified Drift	SP	1	2
	1449.6-1447.6	58	Stratified Drift	SP	1	2
	1439.6-1437.9	59	Stratified Drift	SP	3	4
	1429.6-1428.6	60	Stratified Drift	SP-ML	1	2
	1419.6-1418.8	61	Stratified Drift	SP-ML	5	4
	1409.6-1408.6	62	Stratified Drift	ML	5	4
	1399.6-1398.3	63	Stratified Drift	SP	4	4

See footnotes at end of table.

TABLE C.1
(Continued)

BORING	SAMPLE INTERVAL (feet above Mean Sea Level)	SAMPLE NO.(1)	LITHOLOGIC DESCRIPTION(2)	SOIL TYPE(2) (Unified Soil Classification System)	CARBONATE EFFERVESCENCE(3) (Fizz Test - 10% HCl)	COMPOSITING CATEGORY(4)
	1678.8-1676.8	64	Glacial Till	SM	2	3
	1673.8-1671.8	65	Glacial Till	SM	1	4
	1663.8-1661.8	66	Glacial Till	SM	0	1
	NA	67	Glacial Till	SM	1	4
	1643.8-1641.8	68	Stratified Drift	SP	1	4
	1633.8-1631.8	69	Stratified Drift	SP	2	4
	1623.8-1621.8	70	Glacial Till	SM	1	4
	1613.8-1611.8	71	Glacial Till	SM	0	1
	1605.8-1603.8	72	Glacial Till	SM	0	1
	1605.8-1603.8	73	Glacial Till	SM	1	1
▽	1593.8-1591.8	74	Glacial Till	SM	1	4
	1583.8-1581.8	75	Glacial Till	SM	1	1
	1573.8-1571.8	76	Stratified Drift	SP	1	2
	1563.8-1561.8	77	Glacial Till	SM	0	4
G41-H18B	1553.8-1551.8	78	Glacial Till	SM	0	1
	1543.8-1541.8	79	Glacial Till	SM	1	1
	1533.8-1531.8	80	Stratified Drift	SP	0	2
	1523.8-1521.8	81	Stratified Drift	SP	1	2
	1513.8-1511.8	82	Stratified Drift	SP	0	2
	1503.8-1501.8	83	Stratified Drift	SP	1	2
	1493.8-1491.8	84	Glacial Till	SM	1	4
	1483.8-1481.8	85	Stratified Drift	SP	0	4
	1473.8-1472.3	86	Glacial Till	SM	1	4
	1463.8-1462.3	87	Glacial Till	SM	1	1
	1453.8-1452.8	88	Glacial Till	SM	1	1
	1441.8-1440.8	89	Glacial Till	SM	1	1
	1433.8-1432.8	90	Glacial Till	SM	1	1
	1423.8-1422.8	91	Stratified Drift	ML	0	4
	1413.8-1412.8	92	Stratified Drift	ML	1	4

See footnotes at end of table.

TABLE C.1
(Continued)

BORING	SAMPLE INTERVAL (feet above Mean Sea Level)	SAMPLE NO.(1)	LITHOLOGIC DESCRIPTION(2)	SOIL TYPE(2) (Unified Soil Classification System)	CARBONATE EFFERVESCENCE(3) (Fizz Test - 10% HCl)	COMPOSITING CATEGORY(4)
G41-K21A	1675.4-1673.9	93	Glacial Till	SM	1	1
	1670.4-1668.9	94	Glacial Till	SM	1	4
	1660.4-1658.9	95	Glacial Till	SM	1	4
	1650.4-1648.9	96	Glacial Till	SM	1	4
	1640.4-1639.2	97	Glacial Till	SM	2	3
	1630.4-1629.3	98	Glacial Till	SM	1	4
	1620.4-1618.9	99	Stratified Drift	SP	0	2
	1608.4-1607.3	100	Stratified Drift	SP	0	2
	1606.4-1604.1	101	Stratified Drift	SP	0	2
	1602.4-1600.9	102	Stratified Drift	SP	0	2
	1600.9-1600.4	103	Stratified Drift	SP	0	2
▽	1588.9-1587.2	104	Stratified Drift	SP	0	2
	1580.4-1578.9	105	Stratified Drift	SP	1	2
	1570.4-1568.9	106	Stratified Drift	SP	0	2
	1560.4-1558.9	107	Glacial Till	SM	0	1
	1550.4-1548.9	108	Glacial Till	SM	1	1
	1540.4-1539.4	109	Glacial Till	SM	4	3
	1530.4-1529.4	110	Glacial Till	SM	2	3
	1520.4-1518.9	111	Stratified Drift	SP	0	4
	1510.4-1508.9	112	Stratified Drift	SP	1	2
	1500.4-1498.9	113	Stratified Drift	SP	1	4
	1490.4-1488.9	114	Stratified Drift	SP	1	2
	1480.4-1479.4	115	Stratified Drift	SP	1	2
	1470.4-1469.4	116	Stratified Drift	SP	1	2
	1460.4-1459.4	117	Stratified Drift	SP	1	2
	1450.4-1449.4	118	Stratified Drift	SP-ML	1	4
	1440.4-1439.4	119	Stratified Drift	SP-ML	3	4
	1430.4-1429.1	120	Stratified Drift	SP-ML	1	[illegible]
	1420.4-1418.9	121	Stratified Drift	SP-ML	3	4
	1410.4-1408.9	122	Stratified Drift	SP	3	4
	1400.4-1398.9	123	Stratified Drift	SP	2	4

(1) Samples 1 and 52 were not available for testing.

(2) Lithologic descriptions and soil classifications (ASTM D 2487-69[75]) from Golder Associates (1981b) boring logs and sample descriptions.

(3) Visual numeric estimation showing the presence of carbonates (higher numeric rating correlates to higher carbonate content) after the addition of a few drops of 10% HCl (Sobek, et al., 1978):

0 = No reaction	3 = Moderate reaction
1 = Very slight reaction	4 = Strong reaction
2 = Slight reaction	5 = Very strong reaction

(4) Sample grouping by visual inspection, grain-size feel of samples, and carbonate effervescence test:

1 = Fine grain glacial till with low neutralization capacity.
2 = Coarse grain stratified drift with low neutralization capacity.
3 = Glacial till with high neutralization capacity.
4 = None of the above.

(5) Approximate groundwater table location; contact between samples collected above and below the groundwater table.

(6) Not Available (NA).

TABLE C.2
RESULTS OF INDEX TESTING

LITHOLOGIC DESCRIPTION(1)	BORING	SAMPLE INTERVAL(1) (feet above Mean Sea Level)	SAMPLE NO.	COMPOSITING CATEGORY(2)	1:1 REACTION pH(3)	NEUTRALIZATION CAPACITY(4) (% $CaCO_3$ Equivalent)	GRAIN SIZE DISTRIBUTION(5)								DRY DENSITY(6) (g/cm^3)	WATER CONTENT(7) (%)
							COARSE GRAVEL (76.2-19.05 mm)	FINE GRAVEL (19.05-4.75 mm)	COARSE SAND (4.75-2.0 mm)	MEDIUM SAND (2.0-0.425 mm)	FINE SAND (0.425-0.075 mm)	UNDIFFERENTIATED SILT AND CLAY (<0.075 mm)	SILT (0.075-0.002 mm)	CLAY (<0.002 mm)		
Glacial Till	G41-H9	1662.0-1640.7	7	3	9.65	9.0	0	7.7	9.9	27.1	41.0	14.3	-(8)	-	-	-
Glacial Till	G41-H9	1572.0-1571.7	14	3	10.20	7.2	0	5.0	5.0	21.2	50.0	18.8	14.3	4.5	-	-
Glacial Till	G41-H9	1541.0-1540.3	17	3	9.70	11.0	0	3.1	7.0	21.7	45.0	23.2	18.1	5.1	-	-
Glacial Till	G41-H9	1491.5-1490.6	22	1	10.05	0.8	0	4.1	7.4	20.8	45.3	22.4	-	-	-	-
Glacial Till	G41-G13	1629.6-1628.6	35	3	9.95	7.5	12.0	9.2	7.2	19.7	36.0	15.9	-	-	-	-
Glacial Till	G41-G13	1619.6-1617.6	41	3	10.40	3.0	0	0	1	31.4	64.5	3.2	-	-	-	-
Glacial Till	G41-G13	1579.6-1577.6	45	1	9.85	1.0	0	8.8	5.7	19.5	45.0	21.0	-	-	-	-
Glacial Till	G41-G13	1539.6-1538.7	49	3	10.15	9.0	0	9.0	4.9	19.1	45.3	21.7	-	-	-	-
Glacial Till	G41-G13	1499.6-1498.9	53	3	9.70	7.5	0	5.6	6.3	18.8	47.6	21.7	8.7	13.0	-	-
Glacial Till	G41-H18B	1613.8-1611.8	71	1	9.90	0.2	0	3.1	3.7	17.1	50.5	25.6	-	-	-	-
Glacial Till	G41-H18B	1583.8-1581.8	75	1	10.10	0.5	0	12.9	6.5	13.3	34.5	32.8	13.6	19.2	-	-
Glacial Till	G41-H18B	1553.8-1551.8	78	1	9.80	0.7	0	10.7	4.9	19.0	47.1	18.3	-	-	-	-
Glacial Till	G41-K21A	1650.4-1648.9	96	4	10.15	1.8	20.1	10.4	8.4	15.8	31.9	13.4	-	-	-	-
Glacial Till	G41-K21A	1550.4-1548.9	108	1	9.80	0.4	0	1.1	3.3	20.4	56.8	18.4	-	-	-	-
Stratified Drift	G41-H9	1602.0-1600.0	11	2	9.55	0.9	0	1.5	14.3	58.8	19.7	5.7	3.7	2.0	-	-
Stratified Drift	G41-H9	1472.0-1470.5	24	2	9.70	1.1	0	5.4	14.5	30.8	39.8	9.5	-	-	-	-
Stratified Drift	G41-H9	1452.0-1450.5	26	2	10.20	1.0	0	3.5	4.2	32.6	51.9	7.8	-	-	-	-
Stratified Drift	G41-H9	1432.0-1430.5	28	4	10.05	0.3	-	-	-	-	65.6	34.4	27.7	6.7	-	-
Stratified Drift	G41-H9	1412.0-1410.5	30	4	10.05	1.0	0	0	0.1	0.1	55.9	43.9	25.9	18.0	-	-
Stratified Drift	G41-G13	1459.6-1457.9	57	2	10.10	1.2	0	6.7	5.2	25.5	56.8	5.8	-	-	-	-
Stratified Drift	G41-G13	1439.6-1437.9	59	4	10.30	2.2	0	3.3	2.8	24.5	64.2	5.2	-	-	-	-
Stratified Drift	G41-G13	1419.6-1418.8	61	4	10.00	12.0	0	0	0	3.3	50.7	46.0	34.0	12.0	-	-
Stratified Drift	G41-H18B	1633.8-1631.8	69	4	10.35	7.6	8.1	55.3	13.6	12.6	7.2	3.2	-	-	-	-
Stratified Drift	G41-H18B	1533.8-1531.8	80	2	10.20	0.4	0	0.8	3.1	60.0	31.6	4.5	-	-	-	-
Stratified Drift	G41-H18B	1513.8-1511.8	82	2	9.65	1.3	0	22.2	17.5	29.2	21.5	9.6	-	-	-	-
Stratified Drift	G41-K21A	1580.4-1578.9	105	2	9.75	0.8	0	1.7	3.0	48.0	45.4	1.9	-	-	-	-
Stratified Drift	G41-K21A	1500.4-1498.9	113	4	10.40	3.2	0	0	0	1.4	90.0	8.6	-	-	-	-
Stratified Drift	G41-K21A	1460.4-1459.4	117	2	10.70	1.2	0	0.7	0.4	8.9	85.9	4.1	-	-	-	-
Stratified Drift	G41-K21A	1440.4-1439.4	119	4	10.10	8.0	0	0	0	1.2	66.0	32.8	-	-	-	-
Stratified Drift	G41-K21A	1410.4-1408.9	122	4	10.40	3.6	0	0	0.1	17.2	78.7	4.0	-	-	-	-
Glacial Till	G41-H9	1531.0-1530.4	18	1	-	-	-	-	-	-	-	-	-	-	1.94	10.1
Glacial Till	G41-G13	1528.6-1527.8	50	4	-	-	-	-	-	-	-	-	-	-	2.07	8.5
Glacial Till	G41-K21A	1560.4-1558.9	107	1	-	-	-	-	-	-	-	-	-	-	1.99	10.7

(1) Lithologic descriptions and sample interval from Golder Associates (1981b) boring logs and sample descriptions.

(2) See Table C.1 for sample grouping classifications.

(3) pH of a 1:1 soil to distilled water mixture at 25°C (Sobek, et al., 1978).

(4) Sobek, et al. (1978).

(5) ASTM D 422-63(72).

(6) By weight and volume measurements.

(7) ASTM D 2216-71(80).

(8) "-" indicates not determined. In the case of grain size determinations of silt and clay fractions, insufficient fines relative to sample size precluded the use of hydrometer analysis.

TABLE C.3
COMPOSITION OF COMPOSITE SAMPLES

SOURCE BORING	COMPOSITE SAMPLE NO. 1 (Glacial Till)		COMPOSITE SAMPLE NO. 2 (Stratified Drift)		COMPOSITE SAMPLE NO. 3 (High Carbonate Effervescence)	
	SAMPLE NO.(1)	WEIGHT CONTRIBUTED(2) (grams)	SAMPLE NO.(1)	WEIGHT CONTRIBUTED(3) (grams)	SAMPLE NO.(1)	WEIGHT CONTRIBUTED(2) (grams)
G41-H9	2	420	11	440	5	50
	3	420	12	440	7	50
	18	420	23	440	9	50
	20	420	25	440	14	50
	22	420	26	375	17	50
			27	440	19	50
G41-G13	33	420	56	356	34	50
	44	420	57	178	35	50
	45	420	58	440	36	50
	46	420	60	328	37	50
	47	420			41	50
	50	420			49	50
	54	420			51	50
					53	50
					55	50
G41-H18B	66	420	75(4)	440	64	50
	68	420	80	440	69	50
	71	420	81	440		
	72	420	82	440		
	73	420	84(4)	440		
	78	420				
	79	420				
G41-K21A	95	420	103	440	97	50
	96	420	104	440	109	50
	98	420	112	391	110	50
	107	420	114	400		
	108	420	115	440		
			116	440		
			117	437		

(1) Refer to Table C.1 for sample interval and lithologic description.

