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Leachate Reactions With Soils Under Anaerobic Conditions

Franklin S. Tirsch
Aaron A. Jennings

The research upon which this publication is based was supported in part by the Massachusetts Division of Water Pollution Control, Grant Number MDWPC 76-10(2) and by the U.S.D.A. Pinchot Institute, Grant Number 23-591.



ENVIRONMENTAL ENGINEERING PROGRAM
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LEACHATE REACTIONS WITH SOILS
UNDER ANAEROBIC CONDITIONS

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PREFACE

This report was drawn from the Master of Science Theses "Leachate Reactions with Soils" by Franklin S. Tirsch and "The Leachate Attenuation Properties of Soil Under Anaerobic Conditions" by Aaron A. Jennings. Mr. Tirsch and Mr. Jennings served as research assistants on research project "Nonpoint Pollution" supported by the Massachusetts Division of Water Pollution Control and on Research Project "Modeling the Impact of Liquid Wastes on Groundwater Quality in Forests" supported by the U.S. Forest Service, Pinchot Institute.

Faculty guidance for the research projects was through Dr. Donald Dean Adrian, Principal Investigator. In addition, Dr. Enrique J. La Motta, Assistant Professor of Civil Engineering, and Dr. John H. Baker, Professor of Soil Sciences were thesis committee members.

This report is the second Environmental Engineering Program technical report concerning sanitary landfills and leachates. The first, report, prepared by Paul A. Walker, was titled "Effects of Sanitary Landfill Leachate on Algal Growth." Forthcoming will be a report by Robert W. Pease concerning the determination of stability constants between selected metals and organic molecules from sanitary landfill leachate. Also forthcoming will be a report by Ronald L. Lavigne concerning the production, characterization, and movement of landfill leachates in the New England environment.

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INTRODUCTION

Sanitary Landfill Leachate

A sanitary landfill is an engineering method of land waste disposal which minimizes nuisances or hazards to public health and safety. The term "sanitary landfill" was first coined nearly 45 years ago at an operation in Fresno, California. Today there are estimates that there are over 14000 landfills in the nation accepting 360×10^6 tons of household, commercial, industrial and municipal refuse per day.

Proper practice calls for the refuse to be spread over a small area, compacted by heavy equipment, and covered with earth at the end of each day's operation. The details of operation are discussed by the American Public Works Association (2). Even when proper procedures are followed the disposal of such large amounts of refuse is not without environmental impact. One of the problems receiving widespread attention is that of leachate generation and movement.

Leachate Composition

When refuse buried in a landfill comes in contact with surface water, groundwater, or infiltrating rainwater, leachate, a mineralized liquid high in organic substances, is produced and may move out of the fill and pollute surface and/or groundwaters. The nature of this pollution depends on whether the decomposition takes place in the presence of atmospheric oxygen or soil air (aerobic) or in the absence of oxygen (anaerobic).

Quite a bit of information is available regarding the composition of leachate generated by landfills. Apgar and Langmuir (4), Ho, Boyle, and Ham (26) and Chian and DeWalle (10) report that leachate composition is influenced by many factors including: composition and amount of refuse, sorting and compaction of refuse, water content, climate, season, temperature, age of site, and hydrogeology of the site. Griffin, Frost, and Shimp (22) present a summary of the chemical characteristics of the leachate used in their study as well as the ranges for more than twenty other leachates. This summary, reproduced in Table 1, demonstrates the strong pollutional strength of leachates. However, as Ham (25) points out, more information in addition to concentration of constituents is needed. We must know the quantity of leachate at these concentrations

TABLE 1
SUMMARY OF CHEMICAL CHARACTERISTICS OF LANDFILL LEACHATES

Component	Range of all Values from Garland and Moshier (4)	Blackwell Forest Preserve Leachate Data from Hughes (2)	Du Page Leachate Used in Sorption Study
	(mg/l)	(mg/l)	(mg/l)
COD	40 to 89,520	39,680.	1,362.
BOD	9 to 54,610	54,610.	-
TOC	256 to 28,000	-	-
Organic acids	-	-	333.
Carbonyls as acetophenone	-	-	57.6
Carbonhydrates as dextrose	-	-	12.
pH	3.7 to 8.5	7.10	6.79
Eh (m.v.)	-	-180.	-155.
TS	0 to 59,200	-	-
TDS	0 to 42,276	19,144.	5,910.
TSS	6 to 2,685	-	-
E.C. (mmhos/cm)	3 to 17	10.90	7.20
Alkalinty (CaCO ₃)	0 to 20,850	3,255.	4,220.
Hardness (CaCO ₃)	0 to 22,800	7,830.	1,100.
Total P	0 to 154	6.	<0.1
Ortho P	6 to 85	-	-
NH ₄ -N	0 to 1,106	-	809.
NO ₃ + NO ₂ -N	0 to 1,300	1.70	-
Al	-	2.20	<0.1
As	-	4.31	0.11
B	-	-	33.
Ca	5 to 4,080	-	49.
Cl	34 to 2,800	1,697.	1,070.
Na	0 to 7,700	900.	822.
K	3 to 3,700	-	516.
Sulfate	1 to 1,826	680.	<0.01
Mn	0 to 1,400	1.66	<0.1
Mg	16 to 15,600	-	204.
Fe	0 to 5,500	5,500.	4.40
Cr	-	0.20	<0.1
Hg	-	-	0.0008
Ni	-	-	0.3
Si	-	-	15.1
Zn	0 to 1,000	-	0.03
Cu	0 to 10	0.05	<0.1
Cd	0 to 17	<0.05	<0.01
Pb	0 to 5	-	<0.1

SOURCE: Griffin, Frost, and Shimp (1976).

to be expected. We must also know how these concentrations change with time. In addition, we must know how changes in landfill design and operation will affect leachate composition.

Ho, Boyle, and Ham (26) report that it is difficult to define a typical leachate because leachate composition varies so much. The variation in analyses of landfill leachates reported in the literature has led to speculation that some of the variation is the result of inadequate techniques of sample collection and preservation. In addition, variation may be due to leachate analysis which is a difficult matter. Special modifications to analytical techniques as described by Pease (40), Chian and DeWalle (9), and Environment Canada (13) must be made.

Leachate Movement

Leachate problems may not be confined to the area immediately under and adjacent to the landfill. Given certain rates of leachate production and hydrogeological conditions leachate may enter the groundwater and travel significant distances. It has been proposed that the leachate-influenced groundwater will assume a plume or lens-like shape as it moves off, following the groundwater streamlines in the general direction of flow.

H. E. LeGrand (33) has termed these plume-like leachate zones in groundwater "leachate enclaves", the bounds of which would be defined by the limits of detectable differences in quality between leachate-influenced waters and ambient groundwaters. He hypothesized that these enclaves should have "regular" shapes and might be describable by theoretical techniques. LeGrand went on to define "malenclaves", which would be that portion of the total enclave which exceeded water quality criteria and could be considered "polluted".

Palmquist and Sendlein (39) were able to map the bounds of the "total contamination enclaves" for five landfill sites in Iowa. They were also able to delineate isoconcentration lines for subenclaves of dissolved solids, chloride, sulfate, alkalinity, and COD at most sites. Kimmel and Braids (27) investigated two landfills in New York and were able to establish the bounds of leachate enclaves extending 16,660 feet (3,200 M) and 5,000 feet (1,500 M) in groundwater that already carried a heavy background contamination load from septic system percolates.

Anderson and Dornbush (3) investigated a landfill site in South Dakota and were able to trace the leachate enclave for nearly 1,200 feet (366 M).

Griffin et al. (19) report that increases in the concentrations of alkaline earth metals in groundwater preceding a leachate plume have been observed in the field during monitoring of groundwater chemistry around landfill sites. This increase has been termed the "hardness halo" and is believed to result from ion exchange reactions.

The flow of leachate in plumes poses a sampling problem. Chian and DeWalle (9) report that substantial differences were noted between leachate obtained from lysimeters as compared to that from test pits. Lysimeters restricted to a specific layer may not provide representative samples. The problem is further complicated by the fact that it is not known whether differences from lysimeter to lysimeter reflect conditions in the soil or different solid waste characteristics within the fill.

Leachate Treatability

Chian and DeWalle (10) evaluated laboratory scale biological and physical-chemical treatment processes for their ability to remove the individual contaminants in leachate. Their biological section included aerobic, anaerobic, and combination aerobic/anaerobic processes. The physical-chemical processes studied included: chemical precipitation, activated carbon adsorption, ion exchange adsorption, chemical oxidation, and reverse osmosis.

They found that treatability was especially related to the nature of the organic matter. Leachate generated from young fills in which the organic matter mainly consists of free volatile fatty acids could be readily degraded by biological means. Leachate from old fills containing refractory organics was more amenable to physical chemical treatment.

Ho, Boyle, and Ham (26) also report on chemical treatment of sanitary landfill leachate. They examined treatment by precipitation using lime and sodium sulfide, chemical coagulation using alum and ferric chloride, chemical oxidation using chlorine, potassium permanganate,

ozone, and calcium hypochlorite, and treatment by activated carbon.

Leachate Attenuation

Attenuation may be defined as a decrease in the solution phase mass of a constituent by a physical, chemical, or biological soil/leachate interaction. By this definition, the distribution of material by transport phenomenon (*dilution*) would not be considered an agent of attenuation. Dispersion, for example, does nothing to alter the mass of material in solution. In fact, attenuation acts in direct opposition to the forces of transport in a way analagous to frictional resistance to flow. Although there are exceptions such as negative attenuations which transfer material to the liquid phase, the basic action of attenuation is to resist the dissemination of leachate enclaves.

Leachate may be attenuated in soils by chemical, physical, and biological means. The chemical means include adsorption, cation and anion exchange, precipitation reactions, and oxidation-reduction reactions. Microorganisms may mediate many oxidation-reduction reactions. In addition they are responsible for mineralization and immobilization of constituents and for changes in organic constituents. Physical factors that play a role in attenuation include particle size distribution, pore size distribution, moisture relations and temperature effects. These factors are discussed in detail by Fuller and Korte (17) and Phillips and Nathwani (41).

LITERATURE REVIEW

Expanded research efforts in soil microbiology, soil physics, and soil chemistry are aimed at understanding the ability of the soil to attenuate pollutants. Hajek (24) points out that these studies have established that decontamination of wastewater by soils is usually achieved by a combination of filtration, biological degradation, and physical and chemical adsorption. The soil has a definite assimilation capacity that can be exceeded and Hajek outlines methods used to predict its capacity. The methods include a chemical characterization of the wastewater, characterization of soil, characterization of soil-wastewater interaction by batch equilibrium studies and dynamic column studies, and field studies.

Batch Studies

Griffin and Shimp (23) conducted a study to determine the capacity of kaolinite and montmorillonite for removing Pb from solution and the effect municipal leachate has on that capacity at various pH values. It was found that Pb removal from landfill leachate increased with increasing pH and with increasing concentration of Pb in solution. Several mechanisms were responsible for removal of Pb from solution. Precipitation was found to be important for lead removal from landfill leachates. This was indicated by removal of Pb from blank solutions which contained no clay. The precipitate was identified as lead carbonate.

The decrease in Pb adsorption with decreasing pH, the rapid increase in the amount of Pb adsorbed coinciding with the formation of monovalent Pb-hydroxyl species, and the agreement between adsorption capacity and cation exchange capacity were consistent with a cation exchange mechanism. Further evidence of a cation exchange mechanism was the reduction in Pb adsorption in solutions containing .1 M NaCl and leachates containing higher total salt concentrations. The reduction in Pb adsorption may have been due to high levels of competing cations, but also may have been due to complex formation which would lower the activity of free Pb^{+2} in solution.

The results for Pb adsorption from leachate were plotted according to the Langmuir adsorption equation. Two distinct slopes were observed and were attributed to adsorption at sites of distinctly different energy and possibly competition from other cations.

In another study Griffin, Frost, and Shimp (22) examined the capacities of kaolinite and montmorillonite for removing potentially hazardous heavy metals As, Cd, Cr, Cu, Hg, Pb, Se, and Zn from solution. The effect of leachate at various pH values on these capacities was also examined.

They found that removal of heavy metal cations from landfill leachate generally increased with increasing pH values and with increasing concentration of the heavy metal ion in solution. In sharp contrast, the anionic heavy metals showed a general decrease in removal as pH increased. In addition, no precipitation of the anionic heavy metals was observed over the pH range 1-9.

For anionic heavy metals sorption was greater from leachate than from pure salt solution. The higher adsorption in leachate may have resulted from formation of organic or inorganic polynuclear complexes in the leachate solution that could be adsorbed by the clay minerals.

Solution pH had a pronounced effect on the amount of Cr(VI), Se(IV), and As(V) adsorbed from solution by the clay minerals. It was concluded that the principal adsorption mechanism was anion exchange, and species distribution diagrams indicated that the adsorption was due principally to the monovalent species of each element studied.

In a more detailed study of As(V), As(III), and Se(IV), Frost and Griffin (16) found that As and Se adsorption by montmorillonite was higher than by kaolinite. This was thought to be the result of a higher edge surface area, but may have been due to interlayer hydroxy-aluminum polymers. The results indicated that As and Se in leachate would be quite mobile through beds of relatively pure clay minerals and could easily contaminate groundwaters.

Column Studies

Leighton and Blanc (34) examined the interaction of sodium, potassium, calcium, iron, and magnesium cations in leachate with eight Massachusetts soils. The ability of each soil type to retain the cations in question

decreased as each additional increment of leachate passed through the columns until the removal capacity was exhausted. The soils did not approach exhaustion of removal capacity in the same manner, and the relative order in which each ion was removed varied with respect to each soil type.

In studies undertaken at the University of Wisconsin, as reported by Ham (25), the soil column approach was used to investigate the attenuation properties of soils from a proposed landfill site. Leachate was applied to 1.25 in. (3.2 cm) I.D. disturbed soil columns and samples were generated at depths of 2, 6, and 12 in. (5.1, 15.2, 30.5 cm). Analysis was done for COD, solids, several metallic cations, and for numbers of microorganisms. It should be noted that the method of sample handling did not prevent its oxidation since leachate was allowed to pond at the top of columns exposed to the atmosphere. Observations from the Wisconsin study included:

- 1) Soil permeability was governed by surface clogging and dropped sharply with time. Permeabilities of the order of 10 in/day/unit area (25.4 cm/day/unit area) dropped to less than 0.5 in/day/unit area (1.27 cm/day/unit area) in two weeks. All soils appeared to follow this pattern irrespective of their initial permeability.
- 2) Biological activity (evaluated by the enumeration of the liquid phase organisms population) increased over the first two inches (5.1 cm) of soil. Beyond this depth, activity decreased rapidly and reduced four orders of magnitude after ten inches (25.4 cm). Toxicity effects were not observed.
- 3) Attenuation (as measured by a decrease in COD, solids, and metallic ion concentrations) was considerable but appeared to be concentrated in the first few inches of soil. This was interpreted as indicating that filtration was the predominant attenuation mechanism.

One of the most comprehensive studies reported thus far was conducted by members of the Illinois Geological Survey (19,20,21). The aim was to investigate and evaluate the attenuative properties of several clay minerals and to determine whether they could be used as liners for sanitary landfills.

The three clay minerals selected for study were kaolinite, montmorillonite, and illite and the leachate used was collected from the DuPage County sanitary landfill near Chicago, Illinois. Thirty-two columns containing mixtures of clay minerals and washed quartz sand were prepared. The columns were packed to bulk densities approximating those of naturally occurring glacial tills (~ 1.8 g/cc). The columns were painted black to prevent growth of organisms, such as algae or photosynthetic bacteria, which are not indigenous to deep refuse leachate. Leachate was applied to simulate slow, (less than 2 pore volumes per month) saturated anaerobic flow of leachate as it is thought to occur at the bottom of a landfill. Sixteen of the columns received natural leachate and sixteen received sterilized leachate so that the effects of gross biological activity on pollutant attenuation could be determined. The entire system was maintained under an argon atmosphere to ensure anaerobic conditions. After leaching approximately 15 pore volumes the columns were sectioned and the contents were analyzed to determine the vertical distribution of chemical constituents in each column.

Observations and results of the Illinois Geological Survey studies include:

- 1) All three clays resulted in similar relative attenuation rankings. The following hierarchy of attenuation was developed:
 $Cl < COD < Na < NH_4 < K < Mg < Si < Cd < Zn < Pb < Hg$
- 2) Calcium and manganese were not attenuated but were eluted from the columns. The manganese flush was attributed to the production of more soluble reduced species under the anaerobic conditions. The calcium displacement was attributed to the action of exchangeable ions and interpreted as evidence supporting "Hardness Halo" observations.
- 3) The high removal capacities for Cd, Hg, Pb, and Zn were attributed to favorable cation exchange adsorption and to precipitation at pH values of 5.0 and above.
- 4) A very highly significant linear regression of attenuation numbers as a function of Cation Exchange Capacity (CEC) led to the conclusion that the principle attenuation mechanism for K, Na, NH_4 , and Mg was also cation exchange.

- 5) No significant linear regression of attenuation as a function of either CEC or clay fraction was obtained for B, Cl, COD, Fe, or Si.
- 6) *The soil's hydraulic conductivity decreased with time, but the amount of decrease was highly dependent on the percent of clay present.*

The above studies by the Illinois Geological Survey concentrated on leachate reactions with specific clay minerals. Another body of research, dealing with natural soils, has been published by investigators at the University of Arizona (17,18,28). Anaerobic leachate was applied to soil columns to investigate the transport of selected trace elements.

Leachate was generated in a simulated landfill and was then spiked with eleven potentially hazardous trace elements (As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, Zn) to duplicate the effect of co-disposal of municipal and industrial wastes. In each case, the leachate was acidified to pH 5.0 and spiked with 70 to 120 mg/l of the element of interest. This solution was kept anaerobic by storage under CO₂ gas. Eleven subsoils of some seven major orders were used in the study.

Soils were packed into 5 cm I.D. x 10 cm columns and contacted with the spiked leachate at a rate of one pore volume per day. Saturated flow was established by initial upflow filling of the column. Leachate flow was maintained until one of three conditions was met:

- 1) 100 percent breakthrough occurred (effluent concentration equals influent concentration).
- 2) "Steady State" was achieved (unchanging or very slowly changing effluent concentration at a value below that of the influent concentration).
- 3) Continued absence of the element in the effluent after extended leaching.

The results of this study were analyzed by the preparation of C/Co breakthrough curves. Some very interesting conclusions were extracted:

- 1) Attenuation of these solutes appeared to correlate best with the percent of clay in the soil.
- 2) Surface area and percent free iron oxides provided the next best correlation after clay fraction.

- 3) Considering soil pH did not improve the prediction of attenuation capacity.
- 4) The value of the cation exchange capacity of the soil was not found to be useful in predicting attenuation capacity.
- 5) Most soils possessed a considerable capacity to attenuate these selected trace elements.

Farquhar and Rovers (14) also conducted column studies. Their objectives were to compare the flow and contaminant removal patterns in columns containing both undisturbed and remoulded samples of the same soil, and to investigate the use of dispersed soil experiments for examining soil-contaminant interaction. They concluded that the use of remoulded soil columns to estimate attenuation was acceptable. They also concluded that removal isotherms constructed from the dispersed soil studies could be used to predict the breakthrough curves for some contaminants during remoulded soil column experiments.

Site Studies

At the State College of Pennsylvania Regional Sanitary Landfill Apgar and Langmuir (4) undertook a study of changes in leachate quality with depth in underlying soils to identify the extent and principal mechanism of natural leachate renovation. Soil moisture samples were collected by suction lysimeters, thermistors were installed to measure temperature and soil samples were analyzed for CEC and exchangeable cations.

They concluded that marked decreases in the amounts of leachate contaminants can occur with movement of leachate in unsaturated soils. Study area subsoils showed a decrease in chloride and other species that was attributed to dilution and dispersion. The behavior of redox-sensitive species including BOD, total iron, and ammonia was more complex and less symptomatic with depth than that for specific conductance or chloride. This was partly due to the fact that conditions in unsaturated soils can be both aerobic and anaerobic within a short distance. A phosphate decrease was observed and was believed to be the result of its precipitation as ferric and aluminum phosphates. Ion exchange on soil colloids decreased sulfate and metal cations, and ammonia was considered to be reduced by cation exchange and

bacterial assimilation. The authors report that probably the most significant result of the cation exchange study was the observation that the percent base saturation at a given pH was significantly higher in leachate contaminated soils than in uncontaminated soils.

Kunkle and Shade (29) monitored the groundwater quality at the Hagman Road Landfill in Erie Township, Monroe County, Michigan. They examined the physical-chemical interactions between leachate and the glacial materials and found that the distributions for TDS, SO_4 , total alkalinity, Ca, Mg, Cl, total hardness, and non-carbonate hardness all showed a pattern centering beneath the landfill. Except for alkalinity, which markedly increased, all of the parameters showed a low concentration beneath the landfill site. If the patterns were induced by leachate all of them, except for alkalinity, were directly opposite to the expected kinds of change reported in the literature for other landfills.

The authors postulated that the reduction in sulfate and calcium, and the increase in alkalinity in the carbonate aquifer was related to a sulfate reduction reaction. However, they were faced with an interpretational dilemma. Reductions in total dissolved solids, hardness, and chlorides were not accounted for by the sulfate reduction model. The obvious answer of concentration reductions by local dilution was rejected as being insupportable by known hydrogeologic evidence.

OBJECTIVES

The review of the literature has shown the complex character of leachate and its reactions with soils. The objectives of this investigation were to examine leachate attenuation by soil, with specific interest in understanding the mechanisms involved in attenuation and in determining the magnitudes of the attenuations.

The study was conducted in several steps. Firstly, natural leachates were collected at an operating landfill and were characterized. Secondly, different soil samples from the landfill site were collected and characterized. The third step involved the determination of equilibrium distributions for different constituents in leachate using batch analysis. These results were fitted to models such as the Langmuir and Freundlich adsorption isotherms. The fourth step involved dynamic column breakthrough analysis. Anaerobic saturated leachate flow, saturated "washout" flow, and anaerobic unsaturated leachate flow were considered. Finally, the last step involved the sectioning of the columns and a recharacterization of soil samples from different depths. This determined how cation exchange capacity, exchangeable cations, soil organic matter, and soil pH changed as a result of interaction with leachate.

MATERIALS AND METHODS

Leachate

All leachates used in these experiments were collected in Barre, Massachusetts, from a privately-owned sanitary landfill operated by the Martone Trucking Company. At this site, leachate is generated by a three-acre fill area which received municipal solid wastes from 1970 to 1976. This source was selected since it had previously been studied by Pease (40), Lombardo (35), and Lavigne (32), and was known to occasionally produce substantial volumes of moderate to high strength leachate.