(2) Obtained using a sample splitter (ASTM D 421-58[72]).

(3) Obtained using a sample splitter (ASTM D 421-58[72]) unless indicated weight is below 400 grams. Weights below 440 grams indicate the entire sample (which was less than 440 grams) was contributed to the composite.

(4) Due to a later discovery of interpretation problems between the boring logs and sample identifications, Samples 75 and 84 (glacial till materials) were misappropriately added to Composite Sample No. 2.

APPENDIX C

ATTACHMENT I
GRAIN SIZE DISTRIBUTION CURVES

Grain size distribution curves for composite Samples Numbers 1 (glacial till) and 2 (stratified drift) and the four percent bentonite/till admixture. Grain size distribution curves and other composite characterizations were determined only on the sample fraction passing a Number 4 U.S. standard sieve (4.75 mm). The portions of each sample greater than 4.75 millimeters are shown in Table 3.1.

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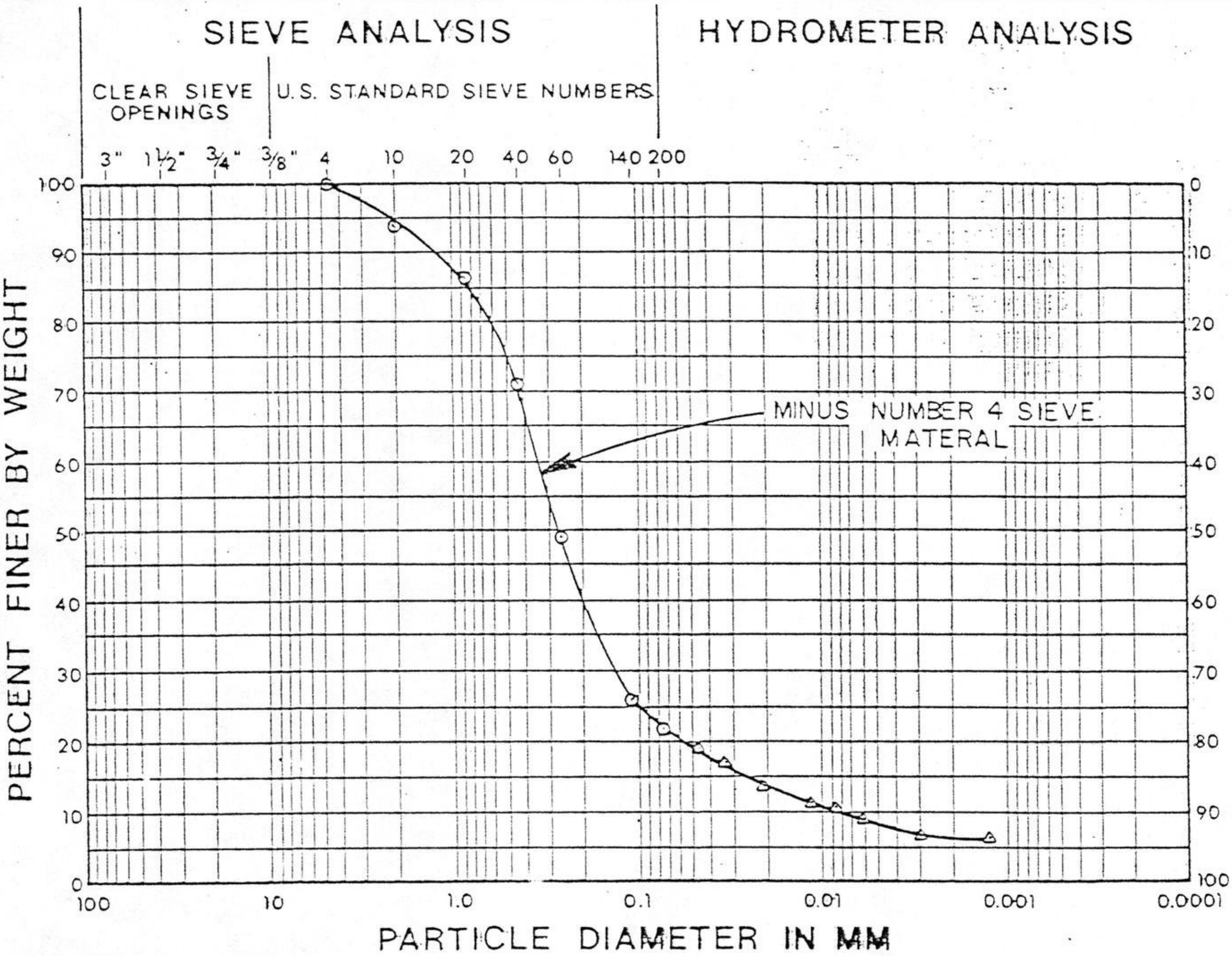


COBBLES	GRAVEL		SAND			SILT AND CLAY FRACTION
	coarse	fine	coarse	medium	fine	

SYMBOL	BORING	SAMPLE	DEPTH	SOIL DESCRIPTION	U.S.C.S.	L.L.	P.L.	W.%
—	—	COMP 1	—	FINE TO COARSE SAND-SOME CLAYEY SILT	SM	—	—	—

FIGURE C.I-1

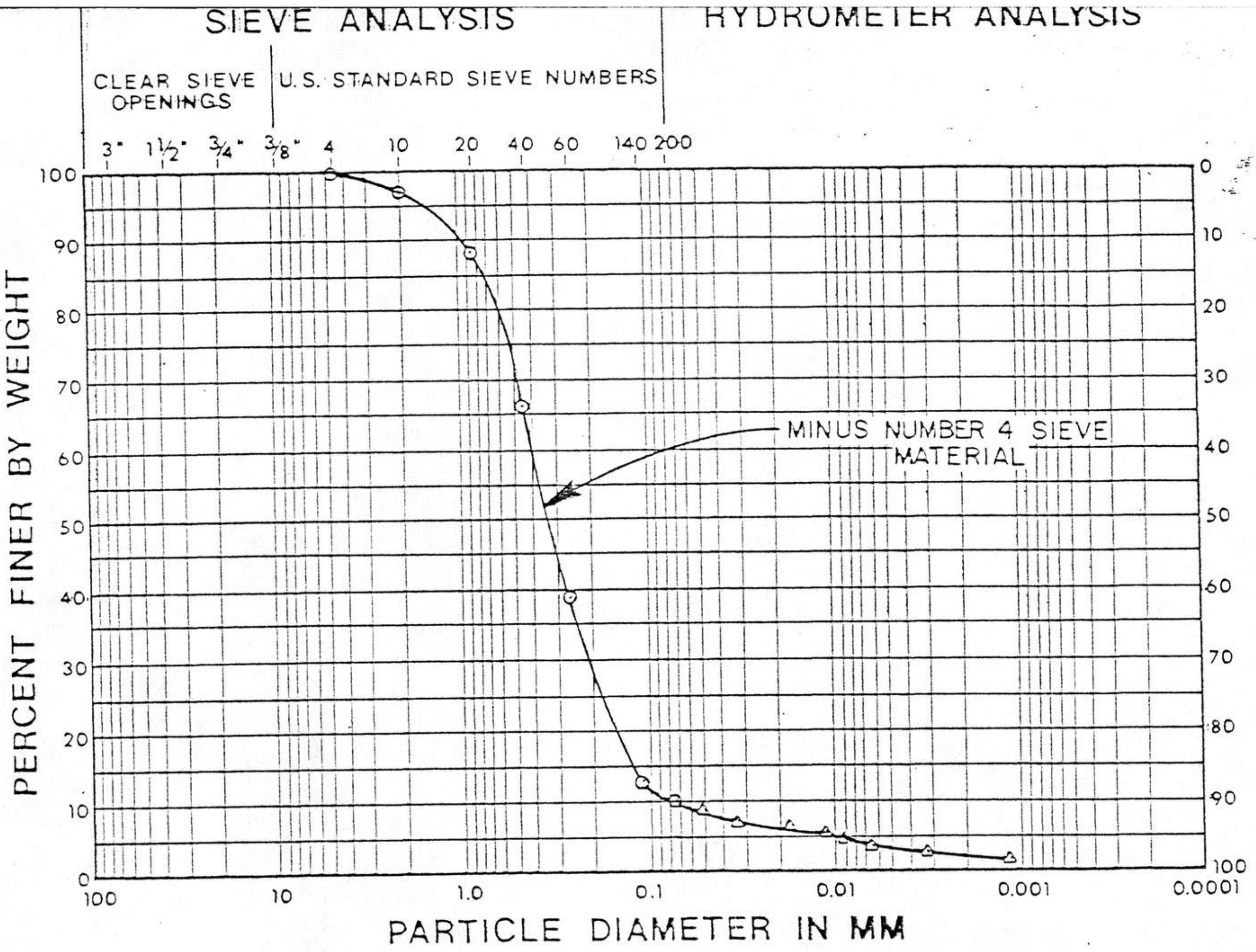
GRAIN SIZE ANALYSIS OF
GLACIAL TILL
(COMPOSITE SAMPLE NO.1)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

BY 4-27-82 APPROVED BY MJT 11.29.82 DRAWING NUMBER 18 1-A



COBBLES	GRAVEL		SAND			SILT AND CLAY FRACTION
	coarse	fine	coarse	medium	fine	

SYMBOL	BORING	SAMPLE	DEPTH	SOIL DESCRIPTION	U.S.C.S.	L.L.	P.L.	W,%
—	—	COMP 2	—	FINE TO MEDIUM SAND-TRACE OF SILT	SP-SM	—	—	—

FIGURE C.I-2

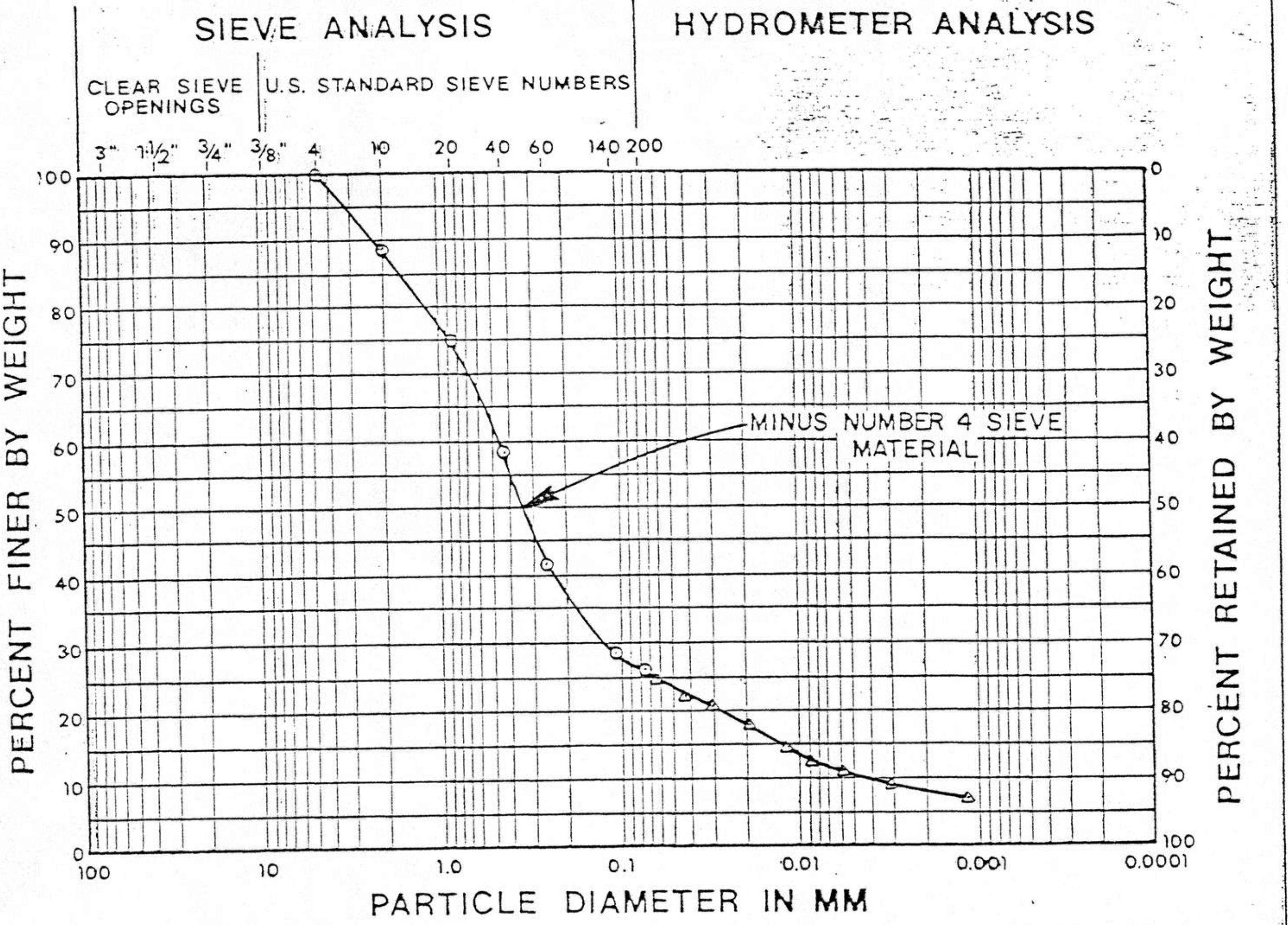
GRAIN SIZE ANALYSIS OF
STRATIFIED DRIFT
(COMPOSITE SAMPLE NO.2)

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

BY 4-27-82 APPROVED BY 11-29-82 NUMBER 1-4 22



COBBLES	GRAVEL		SAND			SILT AND CLAY FRACTION
	coarse	fine	coarse	medium	fine	

SYMBOL	BORING	SAMPLE	DEPTH	SOIL DESCRIPTION	U.S.C.S.	L.L.	P.L.	W.%
——	——	4% BENTONITE/	——	FINE TO COARSE SAND-SOME SILT-TRACE CLAY	SM	—	—	—
		TILL						

FIGURE C.I-3

GRAIN SIZE ANALYSIS OF
4% BENTONITE/TILL ADMIXTURE

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

APPENDIX D

LEACHATE SYNTHESIZATION, STABILITY MONITORING RESULTS, AND ANALYTICAL METHODOLOGY

APPENDIX D
TABLE OF CONTENTS

APPENDIX D

LEACHATE SYNTHESIZATION, STABILITY MONITORING RESULTS, AND ANALYTICAL METHODOLOGY

D.1 INTRODUCTION

This appendix presents the procedures used to create the tailing leachates used in the laboratory testing program. The leachate storage procedures and results of the stability monitoring analyses are also presented. In addition, the analytical methodologies used in the leachate analyses and analytical problems encountered in this study are presented.

D.2 TAILING LEACHATE SYNTHESIZATION

Synthetic leachates were prepared by spiking leachates generated from a constant pH 2 modified ASTM (1981) 1:4 leachate of the Crandon Project Pilot Mill tailings. The leachates were spiked to simulate mill reagents or increase solute levels to significantly above analytical detection limits to aid in solute detection during the attenuation study. The tailings were leached at pH 2 to generate a "worst-case" chemical matrix of the major metals (Ca, Mg, Na, K, Al, Si, etc.) for the synthetic leachates. The MWDF tailing leachates are anticipated to be alkaline with an approximate pH of 10 due to the mill amendments. However, due to the presence of sulfide minerals in the mill tailing, lower pH's are possible. Thus pH 2 was chosen to generate a "worst-case" chemical matrix and three pH's, pH 3, 6, and 9, were selected to study the attenuation characteristics of site sediments over the potential pH range of possible MWDF leachates.

Two leachates were generated for each pH, which have been termed Phase I and Phase II leachates. The Phase II leachates were generated after the supply of Phase I leachates were exhausted so that the column tests could be conducted for a longer time period than was first considered. The same procedures were used to generate both the Phase I and Phase II leachates.

D.2.1 Tailing Leaching

The following procedures were used to generate a tailings chemical matrix for both the Phase I and Phase II leachates:

- Dry tailings - The Pilot Mill tailings were air dried.
- Mix tailings with distilled water - The dried tailings were mixed at a 1:4 ratio with distilled water in a large 30-gallon plastic container.
- Acidify mixture - The pH of the tailings-distilled water mixture was adjusted to and maintained at pH 2 using H_2SO_4.
- Leach tailings - The tailings were leachated for 48 hours at pH 2 with constant stirring during the first 24 hours.
- Separation of tailings and leachate - The leachate was filtered through glass fiber filters to separate the tailings and leachate after the 48-hour leach period.
- pH adjustment - Three equal aliquots of leachate were placed in five-gallon plastic containers and the pH adjusted with lime to pH 3, 6, and 9.
- Leachate oxidation-matrix stabilization - The three different pH leachates were periodically stirred for 24 hours to oxidize the leachates and induce precipitation. This procedure was employed to remove solutes in the leachate chemical matrix which were at a state of saturation with readily formed mineral phases to help promote the long-term stability of the leachates.
- Precipitate removal - Each of the three leachates were filtered through 0.45 m membrane filters and placed in closed five-gallon containers. For the Phase I leachates, the containers were plastic; while glass containers were used for the Phase II leachates to help prevent oxygen diffusion through the container. Additionally, a 12-gallon closed glass container was used for the pH 9, Phase II leachate, as a larger volume of this leachate was required.
- Oxygen removal - The three leachates were purged of oxygen by bubbling nitrogen through the leachates for 60 hours.

D.2.2 Leachate Synthesization

The pH adjusted leachates (Section D.2.1) were spiked with several target chemical species, specified by Exxon, to simulate mill reagents or increase solute levels to significantly above analytical detection limits to aid the attenuation study. The spiking occurred after the oxygen was purged from the leachates. The spiking concentrations of each chemical species and the parent compounds used for spiking are shown in Table D.1.

The spiking was carried out under a nitrogen atmosphere to maintain the semi-anoxic state of the three leachates. In addition, because reduced valence state salts were used in some of the spiking solutions, the time between spike preparation and addition to the leachate was kept to a minimum.

The following solutions were prepared for spiking 17 liter aliquots of three leachate solutions. As three solutions of leachate at pH 3, 6, and 9 are to be used, the spiking solutions needed to be prepared which differed in certain details to promote the leachate stability as follows:

- For pH 3 leachate, sodium tetrathionate ($Na_2S_4O_6$) and all the metal salts were used in the spike.
- For pH 6 leachate, sodium thiosulfate ($Na_2S_2O_3$) and all the metal salts were used in the spike.
- For pH 9 leachate, ferrous sulfate was omitted from the spike and sodium thiosulfate was used.

The reagents' weights indicated in Table D.1 were weighed on an analytical balance and were transferred to different volumetric flasks, as explained below, to prepare stock spiking solutions. There were a total of eight spiking solutions for each leachate pH. The methods of their preparation follow:

Solution A - KCN was dissolved in 50 ml of distilled water in volumetric flask.

Solution B - The nitrate salts of cadmium, mercury (II), and silver were dissolved in 100 ml of distilled water in a volumetric flask.

Solution C.1 - Sodium thiosulfate was dissolved in 250 ml of distilled water in a volumetric flask for the pH 6 and 9 leachates.

Solution C.2 - Sodium tetrathionate was dissolved in 250 ml of distilled water in a volumetric flask for the pH 3 leachate.

Solution D - The indicated amount of lead nitrate was dissolved in 50 ml of distilled water in a volumetric flask.

Solution E - The indicated amounts of the sulfates of copper (II), manganese (II), and zinc, along with potassium chloride and potassium fluoride, were dissolved in 500 ml of distilled water in a volumetric flask.

Solution F.1 - For pH 3 and pH 6 leachates, a solution of $FeSO_4$ $7H_2O$, $MgSO_4$ $7H_2O$, and Na_2SO_4 $10H_2O$ was prepared in one liter of distilled water in a volumetric flask.

Solution F.2 - for pH 9 leachate, a solution of $MgSO_4$ $7H_2O$ and Na_2SO_4 $7H_2O$ was prepared in one liter of distilled water in a volumetric flask.

Solution G - The indicated amounts of selenous acid and arsenic trioxide were dissolved in 100 ml of distilled water in a volumetric flask.

Solution H - The indicated quantity of potassium chromate was dissolved in 200 ml of distilled water in a volumetric flask.

Each of the eight spiking solutions discussed above were prepared separately and the total volume of stock spiking solutions amounted to two liters. These solutions were added individully to 17 liters of respective leachates in the alphabetical order, noted above. For the Phase II pH 9 leachate, the spike amounted to four liters, which was added to 41 liters of the bulk pH 9 leachate, totaling 45 liters. To generate the two additional liters of the Phase II, pH 9 leachate spike, the volumes of the eight spiking solutions noted above (Solutions A through H) were doubled. After each addition, the leachates were stirred.

The rationale behind preparing separate stock spike solutions was to avoid any possible precipitation of mineral salts in the stock spiking solution itself. By adding separate spiking solutions, interferences or reactions likely to occur would take place in the batch leachate. Additionally, the order of addition noted above helped to achieve maximum solute levels due to the formation of complexes in the leachate.

The spiked leachates were aged seven days under a positive nitrogen atmosphere at ambient laboratory conditions to help stabilize the leachates before use in any laboratory testing program. In addition, a nitrogen atmosphere was maintained and leachate pH periodically monitored and adjusted (CaO or H_2SO_4) if more than 0.75 pH units off the target pH throughout the leachate storage period. All precipitates which formed in the spiked leachates were allowed to remain in contact with the leachate throughout its storage period.

D.3 LEACHING STABILITY MONITORING

The stability of the leachates was monitored throughout the course of the laboratory studies by analyzing select parameters. Results of the stability analyses are presented in Tables D.2 through D.4 for each of the three different pH leachates. For the analyses dated December 10, 1981 and forward on Tables D.2 through D.4, the analyses were of the leachate permeant reservoirs to the column attenuation tests (Appendix F). In addition, at the conclusion of both the Phase I and Phase II laboratory column testing, the constant head reservoirs to the four percent bentonite/till liner admixture columns (Columns K-1 and K-2), which could not be mechanically sampled during the course of the column testing, were also analyzed for major parameters of importance. These results are presented in Table D.5

D.4 LEACHATE ANALYTICAL METHODOLOGY

The leachate analytical methodologies and detection limits of this study are summarized in Table D.6. In addition, as noted in Tables D.2 through D.4, other analytical methods for total sulfur and ferrous iron determinations were initially used for comparison to the methods listed in Table D.6. The methods shown in Table D.6 for total sulfur and ferrous iron were selected for use throughout the study as they were simpler procedures, which lowered the potential for analytical errors, and/or considered more accurate methods.

As discussed in the text, cation/anion balance calculations for the leachate analyses were in reasonable agreement. However, analytical problems did occur during the study. The most significant analytical problems encountered follow:

- Chloride levels in the effluents from the sediment columns permeated with the pH 3 leachate (Figures 3-1 through 3-3) were two to four times higher than the chloride concentration of the influent pH 3 leachate. Chemical matrix interferences, specifically by ferric iron, did not appear to be causing this problem. Several dilution ratios of the solutions were used in an attempt to resolve the problem, but with no success. Additionally, soil leaching of the chloride did not seem probable; site ground water permeant effluents had only slight chloride concentrations (approximately 5 milligrams per liter). No geochemical or analytical reason for the increased chloride levels in the pH 3 leachate column effluents were found.

- Total sulfur determinations were higher than expected and often variable throughout the leachate storage period. The difference between combined sulfate and thiosulfate concentrations and the total sulfur concentrations would indicate the presence of other sulfur species in the leachates. Total sulfur concentrations, especially in the pH 3 leachate (Table D.2) were also very variable throughout the study. The cause for this variation is not known, but analytical difficulties are a possible cause.

- Total sulfur, sulfate, and specific conductance levels in some of the column test (Appendix F) effluents (Figures 3.1 through 3.10), were sometimes, like chloride, higher than influent concentrations. Higher sulfate levels may have been due to the oxidation of thiosulfate or other reduced sulfur species in the columns, especially for the earlier column effluent samples (through January 6, 1982, Appendix H) which were inadvertently not stabilized with iodine. However, this would not affect the total sulfur and specific conductance results. These may have been due to analytical problems or slugs of sulfur species moving through the columns after their initial retardation by the sediments.

- Ferrous iron was determined by two standard wet chemical methods (potassium dichromate titration and the phenanthroline-spectrophotometric method) and chemical matrix interferences caused positive errors above the total iron value for every sample analyzed by both methods. Because of the chemical matrix interferences, these results are not quantitative and can only be interpretated as indicating most of the iron present in probably in the ferrous state. The solution equilibrium modeling performed in this study (Table 3.9) confirmed ferrous iron as the dominate iron oxidation state for the pH 2, 3, and 6 leachates.

- Due to solution matrix interferences, some sensitivity in the leachate metal determinations, especially for barium and selenium, was lost in order to compensate for the necessary background corrections. Therefore, low level determinations of these and other metals had poor reproducability.

APPENDIX D
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APPENDIX D
TABLES

TABLE D.1
LEACHATE SPIKING COMPOUNDS AND AMOUNTS

CHEMICAL SPECIES	LEACHATE TARGET CONCENTRATION		SPIKING COMPOUND	MOLECULAR WEIGHT (g)	TOTAL WEIGHT OF SPIKING COMPOUND		
	mg/l	MOLES/LITER			mg/l	GRAMS PER 19 LITERS	GRAMS PER 45 LITERS
Cations:							
As	2	2.67×10^{-5}	As_2O_3	197.8	2.64	0.0502	0.1188
Cd	1	8.90×10^{-6}	$Cd(NO_3)_2 . 4H_2O$	308.5	2.74	0.0521	0.1235
Cr (VI)	0.5	9.62×10^{-6}	K_2CrO_4	194.2	1.86	0.0355	0.0841
Cu	10	1.57×10^{-4}	$CuSO_4 . 5H_2O$	249.7	39.3	0.747	1.765
Fe	50	8.96×10^{-4}	$FeSO_4 . 7H_2O$	278.0	249	4.731	-
Pb	2	9.65×10^{-6}	$Pb(NO_3)_2$	331.2	3.20	0.0608	0.1438
Mn	5	9.10×10^{-5}	$MnSO_4 . H_2O$	169.0	15.4	0.293	0.6930
Hg	0.1	4.98×10^{-7}	$Hg(NO_3)_2 . H_2O$	342.6	0.171	0.0032	0.0077
Se	1	1.27×10^{-5}	H_2SeO_3	129.0	1.64	0.0311	0.0737
Ag	0.2	1.85×10^{-6}	$AgNO_3$	169.9	0.315	0.0060	0.0141
Zn	20	3.06×10^{-4}	$ZnSO_4 . 7H_2O$	287.5	87.9	1.670	3.958
Mg	50	2.06×10^{-3}	$MgSO_4 . 7H_2O$	246.5	507.2	9.637	22.84
Na	270	-	$Na_2SO_4 . 10H_2O$	322.2	3,899	74.07	-
Na(1)	270	-	$Na_2SO_4 . 10H_2O$	322.2	4,189	-	188.5
K	30	-	KCN, KF, KCl	-	-	-	-
Anions:							
Cl^-	50	1.41×10^{-3}	KCl	74.56	105.2	1.999	4.735
$SO_4^=$	1,500	1.56×10^{-2}	$ZnSO_4$, $MgSO_4$, $MnSO_4$, $FeSO_4$, Na_2SO_4	-	-	-	-
$S_2O_3^=$(2)	500	4.46×10^{-3}	$Na_2S_2O_3 . 5H_2O$	248.1	1,105.6	21.01	49.78
$S_4O_6^=$(3)	500	2.23×10^{-3}	$Na_2S_4O_6 . 2H_2O$	306.2	682.8	12.97	-
NO_3^-	1 (as N)	-	$Cd(NO_3)_2$, $Pb(NO_3)2$, $Hg(NO_3)_2$, $AgNO_3$	-	-	-	-
F^-	2	1.05×10^{-4}	$KF . 2H_2O$	94.1	9.91	0.1880	0.4450
CN^-	0.25	9.61×10^{-6}	KCN	65.1	0.63	0.0119	0.0282

(1) For pH 9 leachate with no $FeSO_4$.