The first leachate stock (Batch "A") was collected on January 6, 1976. Due to the severe cold weather, the leachate pools at the base of the fill area were frozen over with 2"-3" (5 cm-8 cm) of ice. Collection was accomplished by breaking through the ice and intercepting leachate as it flowed directly from the fill. This leachate varied in color from straw yellow to orange, and was intensely malodorous. It was collected in five-gallon containers and transported back to the Environmental Engineering Laboratories at the University of Massachusetts. There the separate containers of leachate were composited into Master Sample "A" and this was placed into the storage reservoir. Upon standing, it clarified to a clear straw yellow.

The second leachate stock (Batch "B") was collected on September 17, 1976 from a diversion ditch that had been installed to drain the leachate pools. In this ditch, leachate was standing under a thick surface crust, and varied from the typical liquid to a black, jelly-like sludge. Again, leachate was collected in five-gallon containers, transported to the laboratories and composited.

For both samples the method of collection allowed for some oxidation. The amount of oxygen supplied during collection, however, was insignificant compared to the massive potential demand, and the overall chemical composition of the leachate altered very little.

A third leachate sample (Batch "C") was collected on June 1, 1977 from the "super funnel" taps at the Barre Research Facility. This leachate was stored under a nitrogen atmosphere and was refrigerated.

Surface Water

The surface water used in the "washout" experiment was collected on June 14, 1976 from the Nourse Brook at the inlet weir to the Atkins Reservoir in the Town of Shutesbury, Massachusetts. This source was selected since it represented a very clean, but otherwise reasonably typical New England surface water.

Soil

A soil sample was collected on November 15, 1975 from the "super funnel" section of the Barre Research Facility. The sample was air dried and a standard sieve analysis was performed. The entire soil sample was then sieved to remove all particles retained by a #4 (U.S. Standard) sieve. This was done to facilitate column packing. Large rocks would cause gaps along the column walls or cause non-uniform flow distribution. All further analyses were performed on this sieved soil.

The percent sand, silt, and clay were determined using the hydrometer method (12). The organic matter content was determined using the Walkely-Black wet chemical method of oxidation with dichromate (1). Cation exchange capacity (CEC) was determined using extraction with 1 N NH_4Ac (pH 7) as described by Chapman (8), and exchangeable calcium and magnesium extracted by the ammonium acetate were determined using atomic absorption spectrophotometry. Manganese coatings on the soil were determined using extraction with acidified hydroxylamine hydrochloride (7). Exchangeable aluminum was determined using the aluminon method (15), and exchangeable acidity was determined by titration of a KCl extract with standard sodium hydroxide to pH 8.3. Soil pH was measured after mixing 10 gm soil samples with 30 ml 0.01 M CaCl_2 for 30 minutes.

The first soil sample was used for the preliminary isotherm experiments and the saturated flow column study, but, there was not enough of this soil remaining to repack all the columns for the unsaturated flow study.

A second soil sample was collected from the super funnel area of the Research Facility in September, 1976. In addition, a sample of the soil used in the construction of the clay sill and dike of the Research Facility was also collected. These two samples were handled and analyzed as described above.

Column Apparatus

For accomplishing the goals of this research, a multiple soil column apparatus was developed. This approach was selected over the single-column, multiple-port sampling technique for two major reasons: (1) a single column would require an unreasonably high surface application rate to produce sufficient sample volume at each depth increment. Also, the withdrawal of samples from depth increments would cause flow to decrease with depth. The result would be a decreasing volume applied per soil mass ratio, thus amplifying the effect of attenuation with depth and distorting breakthrough characteristics. The multiple column approach allows for adequate sample volumes to be generated by lower application rates and maintains uniform "volume applied" conditions with depth. (2) Establishing unsaturated flow conditions dictates that low application rates be used and makes the withdrawal of samples from side ports a difficult operation. The multiple column arrangement can be used to simulate this condition by making only minor piping alterations from the saturated flow setup and solves the sampling problem since no side ports need be sampled.

A schematic flow diagram of the developed apparatus is shown in Figure 1. Leachate of sufficient volume to accomplish one "run" was held in the forty-gallon (150 liter) storage reservoir. Atmospheric oxygen was excluded by a floating seal, which followed the receding fluid level as leachate was withdrawn. For the initial run, this reservoir was left at room temperature (ap. 22°C). It was determined, however, that superior leachate chemical stability could be achieved by cold storage, so for subsequent runs, the storage reservoir was refrigerated to ap. 4.5°C.

From the storage reservoir, leachate was pumped to a constant head feed assembly by a positive displacement tubing pump at a rate of

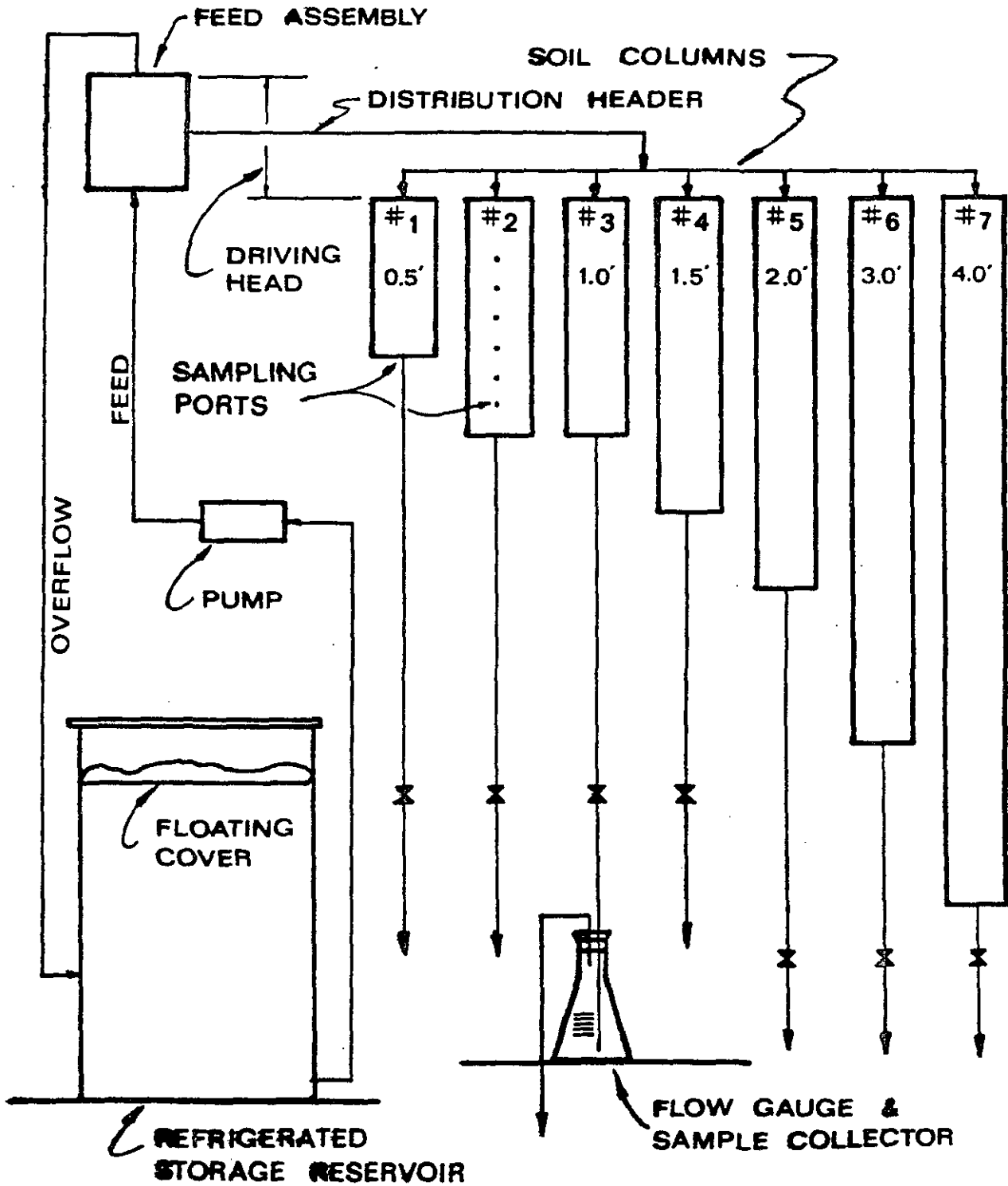


FIGURE 1

SOIL COLUMN APPARATUS

5.0 ml/min. This rate was sufficient to maintain a continuous overflow of the feed assembly and, when recycled, this overflow promoted a modest degree of mixing in the storage reservoir.

The feed assembly allowed sufficient residence time for refrigerated leachate to warm to room temperature. It also provided a constant hydrostatic driving head on the columns. A head of 1.0 foot (30.5 cm) was used throughout all experiments and was found to perform satisfactorily. From the feed assembly, a distribution manifold applied leachate to the 4 in (10.2 cm) I.D. soil columns.

Flow through the columns was controlled by hosecock valves on either the effluent line (for saturated flow) or influent line (for unsaturated flow). Uniform flow was maintained by individual adjustment of these valves as column hydraulic conductivity declined with increasing head loss.

Samples were collected from the column effluent lines by overflow containers designed to gauge flow and minimize sample oxidation.

Intrinsic to this design was the assumption that if columns of varying lengths are run in parallel under identical conditions their effluent data may be composited. In this way, data from several columns may be analyzed as if it originated from depth increments of a single column. The uniformity with which soil was packed into the columns was of considerable importance. Therefore, to aid in achieving consistency with depth and from column to column, a packing apparatus was developed.

This device was, in principle, very similar to one developed by Dr. G. L. Stewart, formerly Professor of Soil Physics in the Plant and Soil Sciences Department of the University of Massachusetts (44). The packing apparatus achieved the desired soil packing effect by vibrating the columns during filling. This made it possible to place disturbed, dried soil into columns at a density more closely resembling its natural state. It also promoted an organized and systematic packing operation so that uniformity from column to column was improved. The packing apparatus consisted of a vibrating column clamp (Fig. 2) which induced vibrations in the column and a support frame (not shown) which simply held the column plumb during packing.

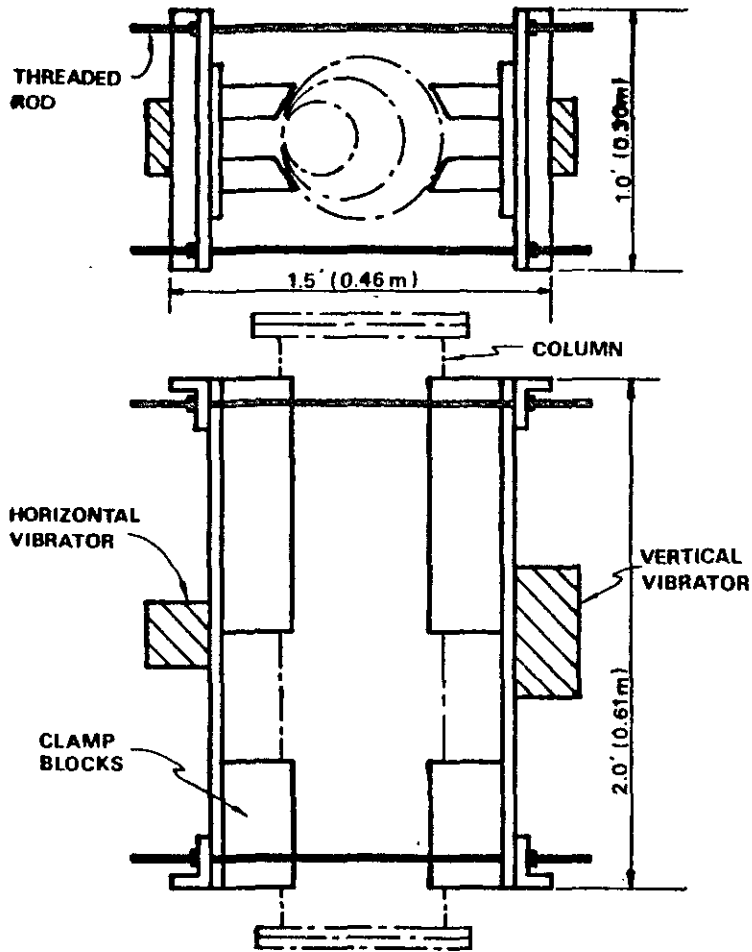


FIGURE 2
VIBRATING COLUMN CLAMP

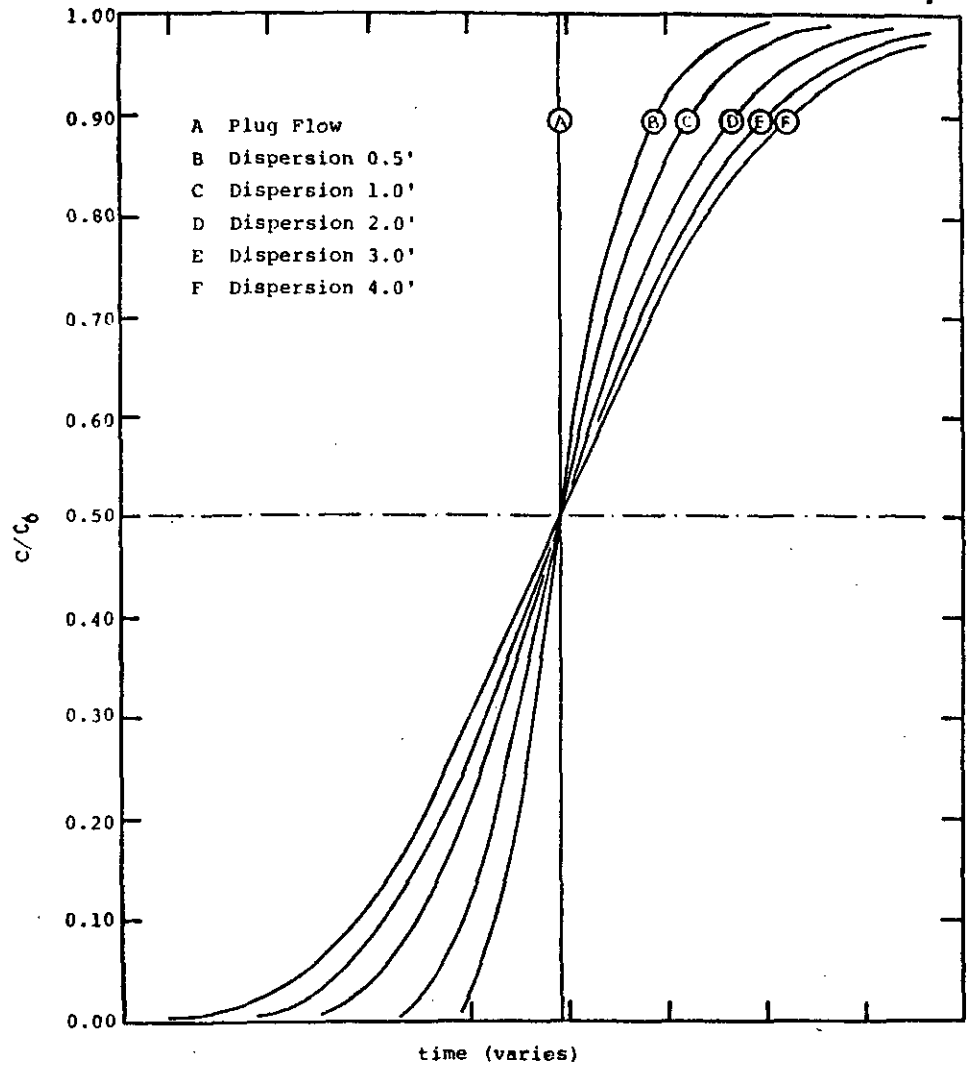


FIGURE 3 - Relative Magnitude of Dispersion Breakthrough Curves for Columns #1 - #7 (Saturated Flow)

For packing a column, the clamp was bracketed into position and the column was secured in an upright position. The support frame positioned the column while isolating it from its surroundings so that it was free to vibrate. Vibrators mounted on the faces of this clamp induced vibrations across the column and, since one was mounted horizontally and one vertically, vibrations in two planes were produced. This prevented destructive interference between the two units. In addition, the electrical input to each vibrator was controlled by a variable resistor so that vibrations could be "tuned" to maximize the effect.

Dry soil was placed into the column through a funnel and pipe, eliminating free fall air classification of the soil. Each column was filled slowly at a rate of approximately 1.0 ft/hour (.30 m/hour). This resulted in a porosity (n) of 29.9 percent and a void ratio (ϵ) of 0.427. This dry soil technique was adopted only after preliminary investigations were made of other techniques. Both wet and slurry packing proved unsatisfactory.

The various phases of this study were accomplished by four separate soil column experiments, each modeling a different leachate/soil interaction condition:

- A. Saturated Flow of Anaerobic Leachate Through Clean Soil (April 9, 1976-May 18, 1976 (937 hours)).
- B. Saturated Flow of Surface Water Through Leachate Equilibrated Soil (June 21, 1976-August 31, 1976 (1680 hrs)).
- C. Unsaturated Flow of Anaerobic Leachate Through Clean Soil (September 28, 1976-November 4, 1976 (844 hrs)).
- D. Saturated and Unsaturated Flow of Chloride Solution Through Clean Soil.

Analysis of Samples

Sampling. Soil columns were sampled by collecting the total effluents of each in one-liter glass bottles until sufficient volume had accumulated. These samples were then removed and partitioned for the analysis of selected parameters.

The very low flow rates at which the experiments were run necessitated a sampling frequency on the order of 48-72 hours since that amount of time was required for sufficient volume to collect.

By this procedure, virtually the entire effluent of each column was delivered for analysis. This allowed for accurate volume measurements and for careful operational control of the flow through velocity. It did, however, dictate that each datum generated by sample analysis represent an average value of the parameter composited over the whole sample interval.

Chemical Parameters. For this research, the following parameters and analytical methods were selected:

<u>Parameter</u>	<u>Method</u>
Alkalinity	Potentiometric Titration
Ammonia	Modified Nesslerization
Chemical Oxygen Demand	Dichromate Reflux
Chloride	Mercuric Nitrate Titration
Metals (Fe, Mn, Ca, Mg, Cu, Zn)	Perkin-Elmer Atomic Absorption
Nitrate	Chromotropic Acid
pH	Accumet pH Meter
Phosphate	Stannous Chloride; also Ascorbic Acid
Specific Conductance	Beckman Solu-Bridge
Sulfate	Barium Sulfate Turbidimetric
Total and Inorganic Carbon	Beckman TOC Analyzer

The methods used to quantify these parameters were modifications of Standard Methods (42), as recommended by Pease (40), and Chian and DeWalle (9).

In addition to method modification, the standard addition technique was employed to enrich results where significant interferences remained.

Biological Parameters. An attempt was made to quantify biological activity in several of the column study samples. The intent of this was the evaluation of the significance of biological activity on leachate substrate rather than the potential for organism transport through the soil.

Analysis was performed on leachate reservoir, column effluent, and column #2 tap samples. Total organism and total coliform counts were done on these samples by both standard agar plate and membrane

filtration techniques. Analysis was also done on soil samples both before packing and upon taking the columns out of service. This quantification was performed by using an elution and enumeration technique as described by Clark (11). Both Clark's soil extract agar and standard plate count agar were used for this purpose.

Soil Analysis of Sectioned Columns

At the end of each stage of column operation the columns were drained and sectioned. Soil samples were collected at different depths as summarized below:

Stage	Column	Sample Depth, ft
Saturated Flow	1	1/2
	4	0,1
	7	0,1,2,3,4
Washout	3	1/2
	5	0,1,2
	6	0,1,2,3
Unsaturated Flow	1	0,1/2
	2	0,1/2
	5	0,1/2,1,2
	6	0,1/2,1,2,3
	7	0,1/2,1,2,3,4

The samples were analyzed for cation exchange capacity, exchangeable cations, pH, organic matter, exchangeable aluminum and exchangeable acidity.

Batch Equilibrations

A preliminary isotherm experiment was started March 10, 1976. A series of approximate dilutions (5,10,20,50,62.5,100,200, and 400X) of batch "A" leachate with deionized distilled water was prepared in 1 liter flasks. Duplicate 250 ml aliquots were equilibrated with 50 gram samples of Barre sand at room temperature for 5 days. A series of blanks containing no soil was equilibrated for the same time. At the end of the five days the samples were filtered using Whatman #42 filter paper. One set of samples was digested for iron and manganese analysis. Another set was analyzed for pH, NH_4^+ , and COD. The sample volume, soil weight, and differences in concentration between the

blank and the sample were used to calculate removals.

This first run was exploratory in nature and immediately problems were encountered. Orange precipitates of ferric hydroxide formed in the samples and blanks as a result of aeration during handling and oxidation with the dissolved oxygen of the dilution water.

A second isotherm was prepared on June 22, 1976. Another series of dilutions (10,20,40,60,80,100, and 142.8X) of batch "A" leachate with deionized distilled water was prepared. This time the dilution water was purged with nitrogen gas so that dissolved oxygen was below 0.1 mg/l. Care was taken to minimize agitation and aeration as 890 ml aliquots were added to 300 gm soil samples in 1 liter sample bottles. Since the dilutions were exact, a sample of raw leachate served as the only control. Duplicate samples were equilibrated in a constant temperature room (27⁰ C) for five days. Another series of dilutions was prepared in the same manner and equilibrated for three days.

At the end of the equilibrations the samples were filtered and analyzed for pH, alkalinity, COD, TOC, NH₄⁺, Fe, Mn, Ca, and Mg. Equilibrium distributions were calculated based on sample volume, weight of soil, and changes in concentration.

A final batch test was prepared June 2, 1977. Three hundred, 400, 500, 600, 700, 800, 900, and 1000 gm samples of Barre sand and Barre clay were placed into 1l sample bottles. While purging with nitrogen gas, Batch "C" leachate was added to fill each bottle. In addition 1500, 2000, and 3000 gm samples of Barre sand were placed into 1 gal bottles and leachate was added to a 1/2 inch depth above the soil. Air remaining in the bottles was displaced with nitrogen gas. Two 1 liter samples with no soil were filled with leachate to serve as blanks. All samples were placed in a constant temperature water bath at 22.5⁰C and equilibrated for 24 hours. Samples were mixed by manual inversion every three hours.

After equilibration the samples were filtered using Whatman #42 filter paper. Sample pH, alkalinity, NH₄⁺ and COD were immediately determined. Samples of the filtrate were acid digested for subsequent metals analysis and other samples were refrigerated for later analysis of total and inorganic carbon.

Changes in constituent concentration were plotted as a function of the soil/leachate mass ratio. In addition, equilibrium distributions were calculated based on changes in concentrations, sample volume, and weight of soil.

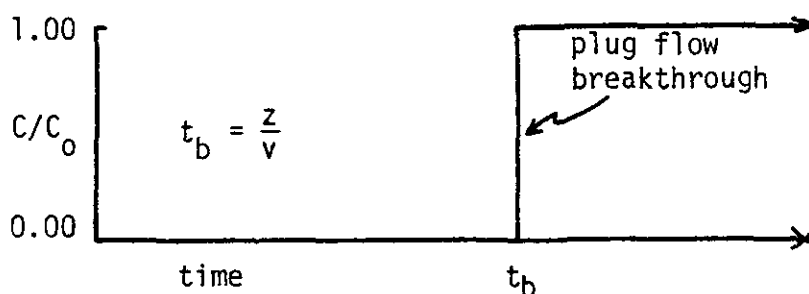
RESULTS AND DATA ANALYSIS

This section contains the results and data analysis for the investigation. First, dispersion modeling and the use of "typical" breakthrough curves are discussed. This is followed by characterizations of the leachates, surface water, and soils used in the study.

The soil/leachate interactions are discussed in terms of the batch equilibrations, the saturated leachate flow, the saturated "washout" flow, the unsaturated flow, and the soil analysis of sectioned columns. The general parameters of specific conductance, pH, alkalinity, chemical oxygen demand, and total carbon are considered first. These are followed by specific parameters of interest including chlorides, ammonia, calcium, magnesium, manganese, iron, and sulfate.

Dispersion Modeling

If solutes moving through soil columns responded only to convective mass transport, their effluent breakthrough curves would be described by a plug-flow model



where: z = length of column (L)
 v = interstitial velocity in Z direction ($L T^{-1}$)
 t_b = time to breakthrough (T)
 C_0 = initial solute concentration (ML^{-3})
 C = solute concentration $C = C(Z,T)$

Given this, any deviation in an empirically-generated breakthrough curve could be attributed to attenuation, and the curve's shape and location could be used to hypothesize the mechanism from which it resulted.

However, this ignores the molecular diffusion and mechanical dispersion that occurs in response to concentration gradients and the dynamics of porous medium flow.

The one-dimensional convective-dispersive mass transport of a solute through a porous medium under conditions of saturated flow is described by the equation:

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial Z} + D \frac{\partial^2 C}{\partial Z^2} \quad (1)$$

where: C = solute concentration (ML^{-3})
 Z = depth (L)
 V = interstitial velocity (LT^{-1})
 D = dispersion coefficient (L^2T^{-1})

Here the effects of both molecular diffusion and mechanical dispersion have been grouped into one term. There is some danger in doing this since the diffusion of the solute would vary with both the solute composition and concentration while its dispersion appears to be independent of solute properties. Typically, however, this simplification is justifiable since the magnitude of diffusion is small compared to dispersion.

The solution of Equation (1), subject to the initial and boundary conditions that

$$C(Z,0) = 0 \quad (2A)$$

$$C(0,t) = C_0 \quad (2B)$$

$$C(\infty,t) = 0 \quad (2C)$$

is given by

$$\frac{C(Z,t)}{C_0} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{(Z-Vt)}{2\sqrt{Dt}} \right) + \exp \left(\frac{VZ}{D} \right) \cdot \operatorname{erfc} \left(\frac{Z+Vt}{2\sqrt{Dt}} \right) \right] \quad (3)$$

This solution produces an "S"-shaped breakthrough curve with 50.0 percent of breakthrough corresponding to a time of (distance/velocity) as in the plug-flow model.

For a constant depth and velocity, the spread of the "S" is determined by the magnitude of the dispersion coefficient. The equation itself simulates mathematically the stochastic nature of the velocities at which discrete molecules will traverse the distance Z , with the most probable velocity being the plug-flow velocity and faster or slower velocities becoming less and less probable as a function of their deviation from the norm.

Equation (3) can be applied directly to the columns used in this study with the only assumption being that it adequately describes the effluent breakthrough of columns of finite length Z rather than the profile about Z in a column of infinite length. It must be remembered, however, that for constant velocity and dispersion coefficient, the shape of the "S" will also vary with depth since as depth increases, the probability of a wider velocity spread also increases.

This model was calibrated to the Barre sand by empirically generating breakthrough curves for a 500 mg/l NaCl solution at a fixed velocity and depth. Breakthrough curves were generated for both saturated and unsaturated flow, the latter of which is only approximated by the differential formulation, Equation (1). Appropriate values of D were then extracted by varying the magnitude of this coefficient until a "best fit" of the empirical data was achieved. Based on these results, the following values of D for the Barre sand were estimated:

	Saturated Flow	Unsaturated Flow
Depth (Z), cm	125.73	125.73
Intersitital Velocity (V), cm/min	8.44×10^{-3}	1.169×10^{-2}
Dispersion Coefficient (D), cm^2/min	7.20×10^{-3}	1.44×10^{-2}

Figure 3 presents the breakthrough curves predicted for columns #1-#7 for the saturated leachate flow experiments. The curves are shown shifted in time so they are coincident at $C/C_0 = 0.50$. From this Figure, the significance of dispersion both in relation to the plug-flow model and in relation to the columns of different length becomes clear. Due to this significance, these curves are used in the subsequent analysis to represent zero attenuation to which the leachate breakthrough curves are compared. Similar curves (not shown) were generated for the unsaturated flow and saturated washout experiments, and are used in a similar context. The latter of these were calculated by complementing a leachate inflow model.

Typical Attenuation Type Curves

In addition to modeling dispersion to yield the baseline for zero attenuation, some typical attenuation "type curves" must be considered

before the laboratory data may be interpreted.

Type curves are modeled by adding to the basic differential formulation (Equation 1) terms which describe attenuative mechanisms. There are, however, only a limited number of cases for which analytical solutions are possible. Nevertheless, by making full use of these and by adding a small measure of insight, "typical" breakthrough curve shapes may be conceptualized for the major proposed mechanisms of attenuation.

Chemical and Biochemical Reactions. Convective-dispersive, reactive mass transport is described by the equation

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial Z} + D \frac{\partial^2 C}{\partial Z^2} \pm KC^n \quad (4)$$

where: K = reaction rate constant
 n = exponent indicating reaction order

For the case of $n = 1.0$ (first order kinetics), the solution to Equation (4), subject to initial and boundary condition equations (2A), (2B), and (2C) is given by Bear (5).

$$\frac{C(Z,t)}{C_0} = \frac{1}{2} \exp\left(\frac{vZ}{2D}\right) \left[\exp(-ZB) \cdot \operatorname{erfc}\left(\frac{Z - \sqrt{v^2 + 4DK} t}{2\sqrt{Dt}}\right) + \exp(ZB) \cdot \operatorname{erfc}\left(\frac{Z + \sqrt{v^2 + 4DK} t}{2\sqrt{Dt}}\right) \right] \quad (5)$$

where: $B = \sqrt{\left(\frac{v}{2D}\right)^2 + \frac{K}{D}}$
 $K > 0$ = consumption reaction
 $K < 0$ = formation reaction

Note that for $K = 0$ (no reaction), this solution reduces to the conservative solute solution, Equation (3).

Figure 4 presents the type curves plotted from Equation (5) for consumptive first order reactions. Similar series of curves may be generated for formative first order reactions. Inspection of these curves

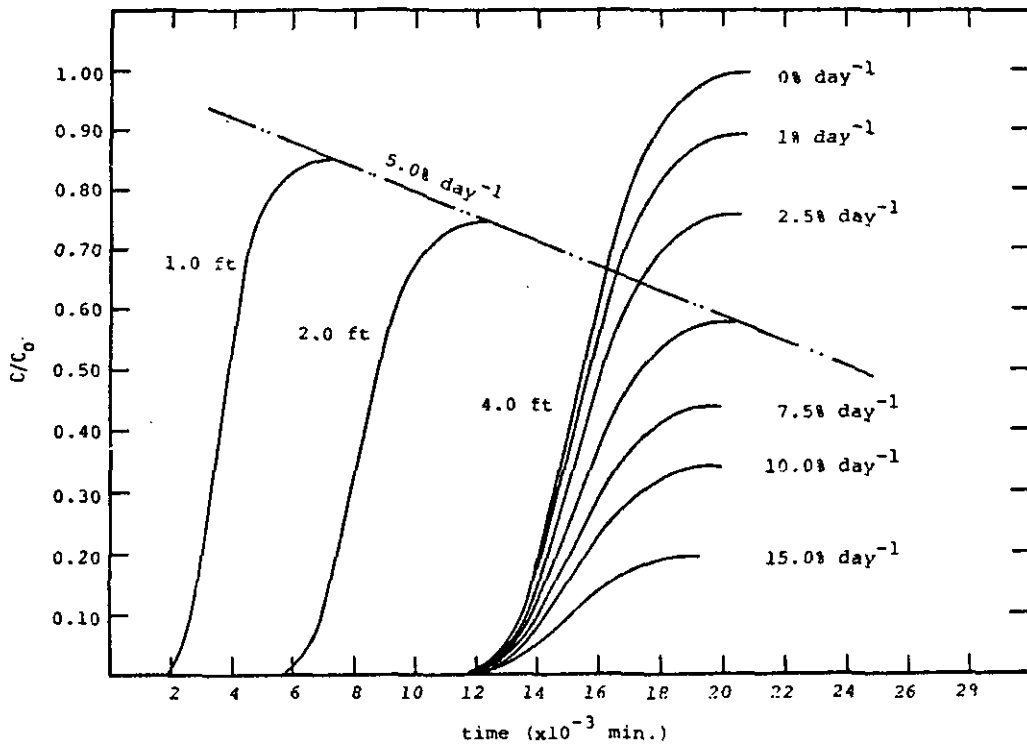


FIGURE 4 - Convective-Dispersive-Consumptive First Order Reactive Mass Transport Type Curves

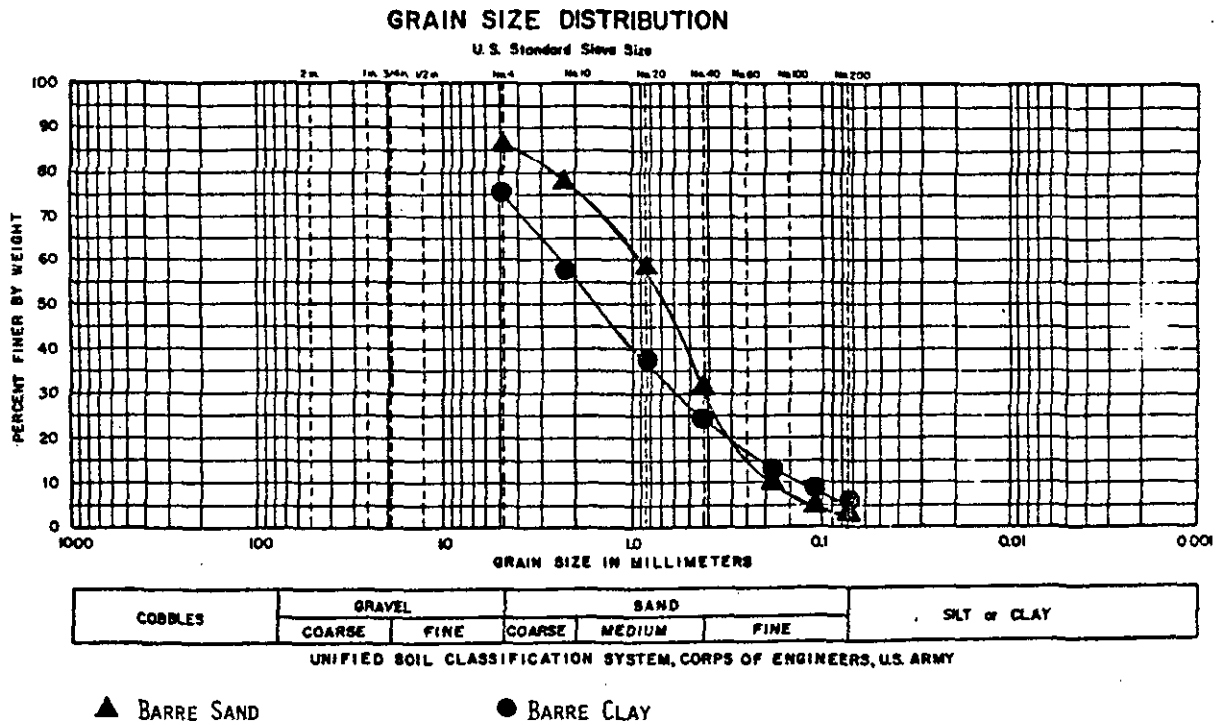


FIGURE 5

yields the two typical characteristics by which reactive attenuation mechanism breakthrough curves may be identified.

1. For $K \neq 0$, the breakthrough curves will not be asymptotic to $C/C_0 = 1.00$. This is the result of mass being permanently added or removed in an amount consistent with the time allowed for the reaction to proceed.
2. For columns of different lengths, the asymptotic C/C_0 values for a constant K will be different. This is due to the difference in reaction times.

Filtration. Although no mathematical formulation is presented to simulate this mechanism, Figure 4 can be used to gain insight into what the curves would look like. For surface straining or shallow depth filtration, characteristic "1" of the reactive solute breakthrough curve would still be manifested. Characteristic "2", however, would not appear.

Sorptive Interactions. Convective-dispersive-sorptive mass transport is described by the equation

$$\frac{\partial C}{\partial t} + \frac{\rho \partial S}{\epsilon \partial t} = -v \frac{\partial C}{\partial Z} + D \frac{\partial^2 C}{\partial Z^2} \quad (6)$$

where: S = mass of solute exchanged with the solid phase per unit mass of exchanger ($M M^{-1}$)

ρ = solid phase (porous medium) bulk density (ML^{-3})

ϵ = medium pore fraction ($L^3 L^{-3}$)

and describes the exchange of material between the solvent and the porous medium due to ion exchange, absorption, physical adsorption, and chemical adsorption, or similar phenomena. Solutions to Equation (6) are developed by substituting for S its functional relationship with the liquid phase solute concentration and then resolving the expression in terms of $C(\text{liquid phase}) = f(Z,t)$.

These functions are generally defined in terms of an equilibrium expression such as a "removal" isotherm. Here removal is used to identify the effect without specifying the mechanism, and negative removal would indicate material addition to the liquid phase. The following are typically encountered removal isotherm models:

<u>Model</u>	<u>Function</u>	<u>Mechanism</u>
Langmuir 1918	$S = \frac{QbC}{1 + bC}$	single layer adsorption or ion exchange
Freundlich 1926	$S = KC^{-n}$	heterogeneous surface energies
Brunauer, Emmett, and Teller (BET) 1938	$S = \frac{BCQ}{(C_S - C)[1 + (B-1)(C/C_S)]}$	multilayer adsorption

Obviously, these cover only simple cases of the possible solid/liquid phase interactions, and far more detailed models may be found in the literature. These do serve, however, to indicate the complexity which may be added to Equation(6) when the substitution is made; a complexity which greatly diminishes the prospects of analytical solution.

Diffusion-Affected Attenuations. It is possible that for some leachate solutes, Equation (3) would not describe their breakthrough curves even if they were truly conservative. This could result from the way the dispersion coefficient was evaluated.

As measured, D describes the dispersion plus diffusion of a 500 mg/l NaCl solution. Although the magnitude of the dispersion portion of this would be the same for any solute, it does not follow that the diffusion portion would be. Since leachate contains several solutes in very high concentrations, their molecular diffusivity combined with the high concentration gradient driving force and relatively low convective transport velocity might yield a much more significant contribution by the diffusion portion of D. If this were the case, the observed breakthrough curves should coincide with the model at $C/C_0 = 0.50$ but diverge elsewhere due to the wider velocity spread a higher D would generate.

Combined Mechanisms. Unfortunately, in a solution as chemically diverse and active as leachate, it is often more probable that a single solute will undergo multiple attenuations rather than respond to any one of these first four groups. It is altogether possible that a single solute may be removed by reactions, filtrations, and sorptions all at the same time or at different times in its column transport.

Obviously, this allows for more combinations and complexities than may be "typed". Nevertheless, by observing the "typical" nature of the selected mechanism curves and by adding to this some knowledge of the solute chemistry, complex breakthrough curves may be used to identify and possibly quantify the mechanisms by which they were formed.

Leachate and Surface Water Characterization

The characterization of the three leachate samples is presented in Table 2. Batch "B" was a little less "potent" than either of the other two but all three fall within the ranges of values presented in Table 1. Batch "B" was a little more stable during storage, and this, no doubt, was due to refrigeration of the whole reservoir. The analysis of the surface water sample used for the washout experiment is presented in Table 3.

Soil Characterization

Throughout this report the two soil samples collected from the super funnel area of the Barre Research Facility will be referred to as "Barre sand" and the soil from the dike will be referred to as "Barre clay". The grain size distributions resulting from the sieve analysis for the first Barre sand sample and the Barre clay sample are shown in Figure 5. When the Barre sand was sieved with a #4 sieve approximately 14.2 percent by weight was removed.

The results of the analyses of the sieved soils are summarized in Table 4. The two Barre sand samples are nearly the same. The sand used in the unsaturated flow study had slightly more clay but a slightly lower CEC. The Barre clay had a CEC nearly three times higher than the sand and significantly higher amounts of exchangeable calcium and magnesium. The manganese content of the clay was also much higher than that of the sand.

Specific Conductance

The specific conductance of leachate reflects the total concentration of ionic solutes. In "young" leachate organic species such as free volatile fatty acids as well as the inorganic species contribute to the conductivity. In "old" leachate the conductivity is mainly attributed to the inorganic ions and to a lesser extent to fulvic acids.

TABLE 2
 Characterization of Leachate Samples

Parameter	Batch "A"	Batch "B"	Batch "C"
Nature	Winter Leachate	Summer Leachate	Summer Leachate
Color	Clear straw yellow	Clear pale yellow	Clear Green-Yellow
Odor	Intense	Moderate	Moderate
Specific conductance ($\mu\text{MHOS cm}^{-1}$)	>18,000	11,800	ND
pH	5.50	6.00	6.22
Alk (mg/l as CaCO_3)	2,100	1,850	4,150
COD (mg/l)	11,100	7,700	13,534
TOC (mgC/l)	ND	2,700	4675
NH_3 (mgN/l)	225	175	378
SO_4 (mg/l)	128	60.5	ND
NO_3 (mg/l)	2.60	ND	ND
PO_4 (mg/l)	0.18	ND	ND
Cl (mg/l)	ND	450	ND
Fe (mg/l)	1,020	362	1095
Mn (mg/l)	32.5	16.2	22.2
Ca (mg/l)	680	480	776
Mg (mg/l)	173	133	117
Cu (mg/l)	2.65	-	-
Zn (mg/l)	0.71	1.00	-
Total Plate Count (Organisms/ml)	60,000	200,000	ND
Source	Surface Pool	Surface Pool	Super Funnel

ND = Not Determined.

TABLE 3

Characterization of Surface Water Sample

Specific Conductance (μ MHOS cm^{-1})	70
pH	5.70
Alkalinity (mg/l as CaCO_3)	2.10
COD (mg/l)	7.40
NH_3 (mgN/l)	0.18
SO_4 (mg/l)	0.0
NO_3 (mg/l)	0.1
PO_4 (mg/l)	0.0
Fe (mg/l)	Trace (<0.05)
Mn (mg/l)	Trace (<0.05)
Ca (mg/l)	1.15
Mg (mg/l)	0.57
Cu (mg/l)	Trace (<0.05)
Zn (mg/l)	0.08
K (mg/l)	0.38
Dissolved Oxygen (mg/l)	8.05
Total Plate Count: organisms/ml	7000

TABLE 4
Summary of Soil Analysis

Soil	Barre Sand	Barre Sand	Barre 'Clay'
Flow	Saturated & Washout	Unsaturated	Unsaturated
pH 10 g + 30 ml .01 M CaCl_2	5.10	4.83	4.82
CEC meq/100 g	1.692	1.478	4.714
Ca meq/100 g	.069	.070	1.644
Mg meq/100 g	.023	.016	.666
Al meq/100 g	.038	.042	.064
Acidity meq/100 g	.088	.103	.082
Organic Matter %	.107	.109	.103
Mn mg/100 g	ND	2.51	9.83
Sand %	96.9	95.0	36.0
Silt %	2.1	1.8	36.8
Clay %	1.0	3.2	27.2

ND = Not Determined.

Chain and DeWalle (9) reported that specific conductance varies as leachate interacts with soil. The specific conductance of biologically stabilized leachate may decrease during seepage through soils as a result of cation exchange in which Ca^{++} and Mg^{++} are replaced by Na^+ . However, values may also increase as a result of nitrification in which NH_4^+ is converted to NO_3^- and H^+ .

The specific conductance breakthrough curves for the three flow situations are shown in Figures 6, 7, and 8. The saturated flow curves follow the conservative dispersion model except that they are representative of a larger dispersion coefficient. This is entirely reasonable since the coefficient is influenced by mechanical dispersion and molecular diffusion. The high concentrations of constituents in leachate would give rise to greater diffusional effects than those observed using 500 ppm NaCl.

For the washout stage there was an initial displacement of leachate that had not drained from the columns. The long tails on these curves are indicative of the gradual release of material from the soil matrix.

The curves for unsaturated flow all show an initial attenuation of specific conductance. This may be the result of cation exchange reactions with the soil. The curve for the one foot depth approaches C/C_0 equal to 1.0 as expected but the curves for 2, 3, and 4 feet appear to level off at C/C_0 values less than 1.0. The 1 1/2 foot curve shows that at greater depths curves may be expected to eventually reach $C/C_0 = 1.0$.

pH

One of the master variables examined was pH. The term "master variable" is used because of the great effect pH has on many of the reactions taking place.

The pH history for the saturated flow experiment is given in Figure 9. During the run the pH of the reservoir varied over the range 5.1 to 5.6. The first samples for the 1, 2, and 3 foot depths showed a sharp drop to pH 4.7. This sharp drop is associated with the first appearance of leachate. The four foot column effluent gradually dropped down to pH 4.65. This gradual drop follows the displacement of the deionized distilled water initially in the column.