(2) For pH 6 and 9 leachates.

(3) For pH 3 leachate.

TABLE D.2

RESULTS OF pH 3 LEACHATE/COLUMN PERMEANT TABILITY MONITORING(1)

PARAMETER	UNITS	PHASE I LEACHATE									PHASE II LEACHATE			
		10/26/81	11/2/81	11/9/81	11/23/81	12/10/81	12/16/81	1/11/82	2/2/82	2/16/82	2/16/82	3/10/82	3/24/82	4/12/82
pH	pH units	3.00	3.01	3.00	2.98	3.01	3.00	2.90	3.06	2.98	3.07	3.00	3.01	2.98
Eh	mV	+586	+578	+545	+556	+752	+641	+600	+521	+387	+609	+536	+511	+587
Specific Conductance	µmhos/cm @ 25°C	8,790	8,080	7,980	7,980	9,220	8,660	8,620	8,440	8,160	7,550	7,370	7,340	7,320
Sulfate	mg/ℓ	6,000	5,000	6,700	-	6,500	-	6,200	5,600	5,100	5,700	5,100	-	5,400
Total Sulfur(2)	mg/ℓ SO$_4$	8,900	-(3)	-	-	-	-	-	-	-	-	-	-	-
Total Sulfur(4)	mg/ℓ SO$_4$	8,200	-	8,900	9,100	13,200	-	6,600	-	8,100	9,100	8,600	-	8,900
Dissolved Metals:(5)														
Ferrous Iron(6)	mg/ℓ	2,100	2,000	2,100	-	-	-	-	-	-	-	-	-	-
Ferrous Iron(7)	mg/ℓ	-	-	1,500	-	-	-	-	-	1,350	940	-	-	-
Total Iron	mg/ℓ	1,360	1,510	1,610	1,720	1,600	-	-	-	1,460	910	1,030	940	940
Arsenic	mg/ℓ	6.8	-	5.8	6.1	6.1	-	-	-	5.1	2.9	3.2	-	3.8
Copper	mg/ℓ	110	120	115	120	110	-	-	-	130	110	110	120	120
Zinc	mg/ℓ	520	550	500	525	500	-	-	-	550	450	450	430	430

(1) Referenced analytical methods presented in Table D.6 unless otherwise noted.

(2) Bromine oxidation in accordance with Furman, ed. (1962); analysis in accordance with APHA (1981).

(3) "-" indicates not determined.

(4) Oxidation with hydrogen peroxide; analysis in accordance with APHA (1981).

(5) Analysis of samples filtered through an 0.45 µm membrane filter.

(6) Potassium dichromate titration (U.S. Steel, 1929).

(7) Phenanthroline, spectrophotometric method (APHA, 1981).

TABLE D.3

RESULTS OF pH 6 LEACHATE/COLUMN PERMEANT STABILITY MONITORING(1)

PARAMETER	UNITS	PHASE I LEACHATE									PHASE II LEACHATE			
		10/26/81	11/2/81	11/9/81	11/23/81	12/10/81	12/16/81	1/11/82	2/2/82	2/16/82	2/16/82	3/10/82	3/24/82	4/12/82
pH	pH units	5.75	5.63	5.69	5.62	5.93	4.94	4.50	5.82	5.22	5.82	5.76	5.46	5.61
Eh	mV	+246	+308	+320	+326	+552	+558	+498	+498	+336	+475	+483	+472	+482
Specific Conductance	µmhos/cm @ 25°C	7,240	6,640	6,700	5,960	7,020	6,570	6,580	6,540	6,750	6,440	6,230	6,120	5,790
Sulfate	mg/ℓ	3,200	2,600	3,600	-(2)	4,050	-	4,200	3,100	3,000	4,140	3,000	-	3,100
Total Sulfur(3)	mg/ℓ SO_4	6,300	-	-	-	-	-	-	-	-	-	-	-	-
Total Sulfur(4)	mg/ℓ SO_4	6,000	-	5,200	-	6,700	-	7,800	-	6,400	6,600	6,300	-	6,100
Dissolved Metals:(5)														
Ferrous Iron(6)	mg/ℓ	1,600	1,200	1,200	-	-	-	-	-	-	-	-	-	-
Ferrous Iron(7)	mg/ℓ	-	-	700	-	-	-	-	-	550	295	-	-	-
Total Iron	mg/ℓ	730	790	660	660	610	-	705	-	610	410	470	410	410
Arsenic	mg/ℓ	0.3	0.33	0.14	0.13	0.21	-	-	-	0.023	0.52	0.38	-	0.84
Copper	mg/ℓ	0.14	0.44	0.11	0.10	0.11	-	-	-	<0.01	0.12	0.8	0.61	0.10
Zinc	mg/ℓ	140	145	135	140	140	-	-	-	140	200	180	180	180

(1) Referenced analytical methods presented in Table D.6 unless otherwise noted.

(2) "-" indicates not determined.

(3) Bromine oxidation in accordance with Furman, ed. (1962); analysis in accordance with APHA (1981).

(4) Oxidation with hydrogen peroxide; analysis in accordance with APHA (1981).

(5) Analysis of samples filtered through an 0.45 µm membrane filter.

(6) Potassium dichromate titration (U.S. Steel, 1929).

(7) Phenanthroline, spectrophotometric method (APHA, 1981).

TABLE D.4

RESULTS OF pH 9 LEACHATE/COLUMN PERMEANT STABILITY MONITORING(1)

PARAMETER	UNITS	PHASE I LEACHATE													PHASE II LEACHATE			
		10/26/81	11/2/81	11/9/81	11/23/81	12/10/81		12/16/81		1/11/82		2/2/82		2/16/82	2/16/82	3/10/82	3/24/82	4/12/82
						9I(2)	9J(3)	9I	9J	9I	9J	9I	9J					
pH	pH units	9.05	9.09	9.06	9.03	9.07	9.07	8.31	8.10	8.80	8.60	8.37	8.29	8.83	8.62	8.83	8.79	8.79
Eh	mV	+276	+318	+335	+346	+412	+412	+351	+365	+438	+459	+332	+321	+308	+487	+496	+486	+506
Specific Conductance	µmhos/cm @ 25°C	5,690	5,090	5,210	4,790	5,460	5,460	4,690	4,900	5,280	5,280	4,850	4,750	4,960	5,360	4,880	4,460	4,470
Sulfate	mg/ℓ	2,200	1,800	3,100	-(4)	2,100	2,100	-	-	2,900	2,800	2,400	2,500	2,300	2,000	2,100	-	2,100
Total Sulfur(5)	mg/ℓ SO_4	4,350	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total Sulfur(6)	mg/ℓ SO_4	3,800	-	4,350	3,800	3,900	3,400	-	-	5,900	5,700	-	-	3,900	4,200	3,900	-	3,800
Fluoride	mg/ℓ	7.6	-	-	-	-	-	-	-	-	-	4.7	5.3	6.8	2.3	-	-	1.9
Dissolved Metals:(7)																		
Ferrous Iron	mg/ℓ	0.2	0.2	0.25	-	-	-	-	-	-	-	-	-	0.5	0.5	-	-	-
Total Iron	mg/ℓ	0.4	0.1	0.1	0.1	0.1	-	-	-	<0.1	-	-	-	1.2	0.4	0.2	0.1	1.6
Arsenic	mg/ℓ	0.091	0.009	0.008	0.007	0.008	-	-	-	-	-	-	-	0.275	0.015	0.075	-	0.009
Copper	mg/ℓ	5.4	5.1	5.3	5.1	4.8	-	-	-	-	-	-	-	7.7	6.8	4.0	5.1	4.4
Zinc	mg/ℓ	0.64	0.15	0.07	0.07	0.12	-	-	-	-	-	-	-	0.27	0.28	0.3	0.04	0.04

(1) Referenced analytical methods presented in Table D.6 unless otherwise noted.

(2) 9I refers to the Phase I pH 9 leachate permeant reservoir for the glacial till (Column Designation I) columns (Appendix F). A larger single pH 9 leachate permeant reservoir was used during the Phase II column testing of the glacial till and stratified drift sediment samples.

(3) 9J refers to the Phase I pH 9 leachate permeant reservoir for the stratified drift (Column Designation J) columns (Appendix F). A larger single pH 9 leachate permeant reservoir was used during the Phase II column testing of the glacial till and stratified drift sediment samples.

(4) "-" indicates not determined.

(5) Bromine oxidation in accordance with Furman, ed. (1962); analysis in accordance with APHA (1981).

(6) Oxidation with hydrogen peroxide; analysis in accordance with APHA (1981).

(7) Analysis of samples filtered through an 0.45 m membrane filter.

TABLE D.5

RESULTS OF ANALYSES FOR PERMEANT RESERVOIRS OF THE FOUR PERCENT BENTONITE/TILL ADMIXTURE COLUMNS (K-1 AND K-2)(1)

PARAMETER	UNITS	RESERVOIR K-1		RESERVOIR K-2	
		PHASE I 2/16/82	PHASE II 4/19/82	PHASE I 2/16/82	PHASE II 4/19/82
Temperature	°C	22.4	23.0	22.4	23.0
pH	pH units	3.16	3.29	6.98	6.49
Eh	mV	+579	+492	+485	+376
Specific Conductance	µmhos/cm @ 25°C	8,230	8,140	5,800	5,740
Available Acidity	mg/ℓ $CaCO_3$	460	520	-(2)	-
Hot Acidity	mg/ℓ $CaCO_3$	760	1,950	-	-
Alkalinity	mg/ℓ $CaCO_3$	0	0	115	90
Chloride	mg/ℓ	110	83	390	260
Fluroide	mg/ℓ	0.16	0.17	6.6	0.05
Sulfate	mg/ℓ	6,800	6,200	2,900	2,700
Total Sulfur	mg/ℓ SO_4	7,600	6,900	3,600	3,400
Dissolved Metals:(3)					
Aluminum	mg/ℓ	75	34	0.3	-
Arsenic	mg/ℓ	5.0	1.1	0.167	-
Calcium	mg/ℓ	455	525	555	-
Copper	mg/ℓ	96	100	2.5	1.8
Iron	mg/ℓ	1,410	990	2.2	0.1
Magnesium	mg/ℓ	-	235	-	-
Silicon	mg/ℓ	190	130	2.4	4
Sodium	mg/ℓ	-	550	-	-
Zinc	mg/ℓ	570	490	0.1	0.1

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(1) Referenced analytical methods presented in Table D.6

(2) "-" indicates not determined.

(3) Analysis of samples filtered through an 0.45 µm membrane filter.

TABLE D.6

REFERENCED ANALYTICAL METHODOLOGIES AND DETECTION LIMITS

PARAMETER	DETECTION LIMIT(1)	ANALYTICAL METHOD	REFERENCE
Temperature	±0.1°C	Thermometric	U.S. EPA, 1979
pH	±0.01 pH units	Potentiometric	U.S. EPA, 1979
Eh	±5 mV	Potentiometric	Wood, 1976
Specific Conductance	1 µmhos/cm @ 25°C	Potentiometric	U.S. EPA, 1979
Filterable Residue	1 mg/ℓ	Gravimetric	U.S. EPA, 1979
Hot Acidity	2 mg/ℓ $CaCO_3$	Titrimetric	U.S. EPA, 1979
Available Acidity	2 mg/ℓ $CaCO_3$	Titrimetric without Oxidation	U.S. EPA, 1979
Alkalinity	2 mg/ℓ $CaCO_3$	Titrimetric	U.S. EPA, 1979
Chloride	0.5 mg/ℓ	Titrimetric	U.S. EPA, 1979
Fluoride	0.01 mg/ℓ	Distillation; Titrimetric	U.S. EPA, 1979
Nitrate	0.1 mg/ℓ N	Brucine; Spectrophotometric	U.S. EPA, 1979
Sulfate	1 mg/ℓ	Thiosulfate Stabilization with Iodine; Turbidimetric; Spectrophotometric	Stabilization Guo and Jank (1980); Analysis APHA (1981)
Thiosulfate	1 mg/ℓ	Iodimetric Titration	Guo and Jank (1980)
Total Sulfur	1 mg/ℓ SO_4	Peroxide Oxidation; Turbidimetric; Spectrophotometric	Analysis APHA (1981)
Cyanide	0.01 mg/ℓ	Colorimetric; Spectrophotometric	U.S. EPA, 1979
Metals:			
Aluminum	0.1 mg/ℓ	AAS,(2) Direct Aspiration	U.S. EPA, 1979
Arsenic	0.002 mg/ℓ	AAS, HGA(3)	U.S. EPA, 1979
Barium	0.01 mg/ℓ	AAS, Direct Aspiration - HGA	U.S. EPA, 1979
Cadmium	0.01 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Calcium	0.005 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Chromium	0.01 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Copper	0.01 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Iron:			
Ferrous	0.1 mg/ℓ	Phenanthroline, Spectrophotometric	APHA, 1981
Total	0.1 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Lead	0.01 mg/ℓ	AAS, HGA	U.S. EPA, 1979
Magnesium	0.005 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Manganese	0.1 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Mercury	0.0005 mg/ℓ	ASS, Cold Vapor	U.S. EPA, 1979
Potassium	0.005 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Selenium	0.001 mg/ℓ	AAS, HGA	U.S. EPA, 1979
Silicon	0.1 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Silver	0.001 mg/ℓ	AAS, HGA	U.S. EPA, 1979
Sodium	0.005 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979
Zinc	0.01 mg/ℓ	AAS, Direct Aspiration	U.S. EPA, 1979

(1) Detection limits for recommended sample volume of analytical method. Due to the limited volume of some samples, especially column effluent samples, detection limits for some analyses were slightly higher due to the dilution requirements to obtain proper sample size for analysis.