The Barre sand had a pH of 5.1 and approximately 0.09 meq/100 g exchangeable acidity. The sharp drop in sample pH may have been due to reactions

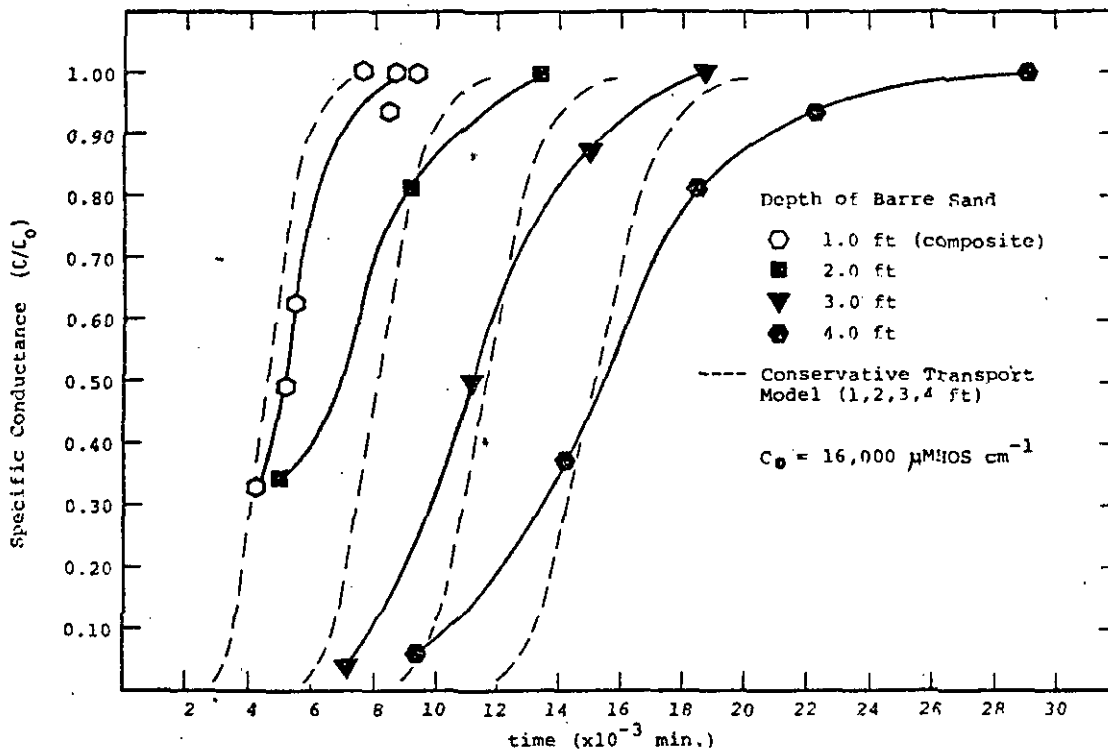


FIGURE 6. SPECIFIC CONDUCTANCE BREAKTHROUGH CURVES (SATURATED FLOW).

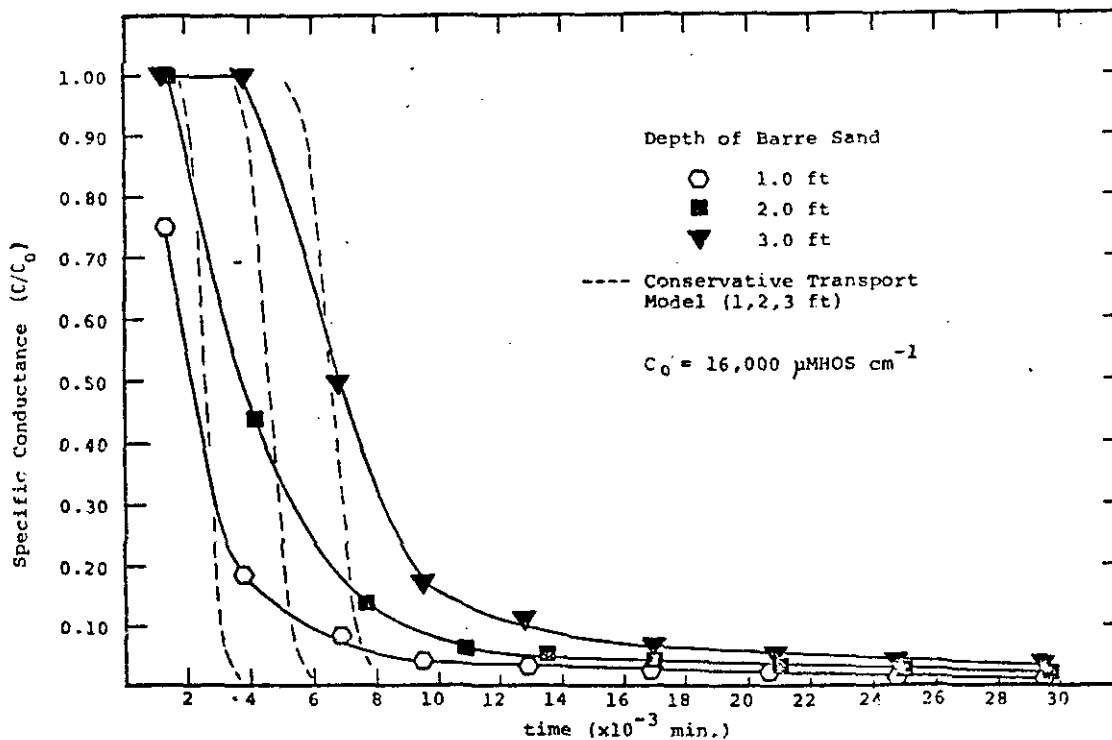


FIGURE 7. SPECIFIC CONDUCTANCE BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW).

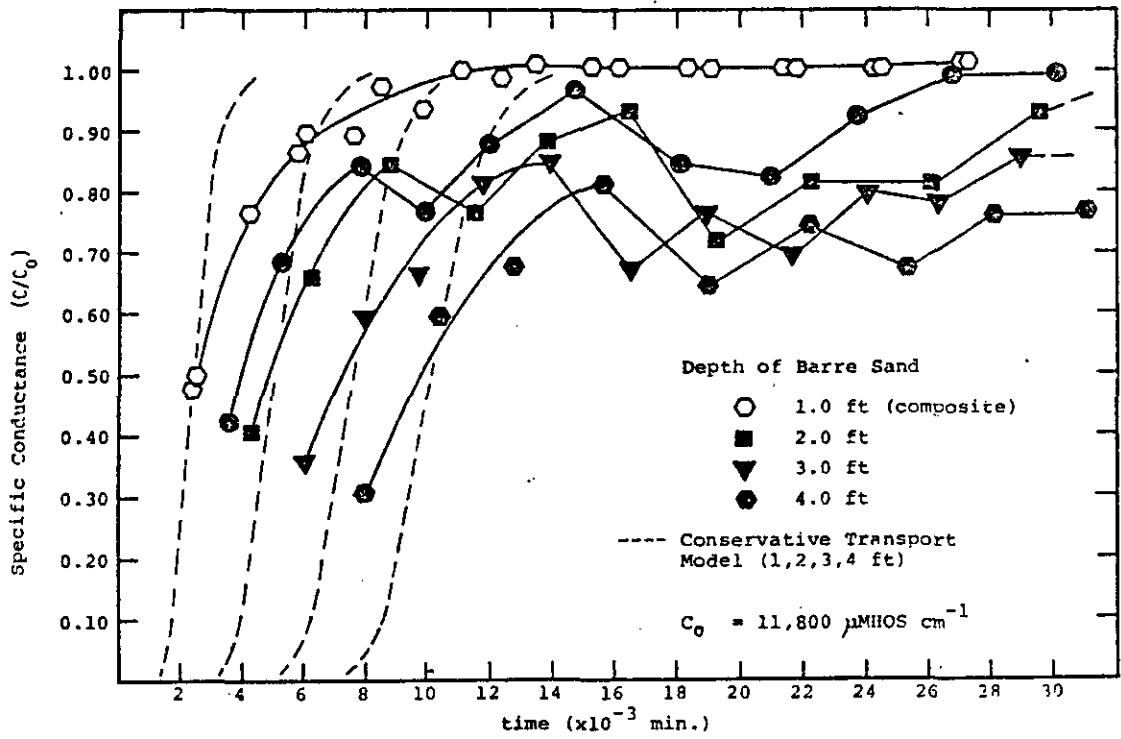


FIGURE 8. SPECIFIC CONDUCTANCE BREAKTHROUGH CURVES (UNSATURATED FLOW).

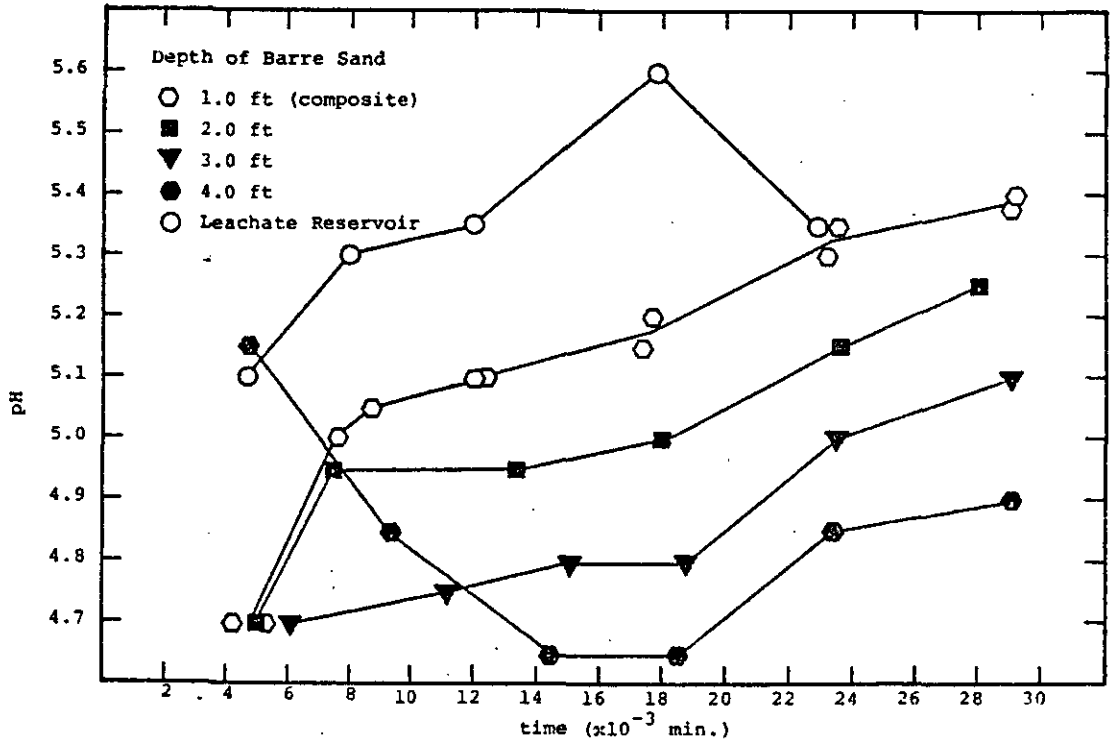
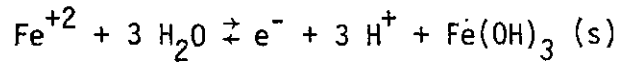


FIGURE 9. COLUMN EFFLUENT pH DURING BREAKTHROUGH CURVE GENERATION (SATURATED FLOW).

with the soil but is more likely due to changes in the samples as they were collected in the 1 liter bottles. As the samples were collected it was observed that they were bright orange and turbid. Atmospheric oxygen in the collection bottles caused some sample oxidation, and in particular, oxidation of ferrous iron to ferric iron. The oxidation and formation of a ferric hydroxide precipitate results in the production of H^+ as shown below



After the initial sharp drop the pH gradually rose towards the reservoir value. This rise was affected by reactions within the column and the oxidation just described. As time progressed, conditions within the columns became more strongly reducing than at the start. A "black layer" (discussed in more detail in the sections on iron and sulfate) developed and progressed down the column. The first 100-200 ml of sample in the collection bottles turned orange as before, but then, due to the strong reducing nature of the incoming liquid and the limited amount of oxygen, the samples gradually turned green-black.

The pH history for the washout run is shown in Figure 10. The pH of the last leachate to enter the columns was approximately 6.0. The columns stood for a while filled with this leachate. Unfortunately, when they were drained the pH of the leachate drained was not measured. The pH of the surface water was fairly constant at 5.8. All three columns showed an initial rise in pH above that of the surface water with the shortest column showing the greatest rise. If the rise were due to cation exchange we might expect the greatest change to occur with the deepest column.

The pH history for the unsaturated flow case is shown in Figure 11 and is similar to that for the saturated flow case. There was a sharp drop followed by a gradual rise to equal the value in the reservoir. Again, this is due to reactions with the soil, oxidation during sample collection, and changing conditions during the run.

Alkalinity

The alkalinity of a water is the capacity to accept protons and is determined by titrating the sample with strong mineral acid to a specified endpoint. The test only indicates general properties of the leachate and cannot be used for the quantitative determination of specific species.

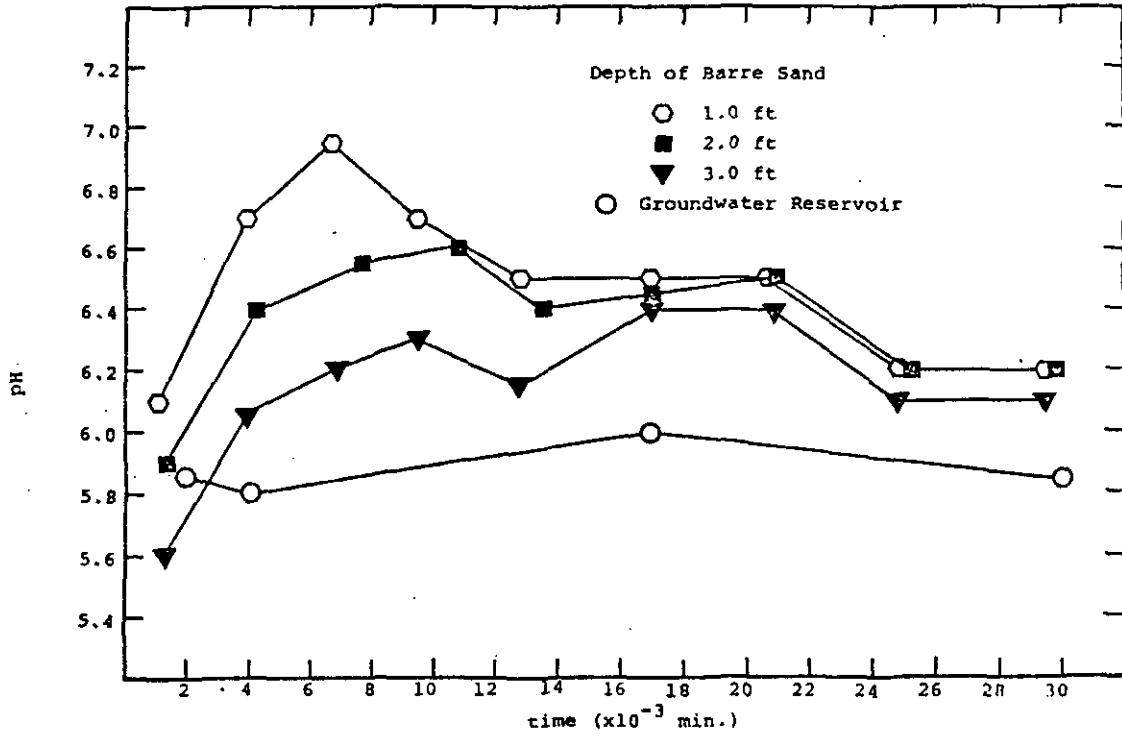


FIGURE 10. COLUMN EFFLUENT pH DURING BREAKTHROUGH CURVE GENERATION (SATURATED "WASHOUT" FLOW).

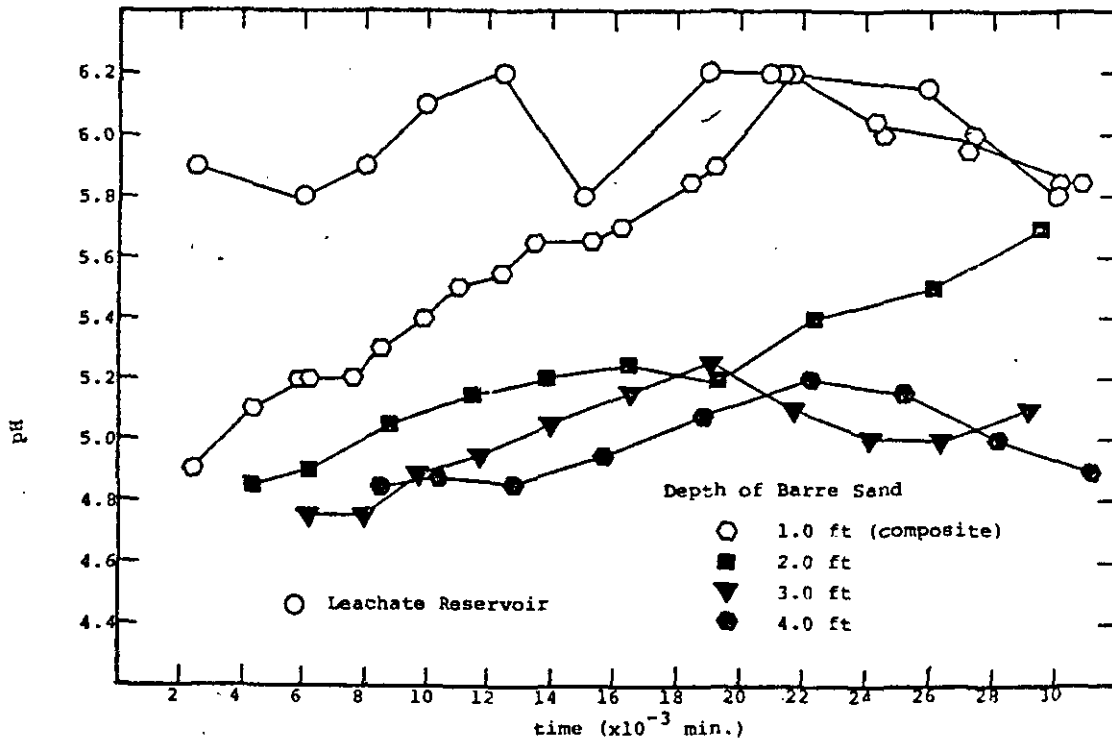


FIGURE 11. COLUMN EFFLUENT pH DURING BREAKTHROUGH CURVE GENERATION. (UNSATURATED FLOW).

Chain and DeWalle (9) reported that in leachate from a recently generating fill, where the pH is acidic, most of the alkalinity was due to the buffering capacity of partially dissociated free volatile fatty acids and carboxyl groups of complex organics. In biologically stabilized leachate where the pH is generally neutral or slightly alkaline, the alkalinity is controlled by the carbonate and bicarbonate species as a result of the dissolution of the CO_2 gas generated during methane fermentation.

The equilibrations of varying amounts of soil with undiluted leachate in which the aeration-oxidation problem was minimized showed alkalinity reductions. For this leachate (Batch "C") approximately 250 mg/l were removed during filtration. It is not clear whether this removal is due to the filtering out of solids that have an acid neutralizing capacity or due to aeration during the filtration and the same reactions discussed earlier.

The reductions in alkalinity are shown in Figure 12. As the soil/leachate ratio increased the sample alkalinity decreased. This decrease was nearly three times greater for the Barre clay than for the Barre sand. Since the changes in alkalinity are closely related to pH changes the variations in pH during these equilibrations are presented in Figure 13. For the samples with Barre sand the pH decreases as the soil/leachate ratio increases. Initially the decrease for the Barre clay is much sharper, but it tends to level off as the ratio increases. Both the Barre sand and Barre clay are mildly acid soils with approximately 0.08 meq/100 g exchangeable acidity. The release of H^+ and aluminum hydroxy ions results in a lowering of solution pH and, thus, a reduction in sample alkalinity.

The alkalinity breakthrough curves for saturated flow conditions are shown in Figure 14. The curves show that alkalinity is attenuated. Some of this attenuation may be ascribed to reactions with the soil as was the case during the batch equilibrations. Most of the attenuation, however, is the result of changes that took place as the samples collected in the 1 liter bottles. During collection, as discussed in the section on pH, there was oxidation of ferrous iron to ferric iron and release of H^+ as ferric hydroxide precipitated. This H^+ reacted with some of the substances contributing to the alkalinity.

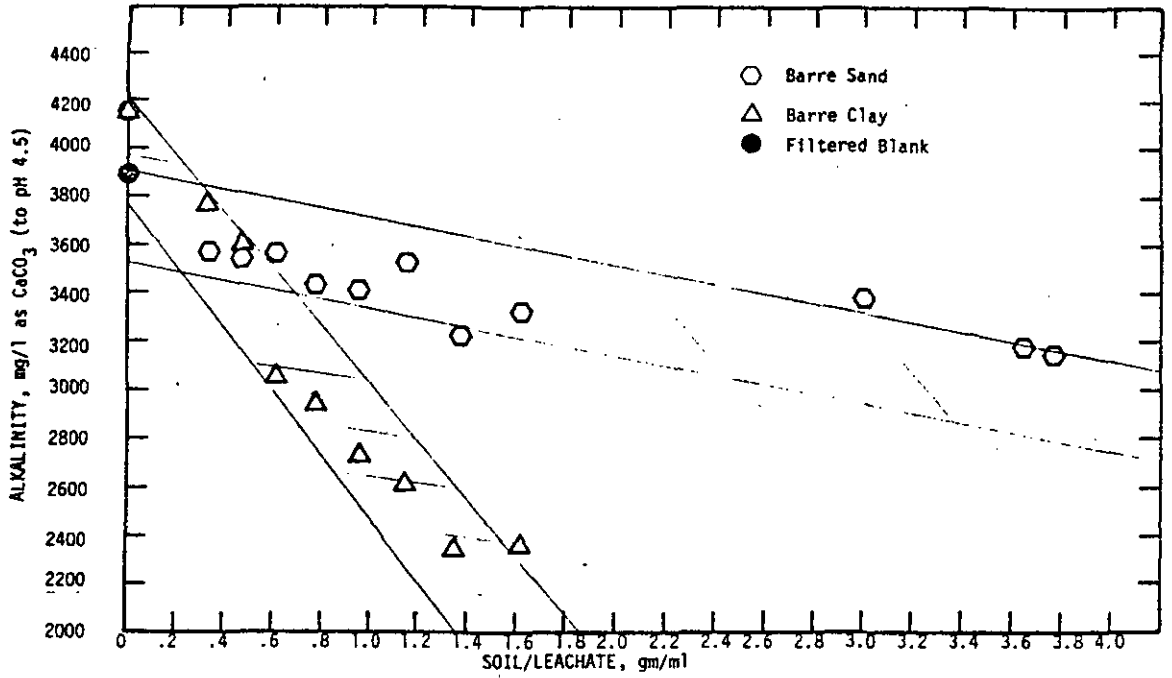


FIGURE 12. ALKALINITY CHANGES IN BATCH EQUILIBRATIONS.