(2) AAS is an abbreviation for Atomic Absorption Spectroscopy.

(3) HGA is an abbreviation for Heated Graphite Atomizer.

APPENDIX E

PROCEDURE FOR THE MEASUREMENT AND CALCULATION OF BATCH DISTRIBUTION RATIOS

APPENDIX E

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APPENDIX E

PROCEDURE FOR THE MEASUREMENT AND CALCULATION OF BATCH DISTRIBUTION RATIOS

E.1 INTRODUCTION

This appendix covers the procedures used for the determination and calculation of batch distribution ratios for mine waste disposal facility (MWDF) foundation soils and the four percent bentonite/till admixture liner material. Results of the distribution ratio determinations are also presented.

A short-term batch method was used to determine constant pH distribution ratios (K_r) for the following chemical species in accordance with the proposed ASTM (1981) method:

- Arsenic
- Cadmium
- Chromium
- Copper
- Iron
- Lead
- Manganese
- Mercury
- Selenium
- Silver
- Zinc
- Cyanide

To enhance the reliability and site-specific characteristics of the K_r determinations, duplicate samples of the four percent bentonite/till liner admixture and two composite foundation soil samples (fine-grained glacial till and coarse-grained stratified drift) from the Site 41 MWDF (Appendix C), and synthetic tailings leachate generated at three pH's (Appendix D) were used in the testing program. Additionally, calcium oxide and sulfuric acid were used to adjust and maintain the leachate pH, as calcium carbonate and sulfuric acid are the probable sources of neutralization potential and acidity, respectively, in the disposal area. Also, the attenuation studies, as far as possible, were carried out under a nitrogen atmosphere to maintain semi-anoxic conditions in the leachates.

E.2 DEFINITIONS AND ASSUMPTIONS

The K_r for a specific chemical species may be defined as the ratio of the mass sorbed onto a solid phase to the mass remaining in solution and can be expressed as (Freeze and Cherry, 1979):

$$K_r = \frac{\text{mass of solute on the solid phase per unit mass of solid phase}}{\text{concentration of solute in solution}}$$

The dimensions of this expression reduce to cubic length per mass (L^3/M). It is conventional to express K_r in units of milliliters (or cubic centimeters) of solution per gram of sediment.

Assumptions of this study included:

- Temperature differences between in situ (approximately 6 degrees to 12 degrees Centigrade) and laboratory experimental (20 degrees to 23 degrees Centigrade) conditions did not significantly affect the experimental results.
- Semi-anoxic conditions were assumed to be the dominant environment during sediment-solute interaction; that is, several interacting species in the leachate were assumed to be in their reduced valence state due to leachate generation techniques and maintenance of a nitrogen atmosphere above the samples during testing.

E.3 SOIL AND LEACHATE PREPARATION

The following three soil samples were used in the batch distribution ratio determinations:

- Glacial Till (Composite Sample No. 1)
- Stratified Drift (Composite Sample No. 2)
- Four Percent Bentonite/Till Liner Admixture

Duplicate samples of each of these three samples were air-dried and disaggregated to their inherent grain size. Detailed procedures employed in the preparation of soils are discussed in Appendix C. The disaggregated soil samples were passed through a "nonbias" riffle splitter and 225.0-gram portions (exact weight recorded) of the split samples were placed in one-liter plastic centrifuge bottles. All plastic and glasswares used in the distribution ratio study were acid cleaned and thoroughly rinsed with distilled water.

Synthetic leachates generated at either two or three pH values, depending on the soil being tested, were used in the distribution ratio determinations. The methods of leachate generation and analysis are presented in Appendix D.

E.4 EXPERIMENTAL

All distribution ratio determinations discussed below were performed at room temperature (20 to 23 degrees Centigrade) and under a nitrogen atmosphere. The nitrogen atmosphere was maintained by placing a positive nitrogen pressure on all reaction bottles before sealing or performing all pH monitoring, filtering, and sample preservations in a glove box maintained under a positive nitrogen atmosphere. The experimental design used for the laboratory measurement of distribution ratios is presented in Table E.1.

Nine hundred milliliter aliquots of respective leachates were added to the bottles containing sediment samples as shown in Table E.1. Out of the six bottles containing fine-grained till, two were filled with pH 3.0 leachates (900 milliliters each), two with pH 6.0 leachates, and the last two with pH 9.0 leachates. Similarly, of the six bottles containing stratified drift, two were filled with pH 3.0 leachates, two with pH 6.0 leachates, and two with pH 9.0 leachates. Out of four bottles containing the four percent bentonite/till liner admixture, two were filled with pH 3.0 leachate and the other two with pH 9.0 leachate. Additionally, one control sample (no soil present) was prepared for each of the three pH leachates (Table E.1) by adding one liter aliquots of each leachate to plastic centrifuge bottles. The exact amounts of leachate and soil sample in each bottle were recorded on data sheets presented in Appendix H (laboratory data).

The bottles (22) with their contents were placed in a tumble agitator and periodically shaken (slow tumbling) for a total of six hours during the first 24-hour period. After shaking, the contents were allowed to stand for the remaining 24-hour reaction period.

During the course of the 48-hour reaction period, each soil-leachate suspension was pH monitored and adjusted at periodic intervals. The pH adjustments were carried out using calcium oxide or sulfuric acid in a glove box maintained under a nitrogen atmosphere. The pH of the suspension at each monitoring period and the amount of acid or base added to bring the suspension to the required pH are presented in the data sheets of Appendix H, along with monitoring time.

After the 48-hour reaction period, the soil-leachate mixtures were centrifuged for 15 to 20 minutes (or until clear in appearance) at 2,500 rpm and the clear supernatants carefully decanted into clean one-liter plastic sample bottles under a nitrogen atmosphere in the glove box. The three control samples were centrifuged, but not transferred to other bottles. After centrifugation, the supernatants and control samples were filtered through a 0.45 micron membrane filter to remove all suspended solids from the supernatant leachates. A 250-mililiter aliquot of all filtered leachates was immediately preserved with nitric acid for metal analyses. Similarly, a 500-milliliter aliquot of each leachate sample was preserved with sodium hydroxide for cyanide analysis. The remaining leachate sample was used for wet chemical analyses. Results of the leachate analytical determinations are presented in Tables E.2 and E.4.

E.5 DISTRIBUTION RATIO CALCULATION AND SUMMARY OF RESULTS

The distribution ratio, K_T, is calculated by dividing the amount of species-of-interest adsorbed per unit weight of adsorbent by the amount of species-of-interest remaining in a unit volume of reacting solution, as outlined in Table E-5 (ASTM, 1981). The control sample analyses were used to evaluate possible sources of error in the testing procedure, determine losses due to adsorption of trace metals onto container walls, and to calculate the effect of leachate neutralization upon the K_r values determined at higher pH's. A summary of determined K_r values is presented in Tables E.6 through E.8.

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REFERENCES

American Society for Testing Materials (ASTM), 1981, "Proposed Test Method for Distribution Ratios by the Short-Term Batch Method," ASTM Committee D-18.14, Philadelphia, PA.

Freeze, A. R. and J. A. Cherry, 1979, Groundwater, Prentice-Hall, New Jersey, 604 pp.

APPENDIX E
TABLES

TABLE E.1

EXPERIMENTAL DESIGN FOR THE MEASUREMENT OF DISTRIBUTION RATIOS

LEACHATE pH	NUMBER OF BOTTLES/SOIL SAMPLE[1] GLACIAL TILL (Composite No. 1)	STRATIFIED DRIFT (Composite No. 2)	4% BENTONITE/TILL ADMIXTURE	CONTROL SAMPLE	TOTAL
3.0	2	2	2	1	7
6.0	2	2	-[2]	1	5
9.0	2	2	2	1	7
Total	6	6	4	3	19

[1] Except for control samples, each bottle contains 225.0 grams of soil sample and 900 milliliters of leachate. The control samples contained only 1,000 milliliters of leachate. See Appendix C for composition of composite samples.

[2] "-" indicates no batch test at this pH.

TABLE E.2

BATCH DISTRIBUTION RATIO ANALYTICAL RESULTS FOR pH 3 LEACHATE(1)

PARAMETER	UNITS	BULK LEACHATE	CONTROL SAMPLE (No. 7)	GLACIAL TILL (Composite Sample No. 1)		STRATIFIED DRIFT (Composite Sample No. 2)		4% BENTONITE/TILL ADMIXTURE	
				SAMPLE NO. 1	SAMPLE NO. 2	SAMPLE NO. 3	SAMPLE NO. 4	SAMPLE NO. 5	SAMPLE NO. 6
Initial Measurements:									
Temperature	°C	23.4	–(2)	–	–	–	–	–	–
pH(3)	pH units	3.00	–	–	–	–	–	–	–
Eh(3)	mV	+576	–	–	–	–	–	–	–
Specific Conductance	µmhos/cm @ 25°C	8,790	–	–	–	–	–	–	–
Hot Acidity	mg/ℓ $CaCO_3$	4,810	–	–	–	–	–	–	–
Alkalinity	mg/ℓ $CaCO_3$	0	–	–	–	–	–	–	–
Final Measurements:									
Temperature	°C	–	24.3	24.3	24.3	24.3	24.3	24.3	24.3
pH(3)	pH units	–	3.00	3.30	3.40	3.10	3.00	3.00	3.10
Eh(3)	mV	–	+546	+526	+496	+536	+546	+546	+556
Specific Conductance	µmhos/cm @ 25°C	–	7,100	7,350	7,350	7,600	8,370	8,110	7,600
Hot Acidity	mg/ℓ $CaCO_3$	–	5,110	4,540	4,480	4,950	4,900	4,680	4,670
Alkalinity	mg/ℓ $CaCO_3$	–	0	0	0	0	0	0	0
Cyanide	mg/ℓ	0.07	0.09	0.23	0.05	0.06	0.18	0.07	0.08
Dissolved Metals:(4)									
Arsenic	mg/ℓ	6.8	6.6	4.5	3.5	4.1	2.9	3.8	2.0
Cadmium	mg/ℓ	2.31	2.37	2.21	2.19	2.27	2.28	2.17	2.17
Chromium	mg/ℓ	2.60	2.90	0.61	0.55	1.30	1.30	0.96	1.10
Copper	mg/ℓ	110	110	92	73	100	100	94	97
Iron	mg/ℓ	1,100	1,200	1,100	1,100	1,100	1,100	1,000	1,000
Lead	mg/ℓ	2.0	2.1	0.5	0.4	0.8	0.8	0.5	0.5
Manganese	mg/ℓ	49	49	64	62	60	58	67	66
Mercury	mg/ℓ	0.0022	0.0028	<0.0005	<0.0005	<0.0005	<0.0005	0.0023	0.0009
Selenium	mg/ℓ	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silver	mg/ℓ	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Zinc	mg/ℓ	520	510	500	490	520	510	480	480

(1) Referenced analytical methods presented in Appendix D.

(2) "–" indicates not determined.

(3) Determined under a nitrogen atmosphere.

(4) Analysis of sample filtered through an 0.45 µm membrane filter. Filtering and preservation conducted under a nitrogen atmosphere.

TABLE E.3

BATCH DISTRIBUTION RATIO ANALYTICAL RESULTS FOR pH 6 LEACHATE(1)

PARAMETER	UNITS	BULK LEACHATE	CONTROL SAMPLE (No. 12)	GLACIAL TILL (Composite Sample No. 1)		STRATIFIED DRIFT (Composite Sample No. 2)	
				SAMPLE NO. 8	SAMPLE NO. 9	SAMPLE NO. 10	SAMPLE NO. 11
Initial Measurements:							
Temperature	°C	23.4	-(2)	-	-	-	-
pH(3)	pH units	5.75	-	-	-	-	-
Eh(3)	mV	+236	-	-	-	-	-
Specific Conductance	µmhos/cm @ 25°C	7,240	-	-	-	-	-
Hot Acidity	mg/ℓ CaCO$_3$	1,990	-	-	-	-	-
Alkalinity	mg/ℓ CaCO$_3$	5	-	-	-	-	-
Final Measurements:							
Temperature	°C	-	24.3	24.3	24.3	24.3	24.3
pH(3)	pH units	-	5.50	5.40	5.40	5.40	5.40
Eh(3)	mV	-	+316	+296	+316	+296	+296
Specific Conductance	µmhos/cm @ 25°C	-	7,100	7,100	7,100	6,600	7,100
Hot Acidity	mg/ℓ CaCO$_3$	-	1,860	1,620	1,560	1,670	1,730
Alkalinity	mg/ℓ CaCO$_3$	-	2	10	10	5	7
Cyanide	mg/ℓ	0.11	3.44	2.21	0.19	3.73	5.51
Dissolved Metals:(4)							
Arsenic	mg/ℓ	0.3	0.1	0.091	0.013	0.013	0.014
Cadmium	mg/ℓ	0.10	0.09	0.02	0.02	0.01	0.02
Chromium	mg/ℓ	0.002	<0.001	0.003	<0.001	<0.001	<0.001
Copper	mg/ℓ	0.14	0.10	0.07	<0.001	0.03	0.03
Iron	mg/ℓ	730	690	530	510	630	590
Lead	mg/ℓ	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Manganese	mg/ℓ	43	42	48	49	50	48
Mercury	mg/ℓ	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Selenium	mg/ℓ	0.01	0.01	0.01	0.01	<0.01	<0.01
Silver	mg/ℓ	<0.001	<0.001	0.069	0.029	<0.001	<0.001
Zinc	mg/ℓ	140	120	93	93	110	110

(1) Referenced analytical methods presented in Appendix D.