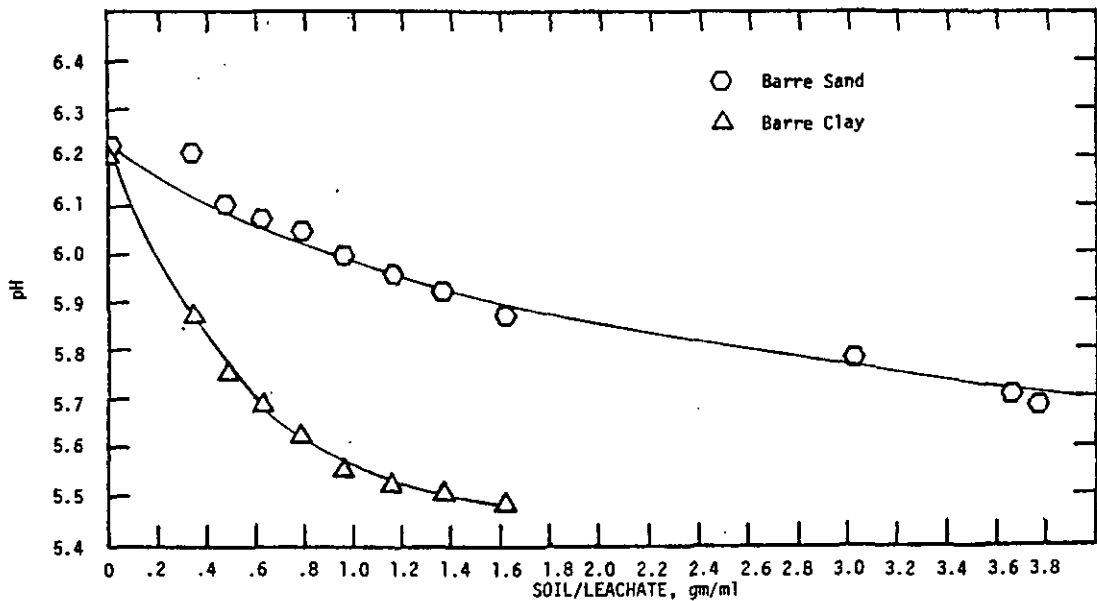


FIGURE 13. pH VARIATIONS IN BATCH EQUILIBRATIONS.

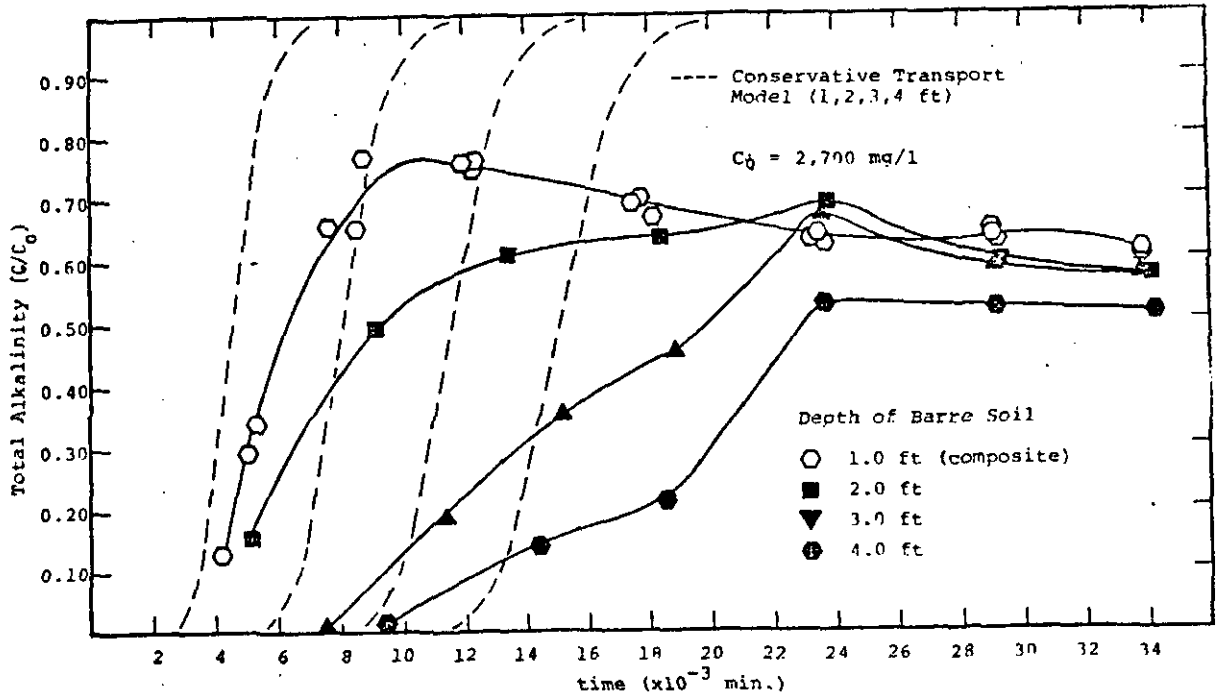


FIGURE 14. TOTAL ALKALINITY BREAKTHROUGH CURVES (SATURATED FLOW).

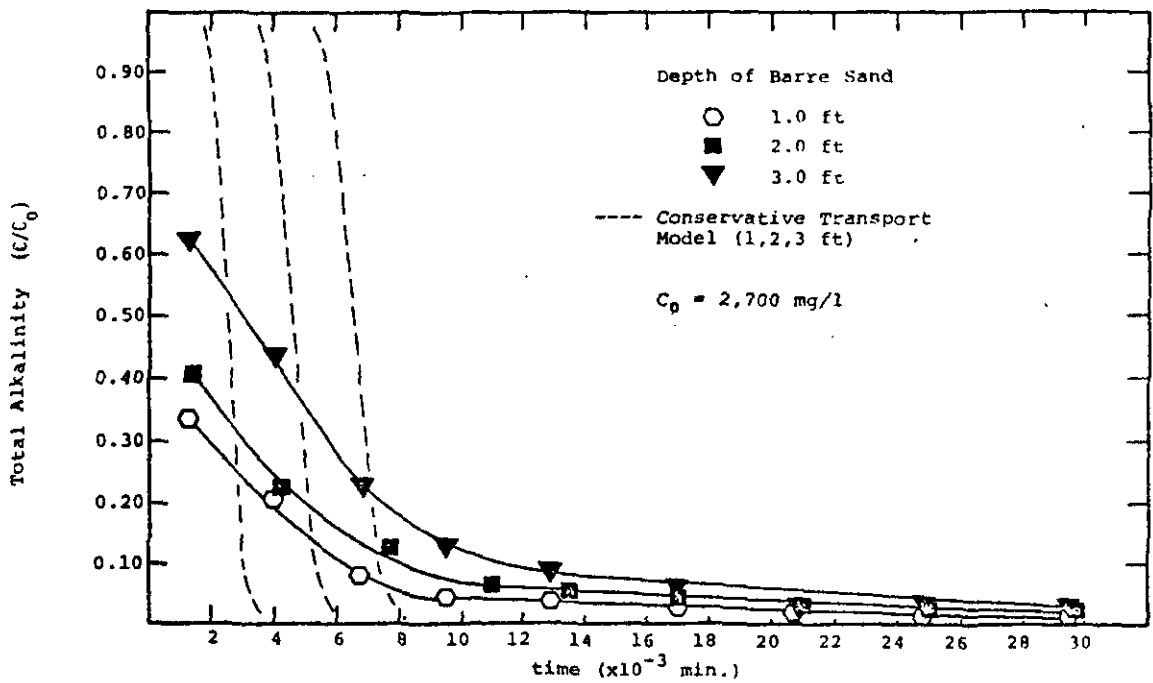


FIGURE 15. TOTAL ALKALINITY BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW).

The alkalinity washout curves are shown in Figure 15. Initially there are some high values resulting from the displacement of leachate that had not drained out. The long tails on the washout curves indicate that substances contributing to the alkalinity are gradually washing off the soil.

Figure 16 summarizes the results for the unsaturated flow experiment which are not very different from the saturated flow case. The soil used in this experiment had a pH of 4.8 and an exchangeable acidity of 0.10 meq/100 g. The sharp initial attenuation was due to reactions with the soil as well as oxidation of the sample in the collection bottles.

Chemical Oxygen Demand

The chemical oxygen demand test performed on leachate provides a measure of organic matter and reduced cationic species. The batch equilibrations using diluted leachate yielded such a scatter of points that no useful information could be extracted. The results for the batch equilibrations using undiluted leachate also had a considerable scatter, however, it was noted that several hundred mg/l may be removed by filtration alone and that there was no appreciable difference between the Barre sand and the Barre clay.

The COD breakthrough curves for saturated flow are shown in Figure 17. There is no indication of any significant COD attenuation. The curves for each depth are not delayed behind the conservative dispersion model and all approach a C/C_0 equal to 1.

The COD washout curves are shown in Figure 18. Note that a new C_0 of 7700 mg/l was used in the construction of this figure as compared to the 12,500 mg/l used in the saturated flow case. This change was due to fluctuations in the COD of the reservoir. These washout curves represent the displacement of leachate that was not removed when the columns were drained. However, it was found that the mg COD washed out was greater than would be predicted. This is in agreement with the fact that more iron washed out than was originally removed since reduced iron contributes to COD.

The unsaturated flow results shown in Figure 19 are a little different than those for the saturated case. There is evidence of some minor depth dependent removal. In addition, the curves initially level

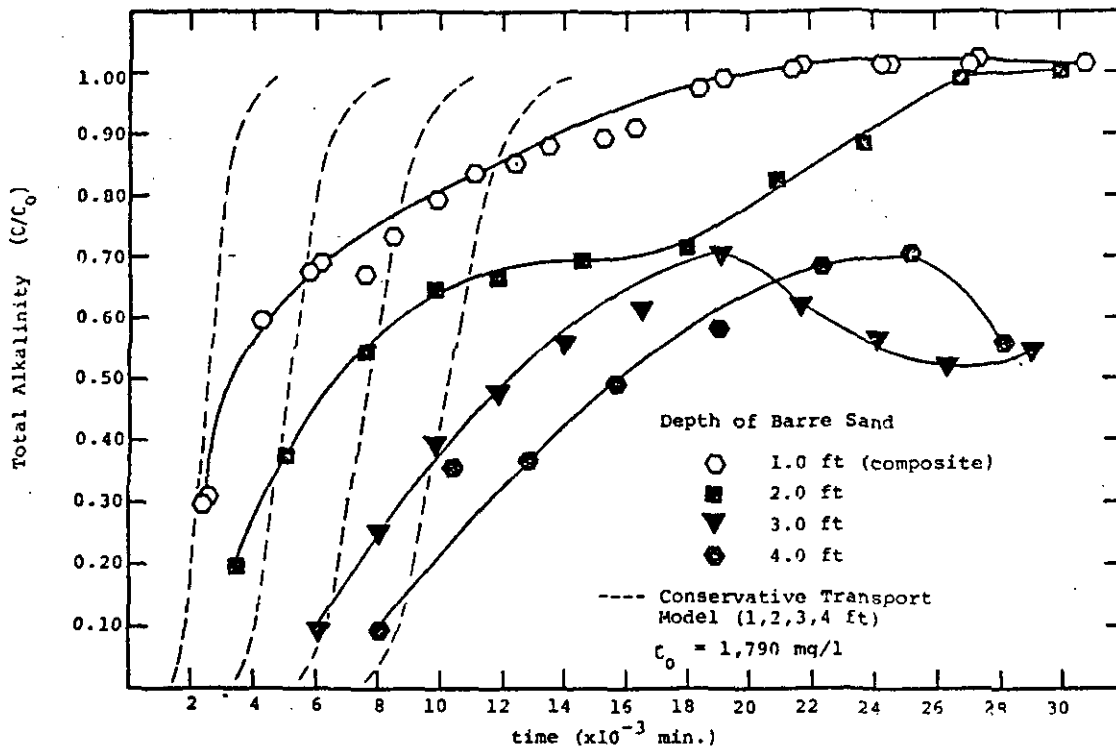


FIGURE 16. TOTAL ALKALINITY BREAKTHROUGH CURVES (UNSATURATED FLOW).

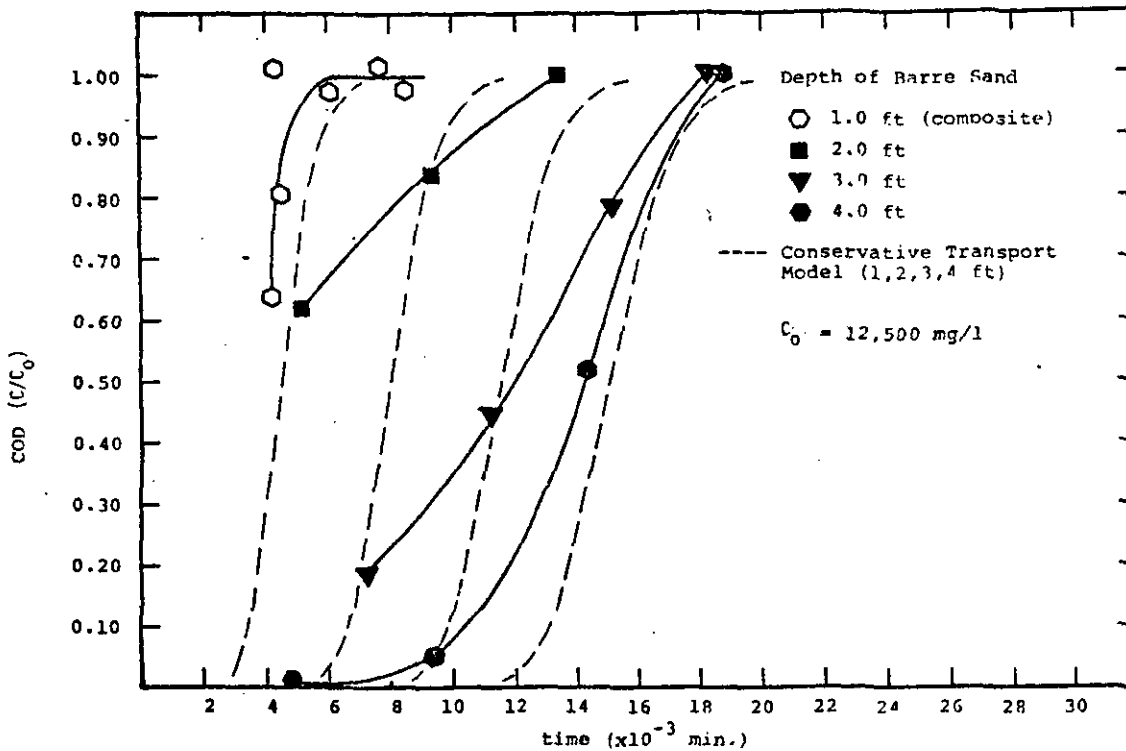


FIGURE 17. CHEMICAL OXYGEN DEMAND BREAKTHROUGH CURVES (SATURATED FLOW).

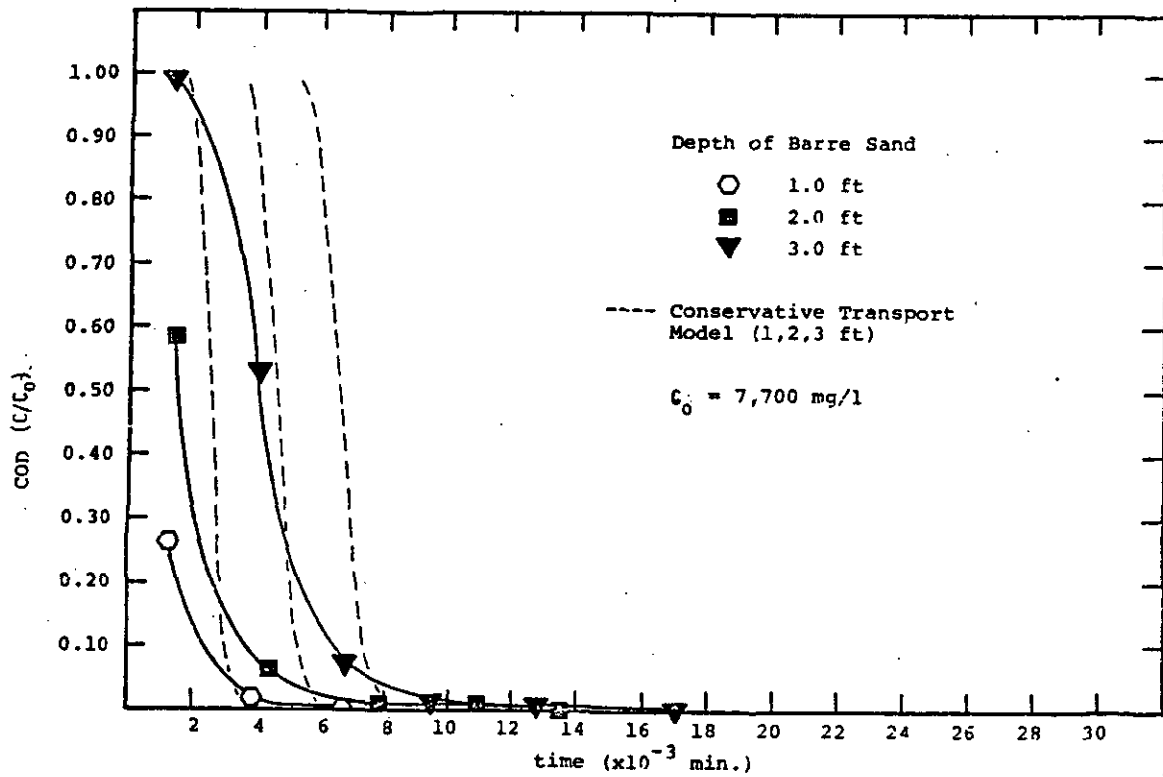


FIGURE 18. CHEMICAL OXYGEN DEMAND BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW).

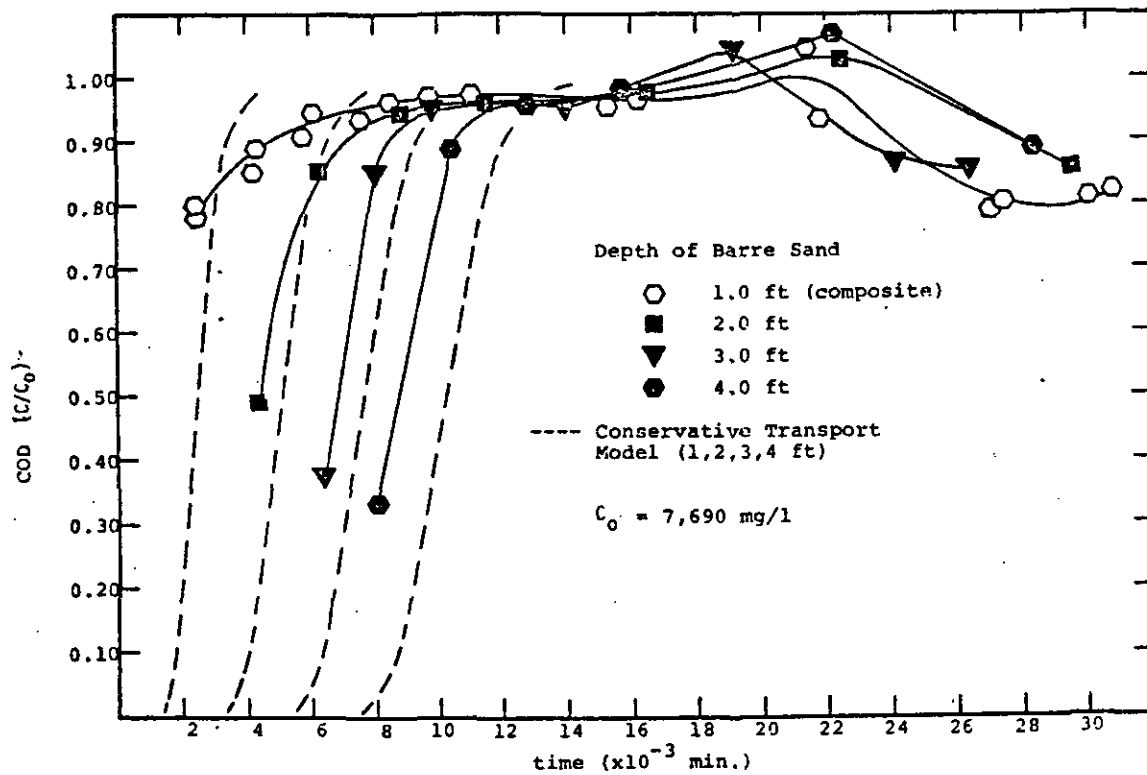


FIGURE 19. CHEMICAL OXYGEN DEMAND BREAKTHROUGH CURVES (UNSATURATED FLOW).

off at a C/C_0 of 0.95 indicating that some depth independent removal is taking place. This depth independent removal may be due to filtration or biological activity at the surface.

It is interesting to note that the curves level off at a lower value, C/C_0 equal to 0.9, as the run progresses. This may be due to the increased activity of a more acclimated biological population.

Total Carbon

In order to get a better measure of attenuation of organic matter than the COD test provided, total carbon (TC) measurements were made. The changes in total carbon resulting from the equilibration of undiluted leachate with varying amounts of soil are shown in Figure 20. The original leachate (Batch "C") had a TC of 4770 mg/l and approximately 300 mg/l were removed by filtration alone. After accounting for this removal by filtration there is a general TC reduction of approximately 0.1 mg/g as the soil/leachate ratio increases. In addition, there does not seem to be any sharp distinction in removal between the Barre sand and the Barre clay soils.

The total carbon breakthrough curves for unsaturated flow conditions are shown in Figure 21. These curves indicate that there is a depth dependent removal of organics. This depth dependent removal amounted to 287 mg/foot or 0.07 mg/g, which is in fairly good agreement with the 0.1 mg/g obtained in the batch equilibrations. Approximately 200 mg are removed independently of depth. This may be due to filtration and/or biological activity at the surface.