(2) "-" indicates not determined.

(3) Determined under a nitrogen atmosphere.

(4) Analysis of samples filtered through an 0.45 µm membrane filter. Filtering and preservation conducted under a nitrogen atmosphere.

TABLE E.4

BATCH DISTRIBUTION RATIO ANALYTICAL RESULTS FOR pH 9 LEACHATE(1)

PARAMETER	UNITS	BULK LEACHATE	CONTROL SAMPLE (No. 19)	GLACIAL TILL (Composite Sample No. 1)		STRATIFIED DRIFT (Composite Sample No. 2)		4% BENTONITE/TILL ADMIXTURE	
				SAMPLE NO. 13	SAMPLE NO. 14	SAMPLE NO. 15	SAMPLE NO. 16	SAMPLE NO. 17	SAMPLE NO. 18
Initial Measurements:									
Temperature	°C	23.4	-(2)	-	-	-	-	-	-
pH(3)	pH units	9.05	-	-	-	-	-	-	-
Eh(3)	mV	+266	-	-	-	-	-	-	-
Specific Conductance	µmhos/cm @ 25°C	5,690	-	-	-	-	-	-	-
Hot Acidity	mg/ℓ $CaCO_3$	0	-	-	-	-	-	-	-
Alkalinity	mg/ℓ $CaCO_3$	30	-	-	-	-	-	-	-
Final Measurements:									
Temperature	°C	-	24.3	24.3	24.3	24.3	24.3	24.3	24.3
pH(3)	pH units	-	9.00	8.90	8.90	8.90	9.00	8.85	8.80
Eh(3)	mV	-	+326	+356	+356	+346	+366	+356	+366
Specific Conductance	µmhos/cm @ 25°C	-	4,560	4,560	4,460	4,560	4,560	4,660	4,660
Hot Acidity	mg/ℓ $CaCO_3$	-	0	0	0	0	0	0	0
Alkalinity	mg/ℓ $CaCO_3$	-	17	19	19	19	18	55	47
Cyanide	mg/ℓ	0.16	0.28	0.15	0.19	1.24	0.52	0.14	1.04
Dissolved Metals:(4)									
Arsenic	mg/ℓ	0.091	0.042	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cadmium	mg/ℓ	0.27	0.24	0.01	0.01	0.01	0.02	0.02	0.01
Chromium	mg/ℓ	0.039	0.031	0.004	0.003	0.004	0.004	0.007	0.010
Copper	mg/ℓ	5.4	5.7	0.46	0.50	1.33	1.08	0.72	0.45
Iron	mg/ℓ	0.4	0.2	0.7	0.2	0.2	0.2	0.2	0.2
Lead	mg/ℓ	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Manganese	mg/ℓ	0.70	0.54	0.07	0.02	0.05	0.28	0.15	0.05
Mercury	mg/ℓ	0.121	0.121	0.019	0.018	0.019	0.011	0.114	0.97
Selenium	mg/ℓ	0.05	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silver	mg/ℓ	0.12	0.13	0.049	0.039	0.039	0,008	0.13	0.12
Zinc	mg/ℓ	0.64	0.34	0.17	0.02	0.03	0.02	0.03	0.02

---

(1) Referenced analytical methods presented in Appendix D.

(2) "-" indicates not determined.

(3) Determined under a nitrogen atmosphere.

(4) Analysis of sample filtered through an 0.45 µm membrane filter. Filtering and preservation conducted under a nitrogen atmosphere.

TABLE E.5

CALCULATION METHOD BATCH DISTRIBUTION RATIO DETERMINATIONS[1]

The distribution ratio is given by:

$$K_r = \frac{(f_m)(V_l)}{(f_s)(W_m)}$$

where

K_r = the distribution ratio in ml/g,

f_s = the fraction of total activity in solution which equals the total concentration in solution assuming the activity coefficients of a given solute were the same before and after reaction of the solution with the soil. In other words, ionic strength remains constant. Making this assumption, f_s is found from the concentrations of the solute after the solution has reacted with the soil divided by the concentration (of the same units) of the solute before the solution was allowed to react with the soil,

f_m = The fraction of activity adsorbed on the mineral (soil), or making the same assumption as to activity coefficients; $f_m = 1 - f_s$,

V_l = The volume of leachate in milliliters equilibrated with W_m (Appendix H), and

W_m = The weight of mineral (soil material) in grams equilibrated with the leachate (Appendix H).

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(1) After ASTM, 1981.

TABLE E.6
SUMMARY OF DISTRIBUTION RATIO (K_r) DETERMINATIONS FOR pH 3 LEACHATE BATCH TESTS

SOLUTE	DISTRIBUTION RATIO(1) (mℓ/g)					
	GLACIAL TILL (Composite Sample No. 1)		STRATIFIED DRIFT (Composite Sample No. 2)		4% BENTONITE/TILL ADMIXTURE	
	SAMPLE NO. 1	SAMPLE NO. 2	SAMPLE NO. 3	SAMPLE NO. 4	SAMPLE NO. 5	SAMPLE NO. 6
Arsenic	1.9	3.5	2.4	5.1	2.9	9.2
Cadmium	0.3	0.3	0.2	0.2	0.4	0.4
Chromium	15	17	4.9	4.9	8.1	6.5
Copper	0.8	2.0	0.4	0.4	0.7	0.5
Iron	0.4	0.4	0.4	0.4	0.8	0.8
Lead	12.8	17	6.5	6.5	12.8	12.8
Manganese	0(2)	0	0	0	0	0
Mercury	>18(3)	>18	>18	>18	0.9	8.4
Selenium	BD(4)	BD	BD	BD	BD	BD
Silver	BD	BD	BD	BD	BD	BD
Zinc	0.1	0.2	0	0	0.3	0.3
Cyanide	0	3.2	2.0	0	1.1	0.5

(1) Distribution ratios calculated using the pH 3 control sample analysis (Sample No. 7, Table E.2) as the initial leachate concentration before contact with the sediment samples.

(2) K_r values reported as "0" represent either no removal of the solute from solution or the solute was leached from the sediment sample; "0" represents no attenuation for this leachate pH.

(3) ">" indicates the concentration in the sediment-reacted leachate was below the analytical detection limit. The lower the K_r values with ">" signs, the lower the initial concentration of that metal in the leachate; i.e., its concentration was near the detection limit before contact with the sediment sample. Therefore, the values reported as greater than are the lower limit, and the detectable concentration of these metals were sorbed or removed from solution.

(4) K_r values reported as "BD" represent soluble metal levels which were below the detection limit in either the control sample or before the leachate was allowed to react with the sediment.

TABLE E.7

SUMMARY OF DISTRIBUTION RATIO (K_r) DETERMINATIONS FOR pH 6 LEACHATE BATCH TESTS

SOLUTE	DISTRIBUTION RATIO (mℓ/g)								
	GLACIAL TILL (Composite Sample No. 1)				STRATIFIED DRIFT (Composite Sample No. 2)				CONTROL SAMPLE (No. 12)
	SAMPLE NO. 8		SAMPLE NO. 9		SAMPLE NO. 10		SAMPLE NO. 11		
	pH 6(1)	pH 3 to 6(2)	pH 6(1)	pH 3 to 6(2)	pH 6(1)	pH 3 to 6(2)	pH 6(1)	pH 3 to 6(2)	pH 3 to 6(2)
Arsenic	0.4	286	27	2,027	27	2,027	25	1,882	260
Cadmium	14	470	14	470	32	944	14	470	101
Chromium	BD(3)	3,863	BD	>11,596(4)	BD	>11,596	BD	>11,596	>11,596
Copper	1.7	6,282	6.0	10,996	9.3	14,663	9.3	14,663	4,396
Iron	1.2	5.1	1.4	5.4	0.4	3.6	0.7	4.1	3.0
Lead	BD	>836	BD	>836	BD	>836	BD	>836	>836
Manganese	0(5)	0.1	0	0	0	0	0	0.1	0.7
Mercury	BD	>18	BD	>18	BD	>18	BD	>18	>18
Selenium	0	0	0	0	BD	BD	BD	BD	0
Silver	0	0	0	0	BD	BD	BD	BD	BD
Zinc	1.2	18	1.2	18	0.4	14	0.4	14	13
Cyanide(6)	0	0	0	0	0	0	0	0	0

(1) Distribution ratios calculated using the pH 6 control sample analysis (Sample No. 12, Table E.3) as the initial leachate concentration before contact with the sediment samples.

(2) Distribution ratios calculated using the pH 3 control sample analysis (Sample No. 7, Table E.2) as the initial leachate concentration before contact with the sediment samples.

(3) K_r values reported as "BD" represent soluble metal levels which were below the detection limit in either the control sample or before the leachate was allowed to react with the sediment.

(4) ">" indicates the concentration in the sediment-reacted leachate was below the analytical detection limit. The lower the K_r values with ">" signs, the lower the initial concentration of that metal in the leachate; i.e., its concentration was near the detection limit before contact with the sediment sample. Therefore, the values reported as greater than are the lower limit, and the detectable concentration of these metals were sorbed or removed from solution.

(5) K_r values reported as "0" represent either no removal of the solute from solution or the solute was leached from the sediment sample; "0" represents no attenuation for this leachate pH.

(6) Control sample and several batch leachates had cyanide concentrations significantly greater than bulk leachate (Table E.3) but near the limits of analytical detection; thus, have conservatively assumed no chemical attenuation of cyanide for pH 6 leachate batch tests.

TABLE E.8

SUMMARY OF DISTRIBUTION RATIO (K_r) DETERMINATIONS FOR pH 9 LEACHATE BATCH TESTS

DISTRIBUTION RATIO(1)
(mℓ/g)

SOLUTE	GLACIAL TILL (Composite Sample No. 1)				STRATIFIED DRIFT (Composite Sample No. 2)				4% BENTONITE/TILL ADMIXTURE				CONTROL SAMPLE (No. 19)
	SAMPLE NO. 13		SAMPLE NO. 14		SAMPLE NO. 15		SAMPLE NO. 16		SAMPLE NO. 17		SAMPLE NO. 18		
	pH 9(1)	pH 3 to 9(2)	pH 9(1)	pH 3 to 9(2)	pH 9(1)	pH 3 to 9(2)	pH 9(1)	pH 3 to 9(2)	pH 9(1)	pH 3 to 9(2)	pH 9(1)	pH 3 to 9(2)	pH 3 to 9(2)
Arsenic	>164(3)	>26,400	>164	>26,400	>164	>26,400	>164	>26,400	>164	>26,400	>164	>26,400	625
Cadmium	92	944	92	944	92	944	44	470	44	470	92	944	36
Chromium	27	2,896	37	3,863	27	2,896	27	2,896	14	1,653	8.4	1,156	370
Copper	46	953	42	876	13	327	17	403	28	607	47	974	73
Iron	0(4)	6,853	0	24,000	0	24,000	0	24,000	0	24,000	0	24,000	24,000
Lead	BD(5)	>836	BD	>836	BD	>836	BD	>836	BD	>836	BD	>836	>836
Manganese	27	2,796	104	9,796	39	3,916	3.7	696	10	1,303	39	3,916	359
Mercury	21	0	23	0	21	0	40	0	0.3	0	0	0	0
Selenium	>8	BD	>8	BD	>8	BD	>8	BD	>8	BD	>8	BD	0
Silver	6.6	0	9.3	0	9.3	0	61	0	0	0	0.3	0	0
Zinc	4.0	12,000	64	102,000	41	68,000	64	102,000	41	68,000	64	102,000	5,996
Cyanide	3.5	0	1.9	0	0	0	0	0	4.0	0	0	0	0

---

(1) Distribution ratios calculated using the pH 9 control sample analysis (Sample No. 19, Table E.4) as the initial leachate concentration before contact with the sediment samples.

(2) Distribution ratios calculated using the pH 3 control sample analysis (Sample No. 7, Table E.2) as the initial leachate concentration before contact with the sediment sample.

(3) ">" indicates the concentration in the sediment-reacted leachate was below the analytical detection limit. The lower the K_r values with ">" signs, the lower the initial concentration of that metal in the leachate; i.e., its concentration was near the detection limit before contact with the sediment sample. Therefore, the values reported as greater than are the lower limit, and the detectable concentration of these metals were sorbed or removed from solution.

(4) K_r values reported as "0" represent either no removal of the solute from solution or the solute was leached from the sediment sample; "0" represents no attenuation for this leachate pH.

(5) K_r values reported as "BD" represent soluble metal levels which were below the detection limit in either the control sample or before the leachate was allowed to react with the sediment.

APPENDIX F

PROCEDURE FOR THE MEASUREMENT OF SOLUTE FRONT ADVANCEMENT AND CALCULATION OF RETARDATION FACTORS

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APPENDIX F

PROCEDURE FOR THE MEASUREMENT OF SOLUTE FRONT ADVANCEMENT AND CALCULATION OF RETARDATION FACTORS

F.1 INTRODUCTION

This Appendix covers the procedures used for the measurement of solute front advancement and calculation of column retardation factors for the composite samples and bentonite/till admixture liner columns permeated with the pH 3, 6, and 9 tailings leachates. It also describes the tests used to assess relative changes in the permeabilities of the column samples after prolonged contract with the leachates.