Chlorides

Chloride analysis was performed only during the unsaturated flow experiment and the results are shown in Figure 22. Chloride is usually considered a conservative material in soil systems. The results here indicate that some chlorides were removed. For the unsaturated flow experiment raw leachate was applied to dry soil. The first sample for each depth (each analyzed at a different time so that it is probably not an analytical error) all had C/C_0 values less than 1. More chloride was removed from the 4 foot column than from the 1 foot column but that amount was not four times as large. The 1/2 foot of Barre clay (shown

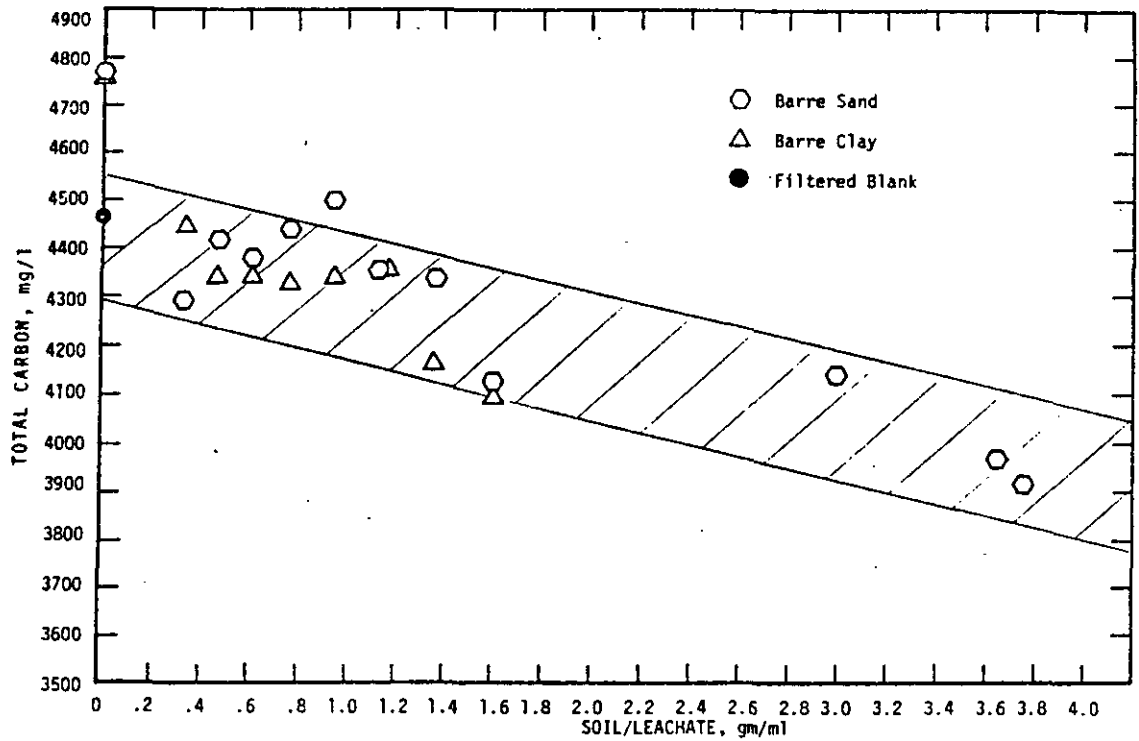


FIGURE 20. TOTAL CARBON REMOVALS IN BATCH EQUILIBRATIONS.

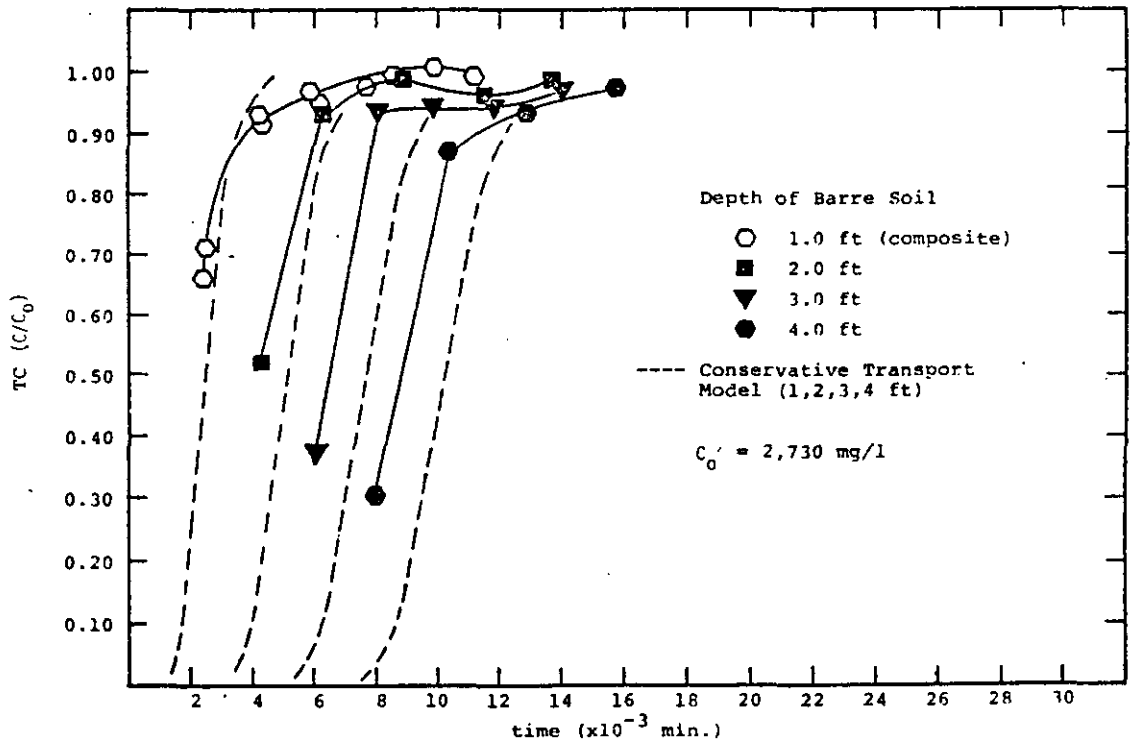


FIGURE 21. TOTAL CARBON BREAKTHROUGH CURVES (UNSATURATED FLOW).

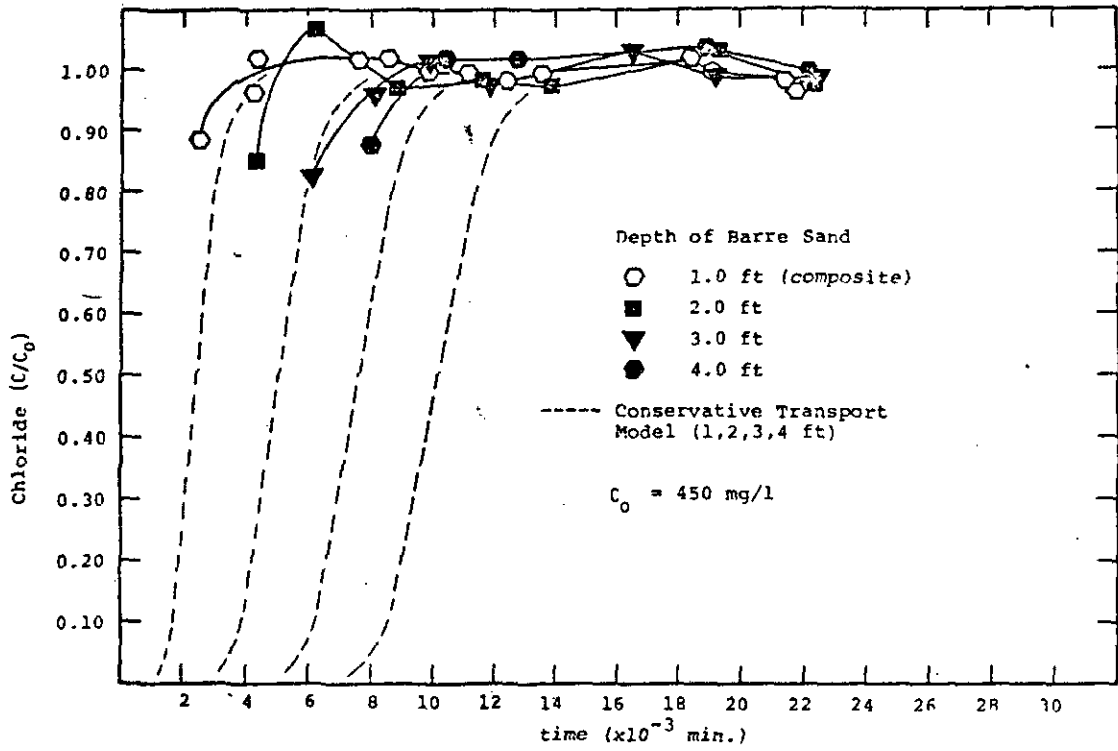


FIGURE 22. CHLORIDE BREAKTHROUGH CURVES (UNSATURATED FLOW).

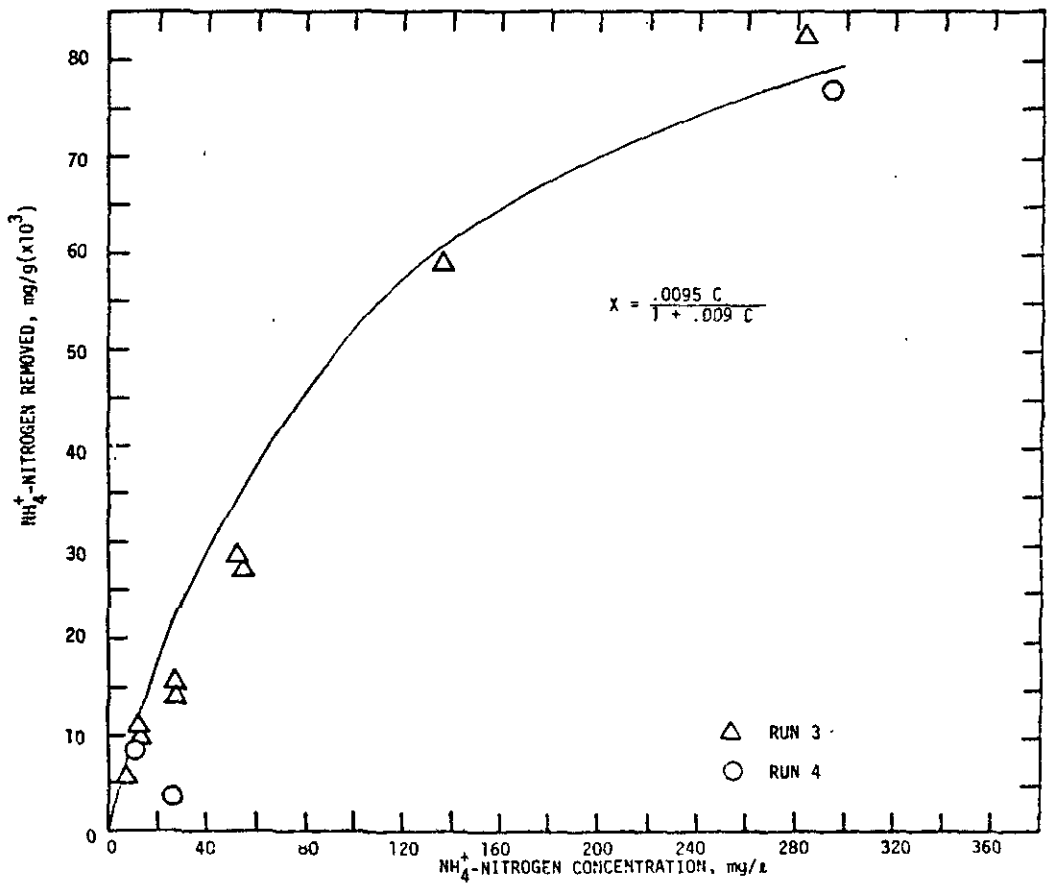


FIGURE 23. AMMONIA REMOVAL ISOTHERM.

in Figure 57) removed more chlorides than the 1 foot columns of Barre sand.

Griffin *et al.* (19) observed some chloride attenuation in their column experiments but report that the attenuation was not a function of the type or amount of clay mineral present. They attributed the removals to interaction at anion exchange sites on the clay and hydrous oxide surfaces and to other chemical reactions.

Ammonia

Because of the reducing environment of the landfill most of the inorganic nitrogen in the leachate is in the NH_4^+ form. The ammonium ion is subject to cation exchange reactions, microbial uptake, and other transformations described by Lance (30) and Lance and Whisler (31).

The equilibrium distribution for NH_4^+ prepared using diluted leachate is shown in Figure 23. The data were fitted to the Langmuir model and the Langmuir equation

$$S = \frac{0.0095 C}{1 + 0.009 C}$$

is shown in the figure.

The Freundlich model was also applied but the fit was not much better. The Freundlich model took the form

$$S = 0.0014 C^{0.71}$$

This may be compared to the results of Farquhar and Rovers (14). For the soil and leachate used in their experiment NH_4^+ removal was described by the equation

$$S = 0.0095 C^{0.346}$$

In the preparation of this isotherm a blank containing no soil was equilibrated along with the soil samples. The NH_4^+ removal calculation was based on the NH_4^+ concentration in this blank at the end of the equilibration. Provided that the dilutions did not stimulate biological activity, NH_4^+ removal by biological uptake was accounted for in the blank. The removals shown in Figure 23, therefore, were due to sorption reactions with the soil.

Ammonium ion removals were also examined using undiluted leachate equilibrated with varying amounts of soil. As the soil/leachate ratio increased the equilibrium NH_4^+ concentration decreased. The decrease for the Barre clay was nearly five times greater than for the Barre sand. At an NH_4^+ concentration (Figure 24) of approximately 350 mg/l removals ranged from 0.01 to 0.06 mg/g. If some of the extremes are neglected a range of removal of 0.02 to 0.03 mg/g might be used as "ball park" guideline for NH_4^+ concentrations in the range of 300 mg/l. This value, however, is not in agreement with the quantity predicted for a concentration of 300 mg/l by the Langmuir equation from the previous batch equilibration. Part of the difference may be ascribed to use of different leachates, but it is most likely due to the use of dilutions in the first run. Farquhar and Rovers (14) point out that because leachate is a complex combination of chemical components attenuation, and specifically sorption, of a specific component will be influenced by the presence of others. Thus, the use of dilutions may affect these influences and lead to higher predictions for NH_4^+ removal than is observed with undiluted leachate.

The saturated flow breakthrough curves for NH_4^+ in Figure 25 are all delayed behind the predicted curve for a conservative material indicating that sorption reactions with the soil are significant. The curves for the 1, 2, and 3 foot columns level off at C/C_0 equal to 0.95 suggesting that NH_4^+ is being removed by some reaction such as microbial uptake.

A mass balance for NH_4^+ was calculated and the NH_4^+ removal as a function of depth is shown in Figure 26. There is quite a bit of scatter for the saturated flow case and the slope of 72.5 mg/ft or 0.016 mg/g indicates that removals are slightly less than the 0.02 to 0.03 mg/g predicted by the isotherm experiment. The intercept is representative of depth independent removal. Approximately 94 mg are removed at the column surfaces, presumably as a result of microbial activity.

When the columns were flushed with clean surface water, NH_4^+ was washed out as shown in Figure 27. Mass balance calculations indicate that more NH_4^+ was washed out during this stage of the experiment than

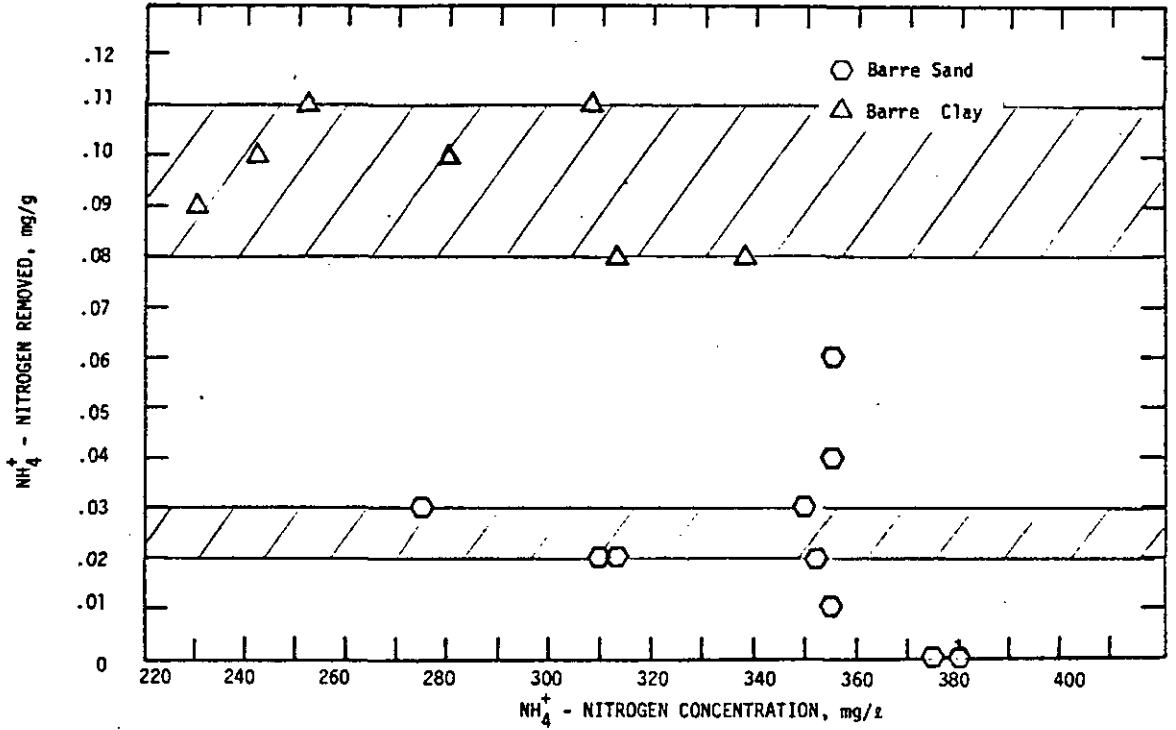


FIGURE 24. AMMONIA REMOVAL IN BATCH EQUILIBRATIONS.

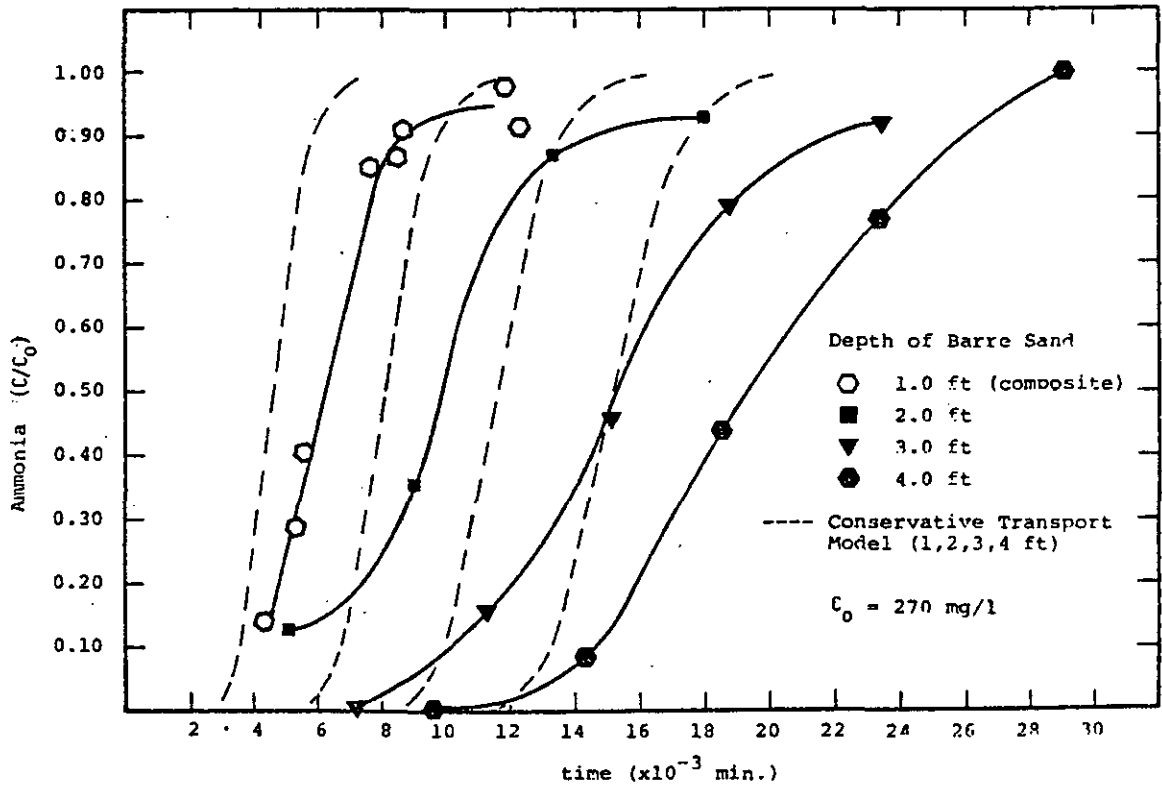


FIGURE 25. AMMONIA BREAKTHROUGH CURVES (SATURATED FLOW).

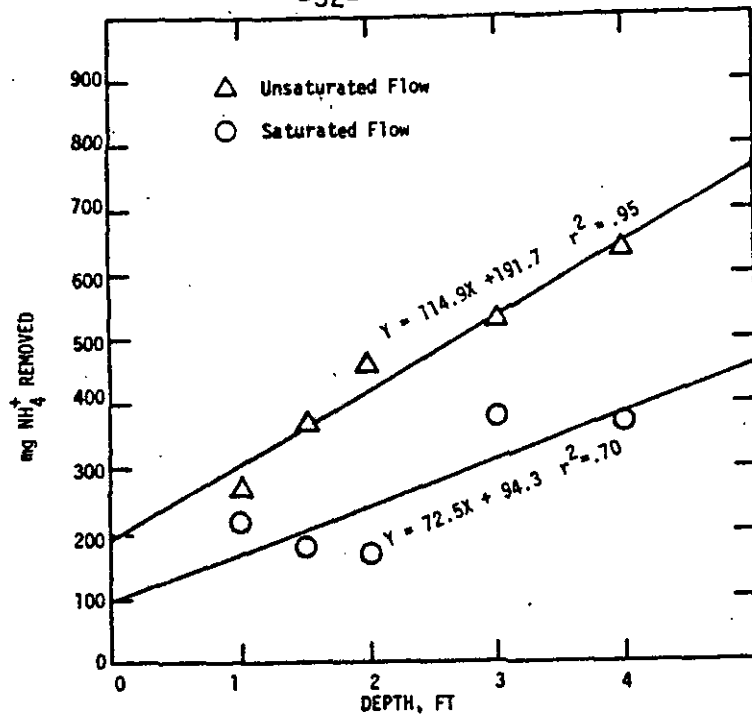


FIGURE 26. AMMONIA REMOVAL IN SATURATED AND UNSATURATED FLOWS.