Distribution ratios are not easily determined for mobile chemical species, total dissolved solids, or acidity. Therefore, it is preferable to directly measure retardation factors for such parameters. To directly measure the retardation factor of chemical parameters, the porous media is permeated with a test solution and the rate of movement of the chemical parameter of interest within the porous media is compared with a selected tracer. (A tracer, such as chloride, is a chemical species which does not significantly react with the geologic media or change its chemical characteristics during the test period.) To calculate the degree of retardation, first the advancement of the half concentration of the tracer is measured and recorded. In addition, effluent samples from the porous media are concurrently monitored for the chemical parameters of interest. The test is continued until the concentration of chemical parameters of interest in the permeant effluent exceeds the half concentration of the source or until sufficient field time has been simulated to show the chemical parameter of interest is essentially immobile. The accumulated flow required for the concentration of the chemical parameters and tracer to reach the half concentration of their original source is noted. The ratio of the flow for the chemical parameters of interest to the flow for the tracer to reach their half concentrations will yield the retardation factor for the chemical parameters of interest.

F.2 STUDY ASSUMPTIONS

Assumptions of this test included:

- Field permeabilities are related to the density of the sediments, such that if disaggregated sediment samples are recompacted to their in situ density, the permeability of the samples should approximate the field permeability. This assumption should be valid unless preferred flow paths (i.e., fractures) control field measured permeabilities.
- The retardation factor for chloride advancement in the permeating leachates is one. This assumption, while not totally true, will be valid within the expected experimental error of testing as chloride does not participate in sorption-precipitation reactions to the extent that other solutes do.
- Specific conductance can be used to estimate the filterable residue/dissolved solids content of the permeant effluents. Because specific conductance is a measure of the electrically charged solutes in a solution and dissolved solids is a measure of the total solute concentration, a correlation between these two measurements is possible. This correlation was determined for the leachates, so that the assumption is considered valid. (A dissolved solids determination requires about 500 milliliters of fluid, which is about three times the pore volume of each column sample. Thus, there is the need for an analysis to approximate the dissolved solids content of each permeant effluent aliquot sampled.)
- Temperature differences between in situ (approximately 6 degrees to 12 degrees C) and laboratory experimental (20 degrees to 23 degrees C) conditions will not significantly affect the experiment result.

F.3 SOIL AND LEACHATE PREPARATION

Column attenuation or solute front advancement tests were conducted using split fractions of the same two composite soil samples and leachates used in the batch attenuation tests (Appendix E). In addition, the four percent bentonite/till admixture was also used in this test, but unlike the liner sample used in the batch test, it was mixed wet (about nine percent water content) to better simulate field placement. A total of 10 column tests were conducted using the experimental design shown in Table F.1. Duplicate column tests of the glacial till and stratified drift were conducted using the pH 9 leachate as a permeant to examine the reproducibility of the tests and because the tailings leachate will likely be alkaline in the MWDF.

The composite samples were recompacted to their field density and water contents (Table F.1) to approximate field permeability. A Proctor test (Figure F-1) was performed on the four percent bentonite/till admixture, and these samples were recompacted to approximately 95 percent of the Standard Proctor (probable field placement). As noted in Chapter 3.0 and Appendix D, the leachate permeants used in this test were maintained under a nitrogen atmosphere and periodically monitored for the parameters of interest.

To determine the correlation between specific conductance and filterable residue/dissolved solids, the leachates were diluted by 20, 30, 40, 45, 50, and 60 percent with distilled water and the specific conductance of each leachate dilution determined. Because distilled water was used as the dilutant, the total dissolved solids of each leachate dilution could be calculated from the nondiluted leachate total dissolved solids concentration. A linear regression between specific conductance (SpC) and total dissolved solids (TDS) of the diluted leachates yielded the following relationships:

- pH 3 leachate:

  $TDS = 0.662 (SpC) - 21.69$ $r = 0.998$

- pH 6 leachate:

  $TDS = 0.782 (SpC) + 40.57$ $r = 0.998$

- pH 9 leachate:

  $$TDS = 0.561\ (SpC) + 278.0 \qquad r = 0.993$$

where

TDS is expressed as mg/ℓ; and
SpC is expressed as μmhos/cm @ 25°C.

F.4 PROCEDURE

Each remolded soil sample was placed inside a latex membrane and consolidated in a triaxial cell as illustrated in Figure F-2. All samples were saturated with Crandon Project ground water and their permeabilities determined prior to introducing leachate as a permeant. An initial Crandon Project ground water permeability of each sample was determined as a reference for comparison to later long-term permeabilities of the samples when leachate was used as the permeant. The Crandon Project ground water permeant effluent was chemically monitored after steady-state flow was achieved to establish baseline soil leachate concentrations for select parameters from each soil sample.

Once the permeability of these soil samples to Crandon Project ground water was established, the permeant to the samples was switched to the leachates. As shown in Table F.1, due to the permeability (Chapter 3.0) of the glacial till and stratified drift samples and the physical constraints of the column test system, a constant head could not be placed upon these samples which would maintain a reasonable flow rate. In this study, an attempt was made to have no more than one pore volume (sample-free space in the column) of flow from each column per week to allow sufficient time for chemical reactions to occur. Therefore, both the glacial till and stratified drift columns were tested under constant flow conditions using a peristaltic pump as the leachate permeant driving force. The bentonite/till liner admixture samples were tested under a constant hydraulic gradient so that changes in the permeability could be continually monitored.

The differential hydraulic pressures applied across the column samples for permeability determinations are presented in Table F.1. Constant head permeability measurements, modified after ASTM [D 2434-68(74)] were used to determine both initial ground water reference and final leachate permeabilities of the glacial till composite and bentonite/till admixture samples. A variable head test (Lambe, 1951) was used to determine the permeability of the more permeable stratified drift composite samples.

Once the leachates started permeating the columns, the column effluents were monitored for time, flow, and chemistry. The primary parameters selected for measurement of solute front advancement retardation factors included the following:

- Specific conductance/total dissolved solids
- Sulfate
- Total sulfur
- Acidity
- Arsenic
- Iron
- Zinc

Chloride was monitored as the water tracer (assumed $R_d = 1$). Column effluent pH and Eh were also continually monitored. In addition, as discussed in Chapter 3.0, other parameters were also periodically analyzed in the column effluents so as to approximate column determined retardation factors. Results of the flow and chemical monitoring and post-column test sample descriptions are presented in Appendix H.

The chemical data were normalized (concentration divided by source concentration) and related to pore volumes of flow from each column. Plots of the normalized concentration versus pore volume of flow (chemical breakthrough curves) were constructed for each column so that solute front advancement R_d values could be calculated.

F.5 CALCULATION OF COLUMN RETARDATION FACTORS

The chemical breakthrough curves constructed from the results of the column tests were prepared on a column pore volume displacement basis. Therefore, the retardation factor (R_d), determined from the chemical breakthrough curves, is calculated by:

$$R_d = \frac{P_{VSI}}{P_{VTR}}$$

where

P_{VSI} = cumulated pore volumes when the half concentration of the solute or parameter of interest has arrived.

P_{VTR} = cumulated pore volumes when the half concentration of the tracer (chloride) has arrived.

APPENDIX F

REFERENCES

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Lambe, T. W., 1951, Soil Testing for Engineers, John Wiley and Sons, Inc., New York, 165 pp.

APPENDIX F
TABLE

TABLE F.1

COLUMN SAMPLE REMOLDING AND TESTING CONDITIONS, AND COLUMN DIMENSIONS

SOIL SAMPLE(1)	COLUMN DESIGNATION	LEACHATE PERMEANT pH	REMOLDING CONDITIONS(2)		DIFFERENTIAL HYDRAULIC PRESSURE(3) (cm H_2O)	SPECIFIC GRAVITY(4) (g/cm^3)	FINAL LENGTH (cm)	TOTAL VOLUME (cm^3)	PORE VOLUME(5) (cm^3)
			DRY DENSITY (g/cm^3)	WATER CONTENT (%)					
Glacial Till (Composite No. 1)	I-1	3	2.01	9.0	200	2.70	13.0	553.3	141.2
	I-2	6	2.00	9.0	200	2.70	12.9	554.6	143.8
	I-3	9	2.01	9.0	200	2.70	12.9	557.4	143.5
	I-4	9	1.97	9.0	200	2.70	12.7	540.6	145.3
Stratified Drift (Composite No. 2)	J-1	3	1.85	5.7	VH	2.67	14.1	611.1	206.2
	J-2	6	1.85	5.7	VH	2.67	13.6	592.1	187.2
	J-3	9	1.85	5.7	VH	2.67	13.9	601.7	195.6
	J-4	9	1.85	5.7	VH	2.67	14.0	605.8	200.6
Four Percent Bentonite/ Till Admixture	K-1	3	1.96	9.0	3,000	2.74	11.6	485.5	138.5
	K-2	9	1.96	9.0	3,000	2.74	11.6	485.5	138.9

(1) See Appendix C for composition of composite samples.

(2) Based upon index testing (Appendix C), previous site investigations (Golder, 1981), and Proctor Curve constructed for the four percent bentonite/till admixture (Figure F-1).

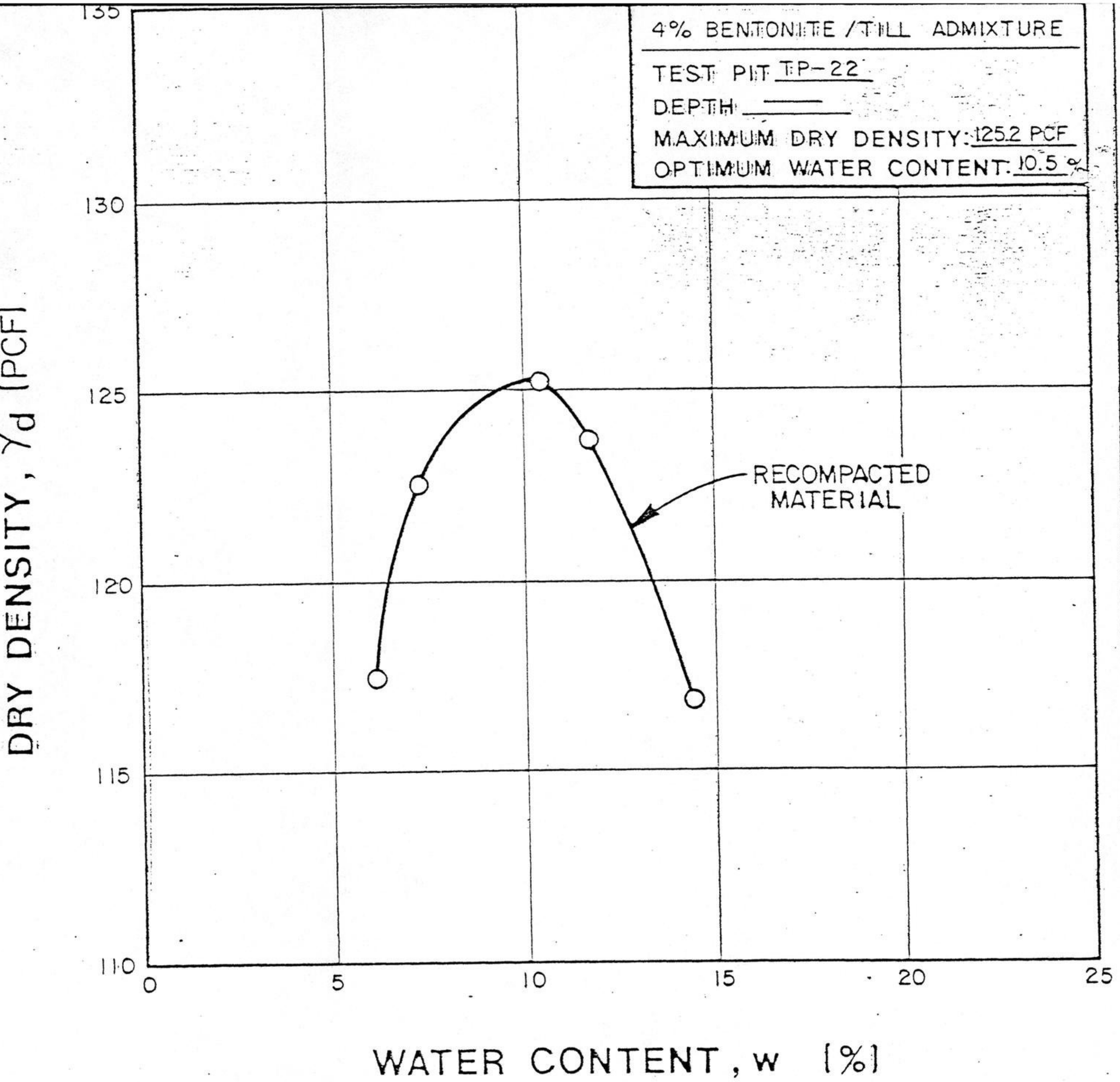
(3) Differential hydraulic pressure across column samples to determine initial and final permeabilities (Table 3.21) of the glacial till. A variable head (VH) test in accordance with Lambe (1951) was used to determine the initial and final permeability of the stratified drift. The differential hydraulic pressure was constant throughout the duration of the column test for the four percent bentonite/till admixture columns.

(4) Specific gravities used for the glacial till and stratified drift columns were estimated from Golder (1981). The specific gravity of the four percent bentonite/till admixture was determined in accordance with ASTM D 854-58(79).

(5) Sample free pore space. Calculation based upon final sample dimensions and specific gravity.

APPENDIX F
FIGURES

AWN BY DBN | CHEC BY | DRA NUMBER RMB 14
BY 4-27-82 | APPROVED BY | 11-27-82


4% BENTONITE/TILL ADMIXTURE

TEST PIT TP-22
DEPTH ______
MAXIMUM DRY DENSITY: 125.2 PCF
OPTIMUM WATER CONTENT: 10.5 %

ASTM DESIGNATION USED STANDARD
**METHOD USED A

ASTM DESIGNATION	HAM./DROP	LAYERS
STANDARD-D698	5.5#/ 12"	3
MODIFIED-D1557	10#/ 18"	5

METHOD**	MATERIAL SIZE	MOLD SIZE	BLOWS*
A	ALL PASSING #4	4" DIA.	25
B	ALL PASSING #4	6" DIA.	56
C	ALL PASSING 3/4"	4" DIA.	25
D	ALL PASSING 3/4"	6" DIA.	56

*BLOWS/LAYER

FIGURE F-1

PROCTOR TEST
4% BENTONITE/TILL ADMIXTURE

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

DRAWN BY	CHECKED BY	APPROVED BY	DRAWING NUMBER
G.J. Graham 6-3-82	11/27/82	11-27-82	RM81-444-A23

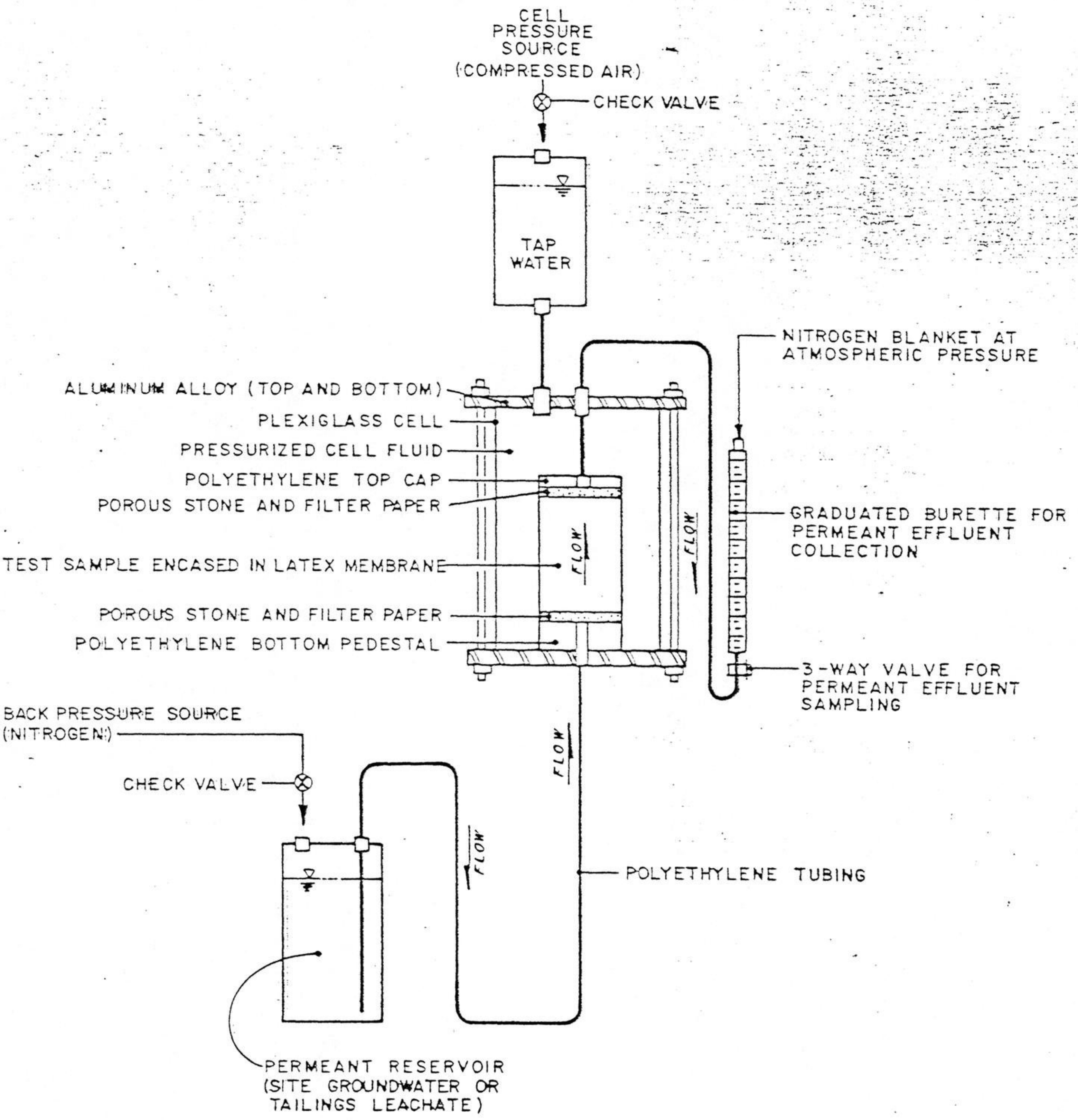


FIGURE F-2

SCHEMATIC OF A CONSTANT HEAD TRIAXIAL CELL PERMEABILITY / SOLUTE FRONT ADVANCEMENT TEST SYSTEM

PREPARED FOR

EXXON MINERALS COMPANY
RHINELANDER, WISCONSIN

D'APPOLONIA

APPENDIX G

RESULTS OF CALCIUM CARBONATE EQUIVALENT DETERMINATIONS

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APPENDIX G

RESULTS OF CALCIUM CARBONATE EQUIVALENT DETERMINATIONS

This appendix presents the results of the calcium carbonate equivalent and carbonate effervescence determinations (Table G.1) used to establish the correlation between carbonate effervescence rating and calcium carbonate equivalent. As discussed in Chapter 3.0, this correlation was then used to evaluate the carbonate minerals distribution in the glacial till and stratified drift in and surrounding the MWDF Site 41 area.

APPENDIX G
REFERENCES

Golder Associates, 1981, "G41 Series Boring Logs, Geotechnical Review, Crandon Project, Waste Disposal System, Project Report 2, Volume 3," Golder Associates, Atlanta, Georgia.

Sobek, A. A., W. A. Schuller, J. R. Freeman, and R. W. Smith, 1978, "Field and Laboratory Methods Applicable to Overburdens and Minesoils," EPA-600/2-78-054, U.S. Environmental Protection Agency (U.S. EPA), Cincinnati, Ohio, 203, pp.

APPENDIX G
TABLE

TABLE G.1

RESULTS OF CALCIUM CARBONATE EQUIVALENT DETERMINATIONS

BORING NO.	SAMPLE INTERVAL ELEVATION(1) (meters)	SAMPLE NO.	CARBONATE EFFERVESCENCE RATING(2)	PERCENT $CaCO_3$ EQUIVALENT(3)
G41-H9	500.5-500.1	7	4(4)	9.0
G41-H9	488.3-487.7	11	0(4)	0.9
G41-H9	479.1-479.0	14	3(4)	7.2
G41-H9	469.7-469.5	17	3(4)	11.0
G41-H9	454.6-454.3	22	0(4)	0.8
G41-H9	448.7-448.2	24	0(4)	1.1
G41-H9	442.6-442.1	26	1(4)	1.0
G41-H9	436.5-436.0	28	0(4)	0.3
G41-H9	430.4-429.9	30	0	1.0
G41-C11	495.1-494.6	4	1	3.8
G41-C11	492.1-491.7	6	1	1.1
G41-C11	490.5-490.1	7	1	0.6
G41-C11	487.5-487.0	9	1	0.8
G41-M11	479.4-478.7	2	0	0.2
G41-M11	461.5-461.1	8	1	4.3
G41-M11	452.8-452.4	11	3	9.9
G41-B12	487.8-487.3	2	1	2.4
G41-B12	475.7-475.4	6	2	5.8
G41-B12	460.4-459.9	11	1	1.6
G41-G13	511.9-511.3	4	3(4)	7.5
G41-G13	493.7-493.0	10	2(4)	3.0
G41-G13	481.5-480.9	14	0(4)	1.0
G41-G13	469.3-469.0	18	3(3)	9.0
G41-G13	457.1-456.9	22	3(4)	7.5
G41-G13	444.9-444.4	26	1(4)	1.2
G41-G13	438.8-438.3	28	3(4)	7.2
G41-G13	432.7-432.5	30	5(4)	12.0
G41-D14	487.5-487.0	4	2	5.3
G41-D14	484.7-484.2	6	2	2.8
G41-D14	481.6-481.1	10	1	3.0
G41-C15	490.2-489.7	3	0	0.2
G41-C15	483.9-483.4	8	1	0.4
G41-C15	472.6-472.1	15	3	10.3
G41-C15	462.0-461.7	22	2	6.2
G41-C15	452.8-452.5	25	1	0.9
G41-G15	494.1-493.8	6	1	0.6
G41-G15	490.9-490.6	8	0	0.8
G41-G15	487.8-487.5	10	0	0.6
G41-G15	484.6-484.5	12	1	0.9
G41-G15	475.4-475.2	15	2	5.5

TABLE G.1
(Continued)

BORING NO.	SAMPLE INTERVAL ELEVATION(1) (meters)	SAMPLE NO.	CARBONATE EFFERVESCENCE RATING(2)	PERCENT $CaCO_3$ EQUIVALENT(3)
G41-G15	456.8-456.6	21	1	0.4
G41-M15	488.6-488.5	6	3	36.7
G41-M15	482.5-482.0	8	1	0.3
G41-M15	464.0-463.6	14	1	0.4
G41-M15	455.0-454.6	17	0	0.2
G41-P16	478.1-477.6	3	2	6.3
G41-P16	462.9-462.4	8	2	7.0
G41-P16	447.7-447.2	13	3	10.7
G41-P16	441.6-441.1	15	2	4.8
G41-E17	493.6-493.1	8	1	0.5
G41-E17	486.4-486.0	13	0	0.6
G41-E17	482.0-481.5	16	1	0.5
G41-E17	470.7-470.4	21	0	0.9
G41-E17	461.1-460.7	24	1	0.8
G41-H18B	497.9-497.3	6	2(4)	7.6
G41-H18B	491.8-491.2	8	0(4)	0.2
G41-H18B	482.6-482.0	11	1(4)	0.5
G41-H18B	473.5-472.9	14	0(4)	0.7
G41-H18B	467.4-466.8	16	0(4)	0.4
G41-H18B	461.3-460.7	18	0(4)	1.3
G41-P18	473.6-473.1	8	2	4.2
G41-E19A	492.5-492.0	4	1	2.2
G41-E19A	483.3-482.9	7	0	0.6
G41-E19A	474.2-473.7	10	2	8.6
G41-E19A	471.0-470.6	11	3	9.1
G41-E19A	455.9-455.6	16	1	0.9
G41-E19A	453.0-452.7	17	1	1.0
G41-E19A	446.7-446.1	19	3	12.6
G41-K21A	503.1-502.6	4	1(4)	1.8
G41-K21A	481.7-481.3	11	1(4)	0.8
G41-K21A	472.6-472.1	14	1(4)	0.4
G41-K21A	457.3-456.9	19	1(4)	3.2
G41-K21A	445.1-444.8	23	1(4)	1.2
G41-K21A	439.0-438.7	25	3(4)	8.0
G41-K21A	429.9-429.4	28	3(4)	3.6
G41-N21	520.4-519.9	5	0	0.4
G41-N21	517.4-517.2	7	2	2.2
G41-N21	509.7-509.4	12	2	2.4
G41-N21	NA(5)	16	3	6.3
G41-E22	484.6-484.2	5	1	1.4
G41-E22	463.2-462.8	12	3	13.0
G41-E22	451.0-450.6	16	0	0.2

TABLE G.1
(Continued)

BORING NO.	SAMPLE INTERVAL ELEVATION(1) (meters)	SAMPLE NO.	CARBONATE EFFERVESCENCE RATING(2)	PERCENT $CaCO_3$ EQUIVALENT(3)
G40-Y22	468.8-468.2	8	1	1.2
G40-Y22	459.4-459.0	11	2	3.9
G41-A23	487.1-486.5	3	0	0.3
G41-A23	482.5-481.9	6	1	0.4
G41-A23	477.9-477.3	9	1	0.4
G41-A24	NA	3	0	0.2
G41-A24	NA	7	0	0.4
G41-A24	NA	9	1	1.4
G41-A24	NA	12	3	13.1
G41-F24	491.8-491.4	8	1	0.4
G41-P24	506.3-506.0	5	1	0.8
G41-P24	491.3-491.2	15	1	0.4
G41-P24	471.5-471.2	25	1	1.2
G41-F24	484.2-483.9	13	2	6.0
G41-F24	481.1-480.7	15	2	3.4
G41-K26	495.6-495.2	7	1	0.5
G41-K26	462.1-461.6	18	0	0.6
G40-Y26	479.1-478.6	3	2	3.4
G40-Y26	466.3-465.8	7	2	3.8
G40-T30	478.7-478.1	3	1	1.0
G40-T30	472.6-472.0	5	0	0.4
G40-T30	469.5-469.2	6	0	0.2
G40-T30	466.3-465.7	7	3	12.0

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(1) Sample interval and numbers from Golder (1981) boring logs and sample descriptions.

(2) Visual numeric rating showing the presence of carbonates after the addition of a few drops of ten percent HCl.

0 - No reaction
1 - Very slight reaction
2 - Slight to moderate reaction
3 - Strong reaction

(3) Sobek, et al. (1978).

(4) Effervescence values for samples from borings G41-H9, G41-G13, G41-H18B and G41-K21A assigned on a numeric rating scale of 0 to 5

0 - No reaction
1 - Very slight reaction
2 - Slight reaction
3 - Moderate reaction
4 - Strong reaction
5 - Very strong reaction

(5) "NA" indicates data not available.