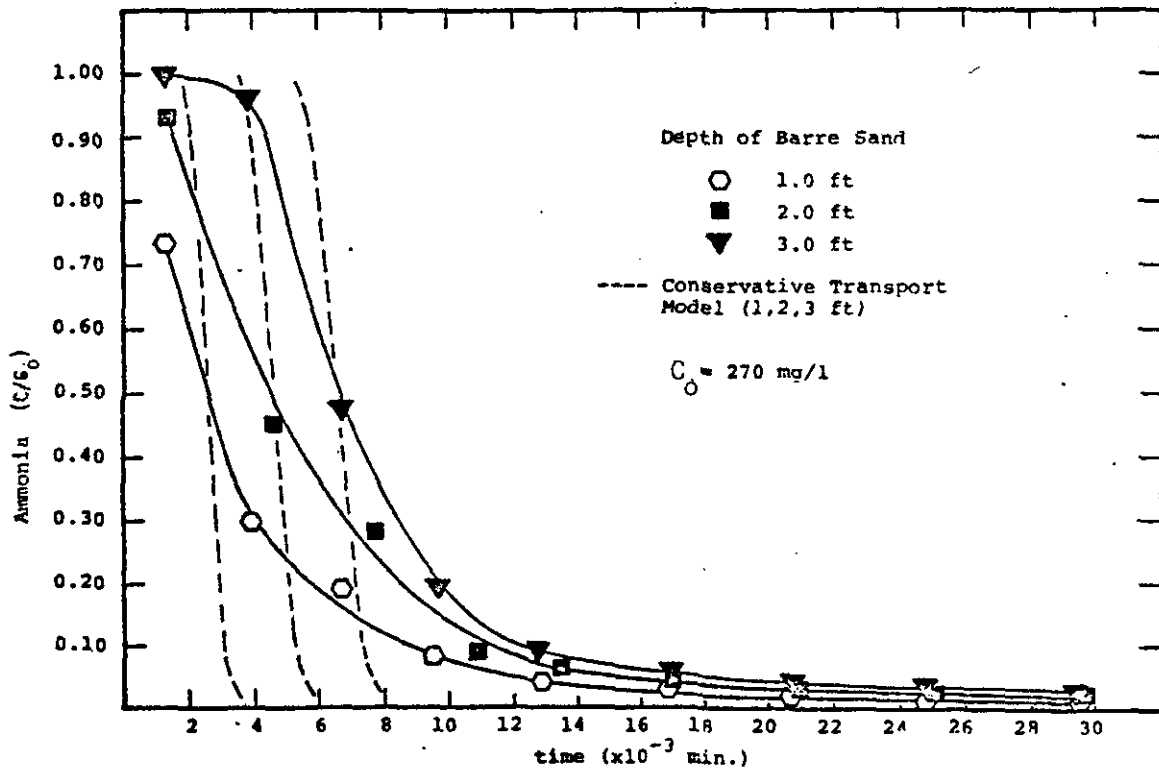


FIGURE 27. AMMONIA BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW)

was removed from the leachate to begin with. In the saturated flow stage 215, 165, and 378 mg NH_4^+ were removed by columns 3, 5, and 6 respectively. In the second stage 406, 492, and 580 mg NH_4^+ were washed out of these columns. This is most likely due to microbial activity in the columns between the time of shut down after saturated flow and the start of washout (May 18 to June 21, 1977). Microbial breakdown of the organics in the leachate would lead to increased NH_4^+ concentrations and could account for these releases. Unfortunately this cannot be substantiated because the leachate that was drained from the columns prior to washout was not analyzed.

The unsaturated flow breakthrough curves for NH_4^+ in Figure 28 are similar to those for saturated flow. The lagging of the curves indicates a depth dependent removal mechanism and the leveling off at C/C_0 equal to 0.9 indicates a depth independent removal mechanism. The y axis intercept in Figure 26 of 190 mg provides a measure of the depth independent removal presumed to be biological uptake. The unsaturated flow case had a slope of 119.4 mg/ft or 0.026 mg/g. This value nicely falls into the range of removals for Barre sand, 0.02 to 0.03 mg/g, predicted by the batch equilibrations.

The curve for the 1/2 foot depth of Barre clay is shown in Figure 57. Approximately 506 mg NH_4^+ were removed to breakthrough. If this removal were evenly distributed over the 1/2 foot depth it would correspond to approximately 0.23 mg/g. This exceeds the range of 0.08 to 0.11 mg/g predicted for the Barre clay by the isotherm experiments.

Calcium

Calcium is one of the principal exchangeable cations in the soil matrix. It is of particular interest in the study of soil-leachate interactions because it may serve as an early warning of approaching leachate plumes. The calcium cation contributes to water hardness and the so-called "hardness halo" has been observed in the field by several researchers.

The calcium isotherm resulting from the equilibration of diluted leachate with soil is shown in Figure 29. The data was fitted to the Langmuir model and the Langmuir equation

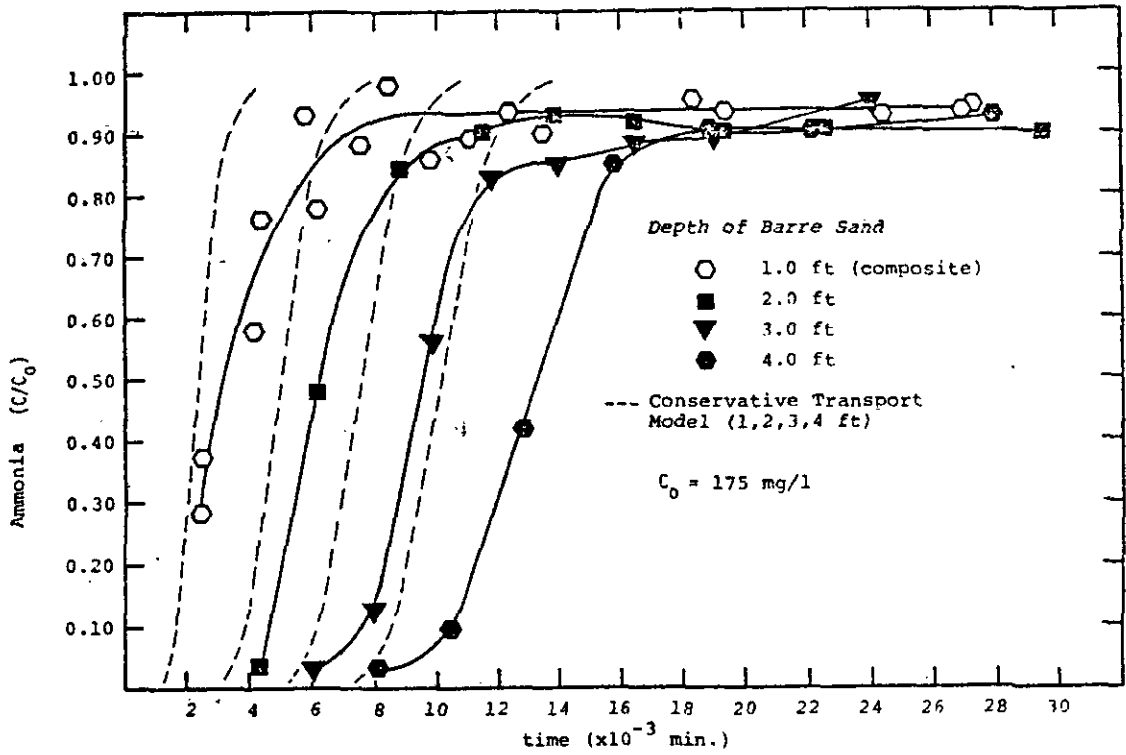


FIGURE 28. AMMONIA BREAKTHROUGH CURVES (UNSATURATION FLOW).

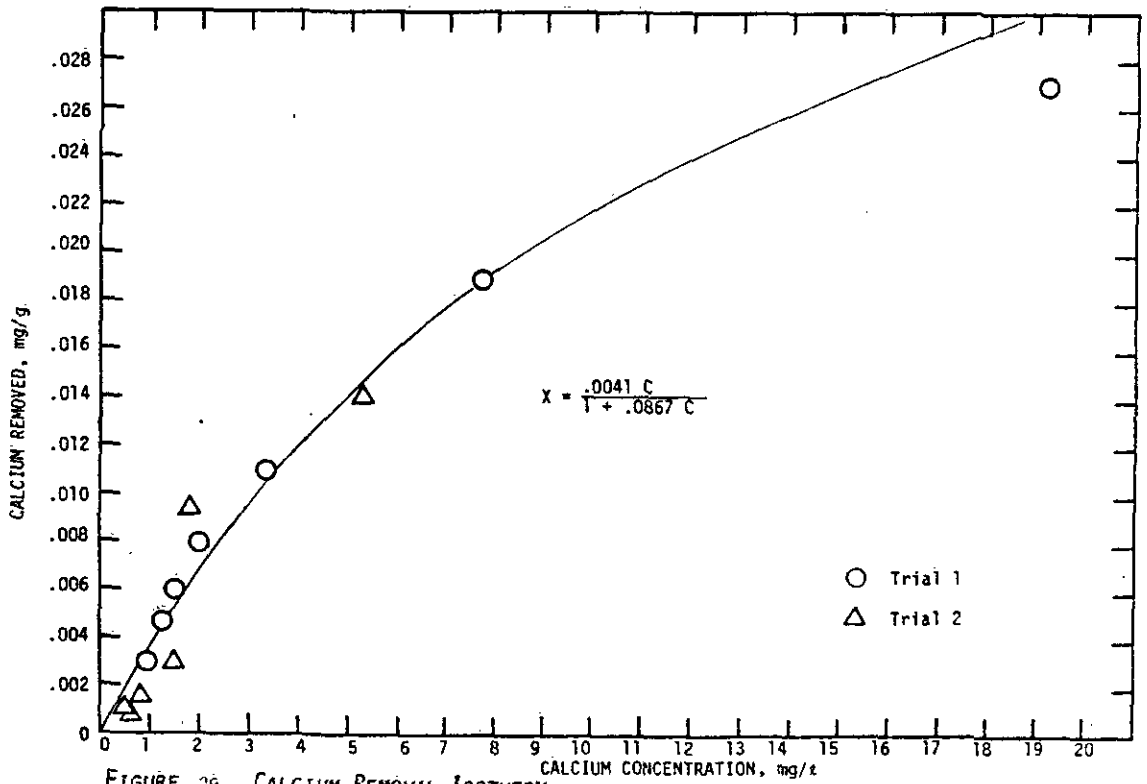


FIGURE 29. CALCIUM REMOVAL ISOTHERM.

$$S = \frac{0.0041 C}{1 + 0.0867 C}$$

is drawn in the figure.

When equilibrations with undiluted leachate were prepared the results shown in Figure 30 were obtained. For the Barre sand the results were scattered about zero removal. The Barre clay, on the other hand, released calcium, and these releases decreased in magnitude as the equilibrium solution concentration increased.

The calcium breakthrough curves for saturated flow conditions are shown in Figure 31 and they are a bit confusing. Initially the curves appear ahead of the convective dispersive prediction for a conservative material. Then the curves cross over behind the prediction and tend to level off at a C/C_0 of approximately 0.95.

A C/C_0 of 0.5 is representative of transport independent of dispersion effects. The C/C_0 values of 0.5 for the 2, 3, and 4 foot columns appear ahead of the prediction model indicating that some release of calcium is taking place. Perhaps the initial conditions in the columns are such that some exchangeable calcium is released.

When the curves cross over behind the prediction this indicates that some removal is taking place. The leveling off of all the curves at the same C/C_0 less than 1 indicates that some depth independent removal is occurring. Perhaps a precipitation reaction at the surface took place as time progressed. Gas formation was noted at the column surfaces as time progressed. If some of this gas were CO_2 resulting from biological activity and if the pH was buffered by the soil and the leachate, conditions for precipitation of calcium carbonate would be more favorable.

The results for calcium breakthrough under unsaturated flow conditions are shown in Figure 32. These curves are indicative of two removal mechanisms. Firstly the curves lag behind each other indicating that a depth dependent removal is taking place. Secondly, all the curves level off at C/C_0 equal to 0.90 indicating that a certain amount of removal is depth independent.

The depth dependent removal may be attributed to ion exchange reactions with the soil. Originally there was 0.07 meq/100 g exchangeable

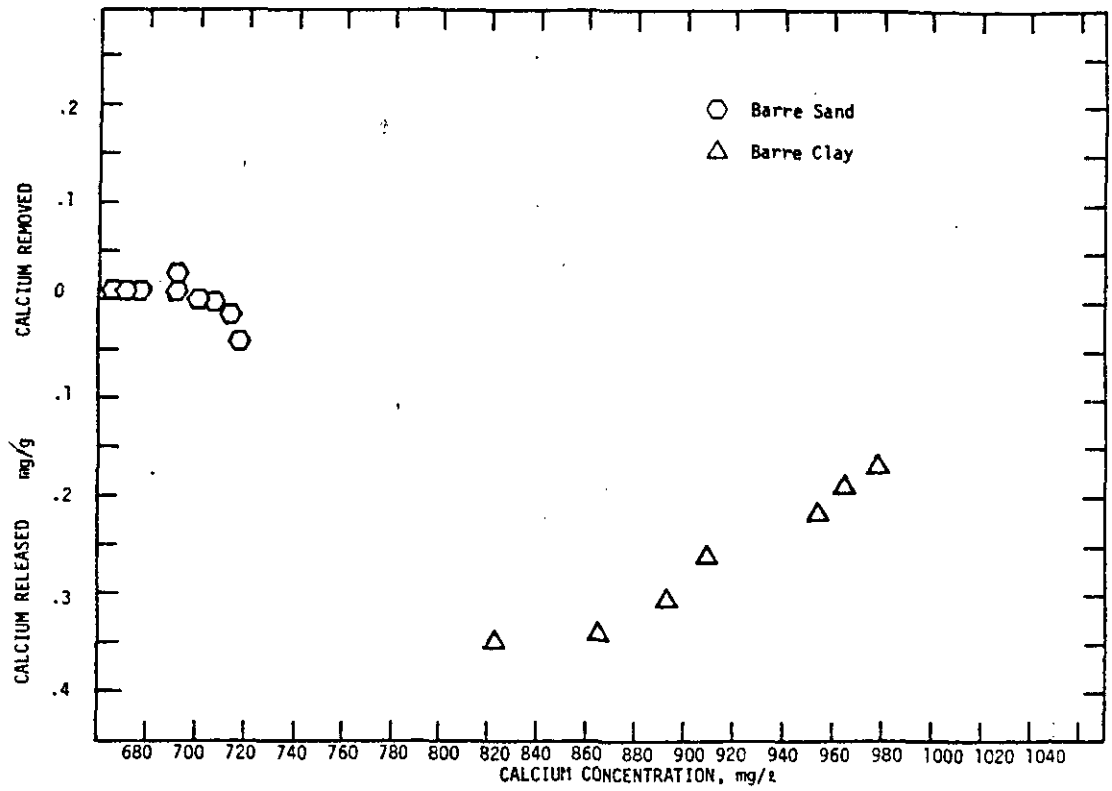


FIGURE 30. CALCIUM REACTIONS IN BATCH EQUILIBRATIONS.

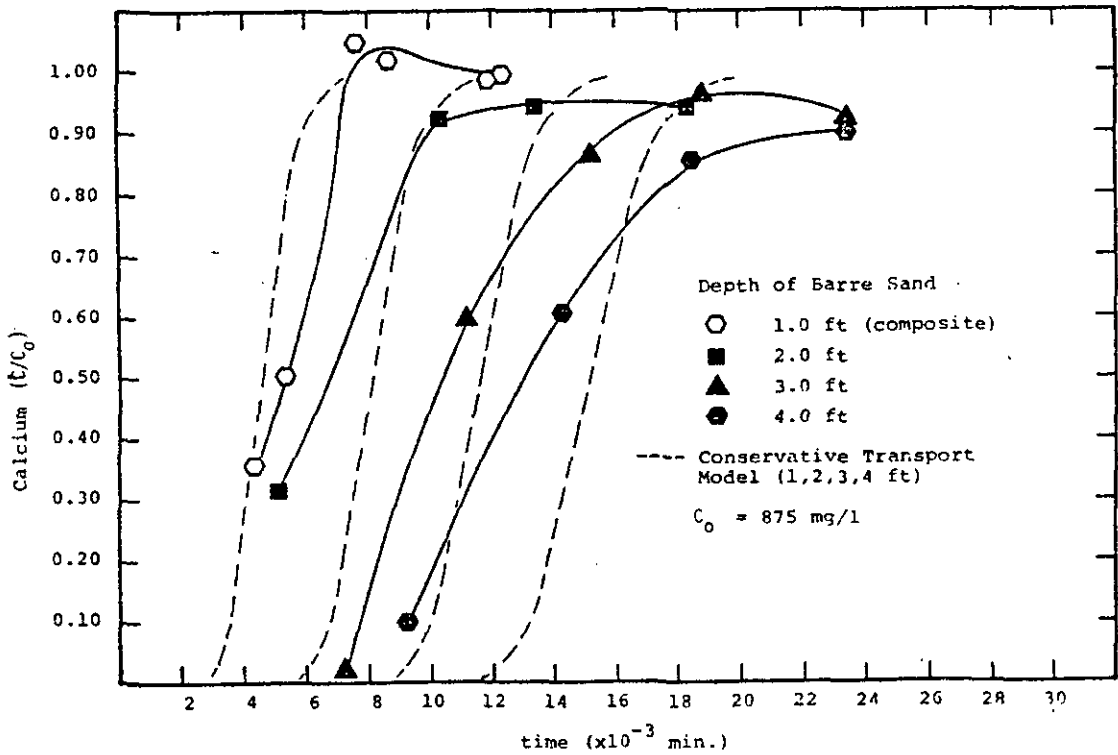


FIGURE 31. CALCIUM BREAKTHROUGH CURVES (SATURATED FLOW).

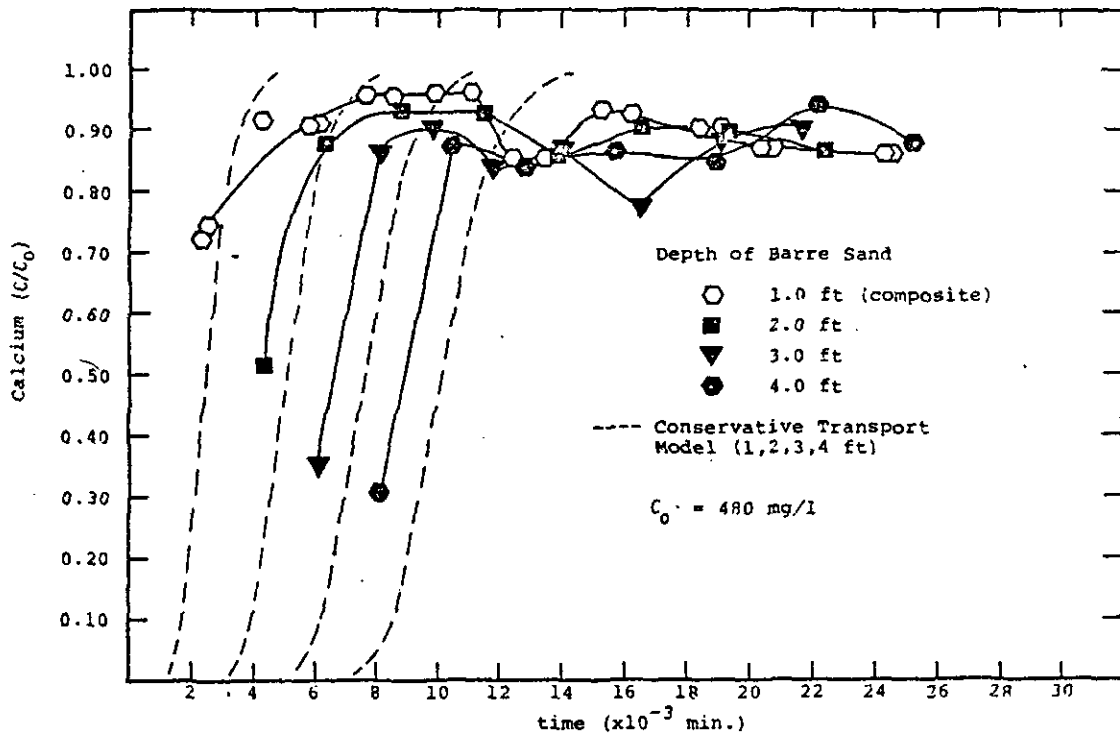


FIGURE 32. CALCIUM BREAKTHROUGH CURVES (UNSATURATED FLOW).

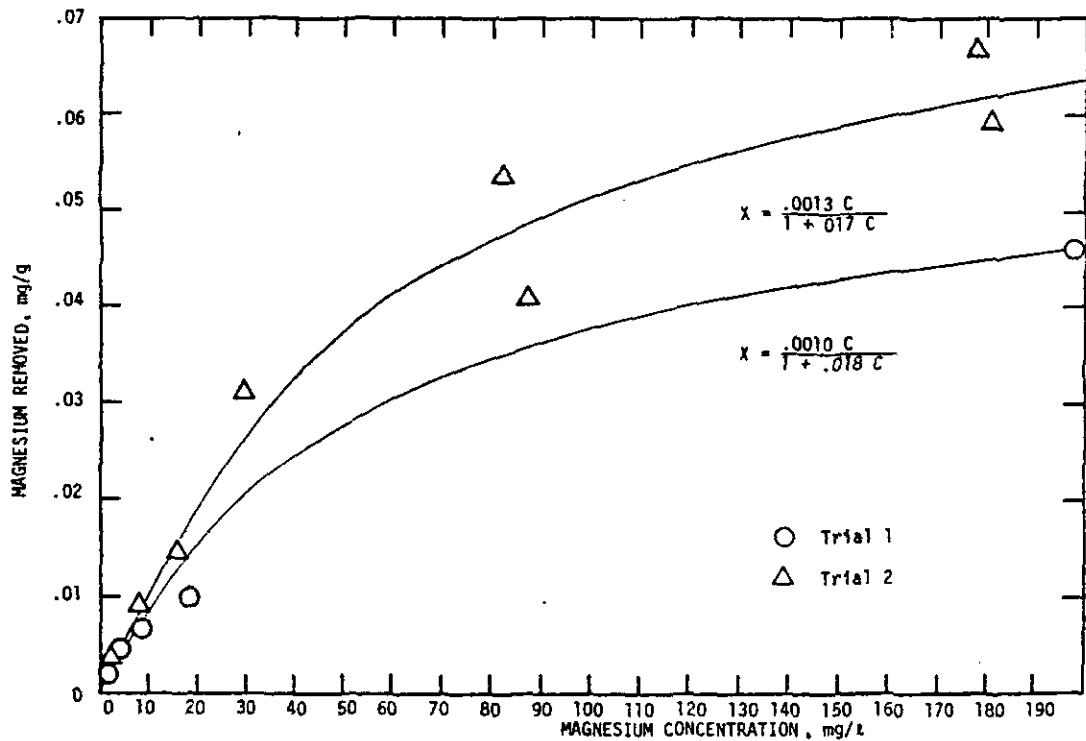


FIGURE 33. MAGNESIUM REMOVAL ISOTHERMS.

calcium in the Barre sand. The soil analyses for the column sections indicate that exchangeable calcium increased markedly.

The depth independent removal mentioned above was probably due to calcium carbonate precipitation at the surface of each column. For the surface samples the calcium measured in the NH_4Ac extract of the CEC determination was nearly ten times the original value and at least double the final values for other depths. In addition, when the columns were sectioned it was observed that the surfaces were hard and crusty as if a cementation had taken place. The solubility relations for CaCO_3 were examined and for the calcium concentration, the amount of inorganic carbon present, and the pH range encountered there is a possibility that CaCO_3 could have precipitated. In addition, if biological activity increased the CO_2 concentration the possibility of CaCO_3 precipitation would be even greater provided that the pH was buffered by the soil and leachate.

Not shown in Figure 32 for the Barre sand is the breakthrough curve for the 1/2 foot of Barre clay packed in column 1 (see Figure 57). The C/C_0 values for the Barre clay progressed in the order 1.37, 1.52, 1.52, 1.17, 1.05 and continued to level off at C/C_0 equal to 1. This release of calcium is in agreement with the isotherm experiment described above. For the column approximately 330 mg Ca were released. This corresponds to 0.15 mg/g. This release of calcium is also verified by the analysis of soil from the sectioned column. Originally the Barre clay had 1.644 meq/100 g exchangeable calcium. This value decreased to 1.387 meq/100 g at the surface and 0.991 meq/100 g at the bottom of the column.

Magnesium

Magnesium is closely linked with calcium. It is of interest because it is one of the principal exchangeable cations in the soil matrix, and because it is related to water hardness and the "hardness halo." The magnesium results for the equilibrations of diluted leachate with soil are shown in Figure 33. The results differed slightly for the two particular trials. Each data set was fitted to the Langmuir model and the resulting equations were

$$S = \frac{0.0010 C}{1 + 0.018 C} \quad \text{and} \quad S = \frac{0.0013 C}{1 + 0.017 C}$$

The constant b, related to the energy of adsorption was essentially the same for each while the constant Q, related to the adsorption maximum was 0.058 mg/g in the first trial and 0.082 mg/g in the second.

When equilibrations with fresh, undiluted leachate were conducted the results shown in Figure 34 were obtained. For the Barre sand a very limited concentration range was covered. All the points were grouped closely together and showed a slight tendency towards release of magnesium. For the Barre clay a larger concentration range was covered and magnesium was definitely released from the soil. This release decreased as the equilibrium solution concentration of magnesium increased (as the soil/leachate ratio increased).

The saturated flow breakthrough curves for magnesium are presented in Figure 35 and are similar to the calcium curves in some respects. The curves precede the prediction for a conservative material indicating that some release is taking place. The curves approach C/C_0 values equal to 1 but for times greater than 20,000 minutes there is a reduction to different C/C_0 values less than 1 for the different depths. These reductions, however, are the reverse of that which a depth dependent reaction would produce, and are most likely the result of reservoir instability.

The early appearance of the breakthrough indicates that magnesium was being released. The isotherm with undiluted leachate also indicated that magnesium would be released. This may be due to the release of exchangeable Mg, but may also be due to the dissolution of some Mg containing compound. However, the soil analysis of sectioned columns indicated that Mg was removed from the leachate. Originally the Barre sand had 0.023 meq/100 g exchangeable Mg. At the column surfaces the Mg in the NH_4Ac extract was as high as 0.28 meq/100 g. Below the surface the increases were not as great, but the Mg was still three to eight times the original value.

The curves for Mg breakthrough under unsaturated flow conditions are shown in Figure 36. These curves are indicative of depth dependent removal. At each depth the curves level off at C/C_0 equal to 1 showing that some finite removal capacity has been exhausted.

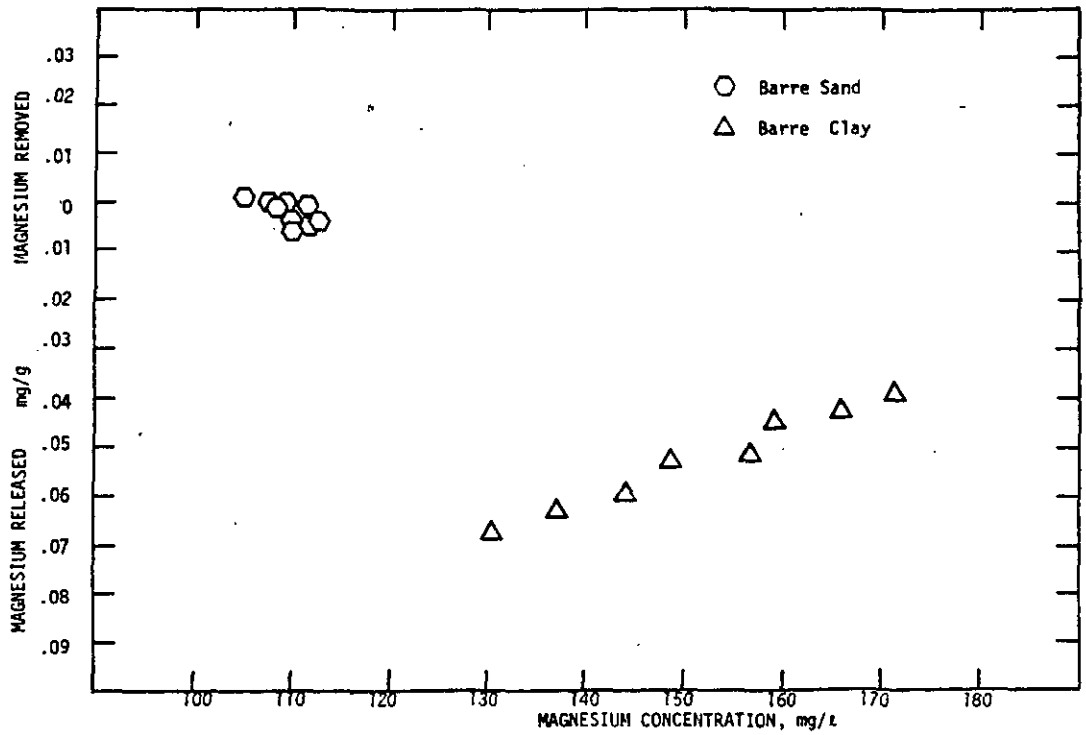


FIGURE 34. MAGNESIUM REACTIONS IN BATCH EQUILIBRATIONS.

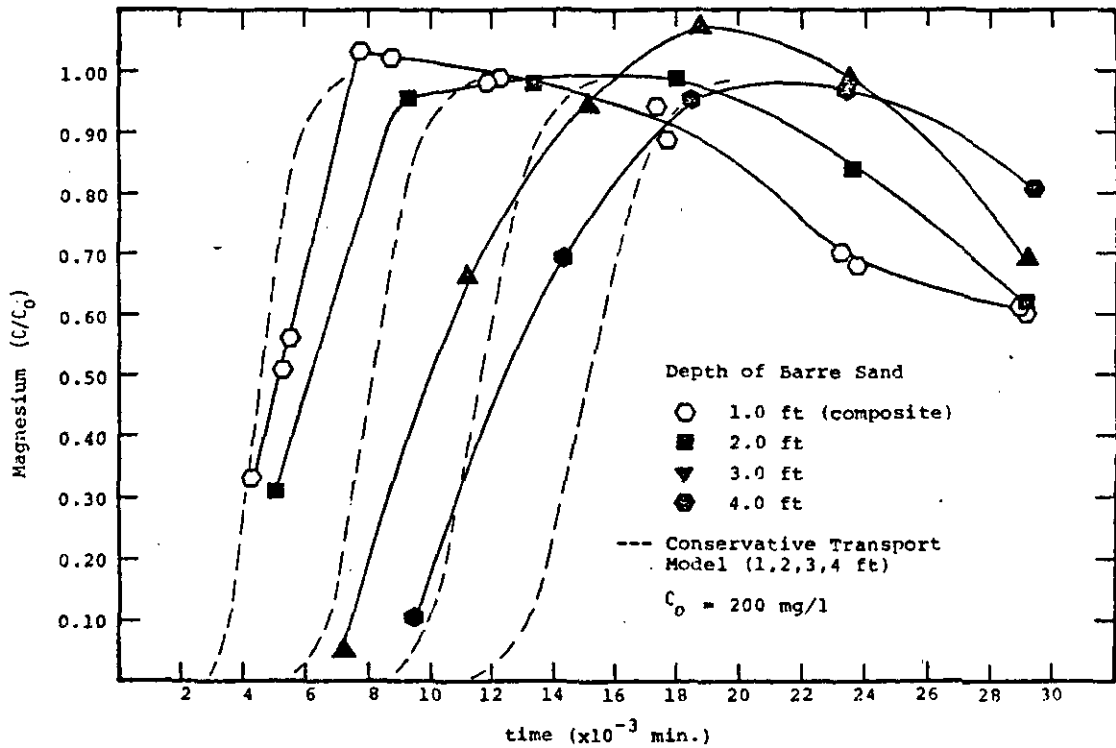


FIGURE 35. MAGNESIUM BREAKTHROUGH CURVES (SATURATED FLOW).

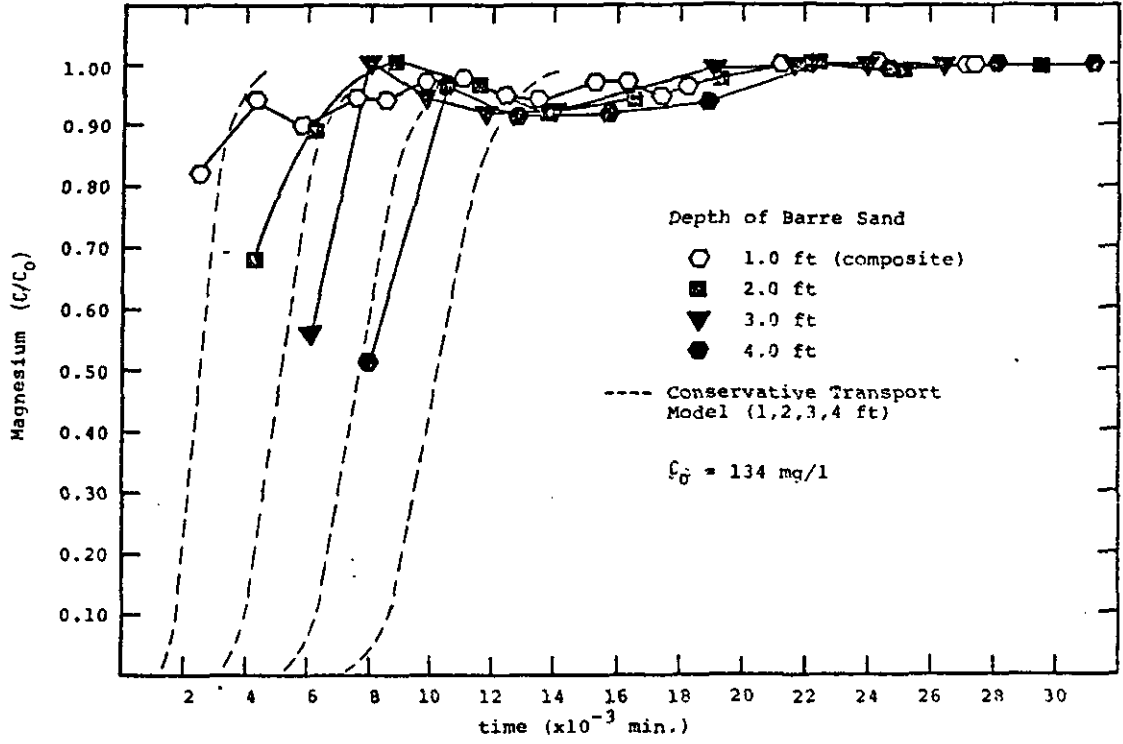


FIGURE 36. MANGESIUM BREAKTHROUGH CURVES (UNSATURATED FLOW)

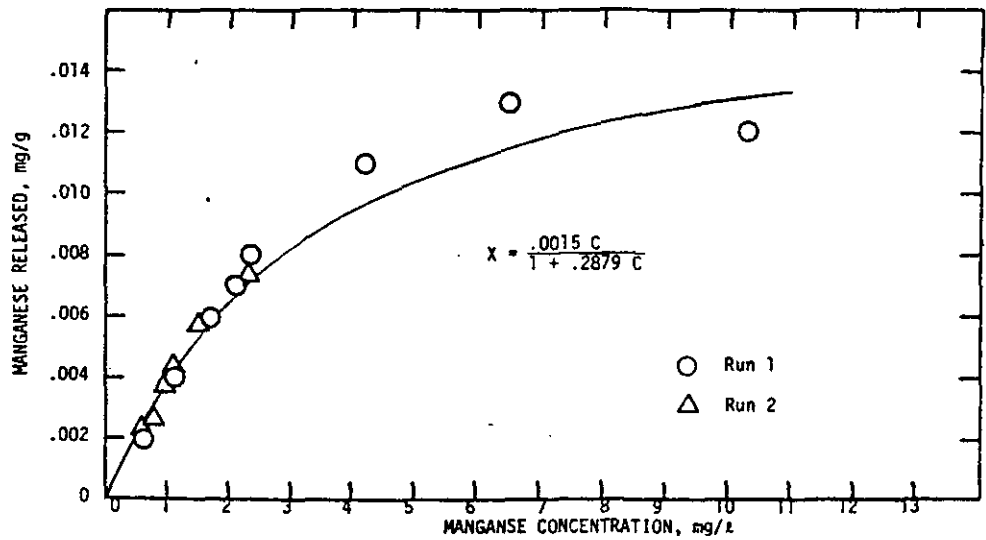


FIGURE 37. MANGANESE DESORPTION ISOTHERM.

The removal was probably due to ion exchange reactions with the soil. The original soil had approximately 0.016 meq/100 g exchangeable magnesium. After exposure to leachate the exchangeable Mg increased as much as 15 times to 0.239 meq/100 g at the surface of column 2. On the whole the increase in exchangeable Mg decreased with depth.

The isotherm results for the Barre clay indicated that Mg would be released. The breakthrough curve for the 1/2 foot depth of Barre clay is included in Figure 57. The C/C_0 values progress in the order 1.15, 1.195, 1.169 and then level off at 1.0. Magnesium was released in the same manner as calcium. Approximately 29 mg or 2.4 meq of Mg were released by the Barre clay. The soil analysis in Table 8 indicates that the exchangeable Mg decreased from 0.666 meq/100 g to an average of 0.572 meq/100 g. Over the column length this release is approximately 2.1 meq, which is in fairly good agreement with the 2.4 meq mentioned above.

Manganese

Manganese is one of the heavy metals present in significant amounts in the Barre landfill leachate. During the preliminary isotherm experiment it was found that Mn was released by the soil rather than removed.

The increase in Mn concentrations is probably due to the solution of manganese compounds coating the soil particles. The high Mn concentration in the raw leachate was due to the fact that the leachate was collected after it had passed through some soil at the site.

The desorption isotherm for soil equilibrated with diluted leachate is shown in Figure 37. The data were fitted to the Langmuir model and the equation took the form

$$S = \frac{0.0051 C}{1 + 0.2879 C}$$

With equilibrations using undiluted leachate the results shown in Figure 38 were obtained. For the Barre sand the manganese release was approximately 0.011 mg/g, slightly less than that predicted using diluted leachate. The Barre clay released a greater amount of Mn and that release was dependent on solution concentration.

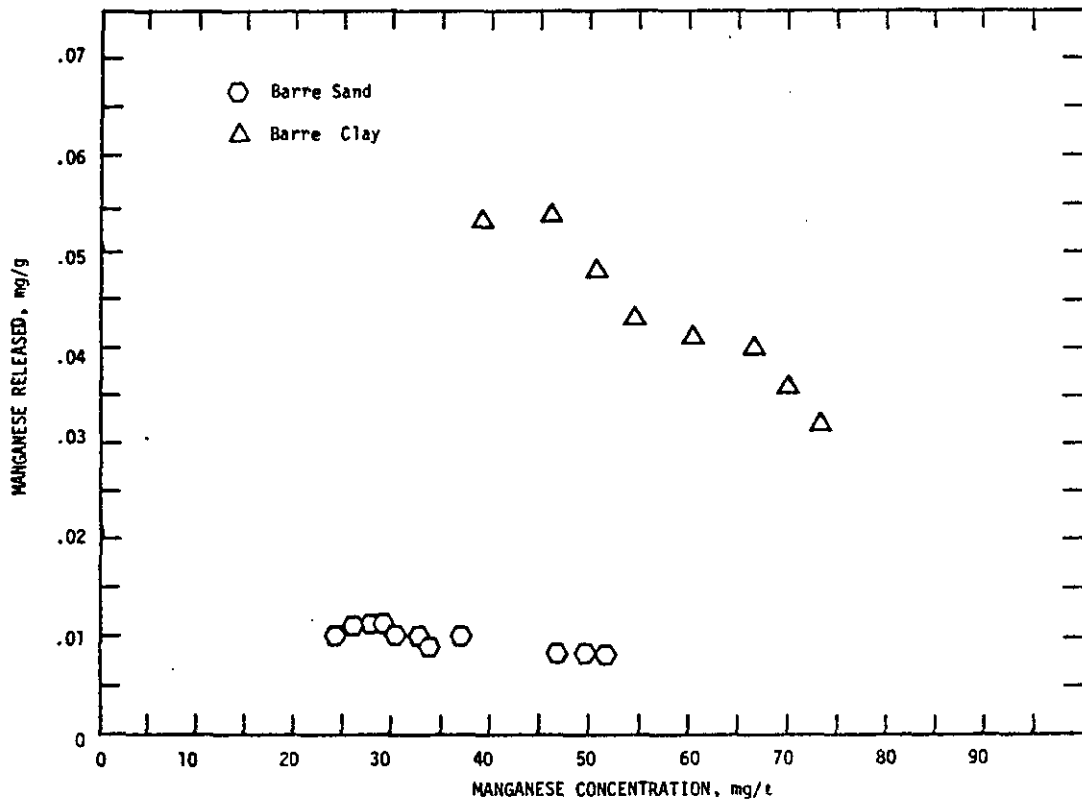


FIGURE 38. MANGANESE RELEASE IN BATCH EQUILIBRATIONS.

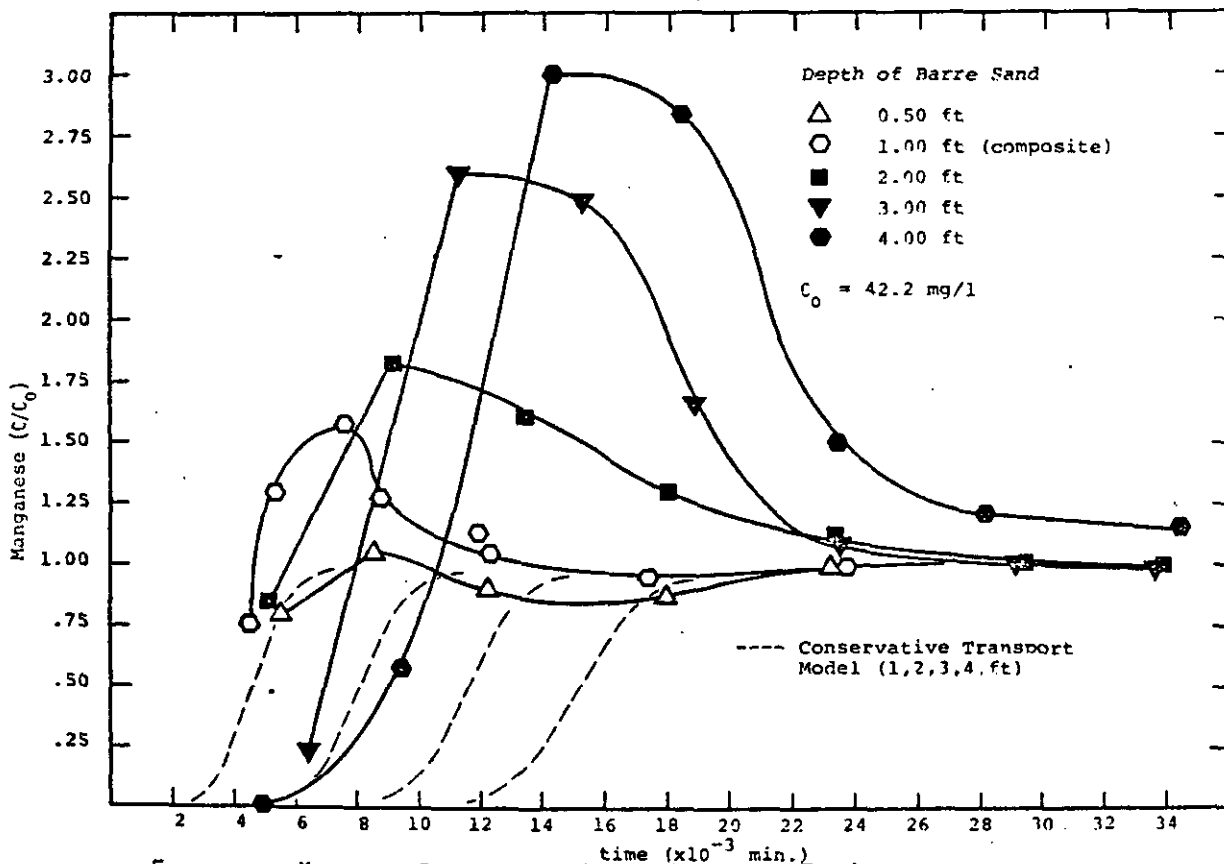


FIGURE 39. MANGANESE BREAKTHROUGH CURVES (SATURATED FLOW).

Chao (7) reported on a method to selectively extract manganese coatings on soil particles. When this method was used approximately 0.025 mg/g were extracted from the Barre sand and approximately 0.098 mg/g from the Barre clay. These values are approximately double the amounts removed from the soils by the leachate.

After noting the manganese release in the batch equilibrations the saturated flow breakthrough curves shown in Figure 39 come as no surprise. Manganese was released in proportion with column length as shown in Figure 40. For the saturated flow data points a least squares best fit through the origin has a slope of 51.1 mg/ft or 0.012 mg/g which is in excellent agreement with the 0.011 mg/g obtained in the undiluted leachate batch equilibrations.

When the saturated flow with leachate was ended, fresh stream water was applied in a washout experiment. No additional Mn was released during this stage of the study.

The unsaturated flow breakthrough curves for manganese are shown in Figure 41. Manganese was released from the soil, but in not nearly as uniform a manner as in the saturated flow situation. In the saturated flow case a larger and larger "hump" peaking at greater and greater C/C_0 values was observed with increasing depth. For this unsaturated flow case the curves initially rise to a C/C_0 of approximately 2.5 and begin a gradual decline. However, as time progresses, the three and four foot columns experience sharp increases in manganese release. These sharp increases paralleled similar sharp increases in the iron and sulfate curves and were probably due to the establishment of even stronger reducing conditions.

On Figure 40 a best fit line through the origin for the unsaturated flow data has a slope of 44.1 mg/ft or 0.01 mg/g. This is in good agreement with the saturated flow and batch results.

Iron

The iron removal isotherm obtained from the preliminary batch equilibration is shown in Figure 42. It is a favorable (concave downward) isotherm. However, it was noted that after the first day an orange turbidity developed in the blanks which contained no soil. It is believed that this turbidity resulted from a colloidal ferric hydroxide precipitate formed as a result of oxidation of the ferrous to the ferric

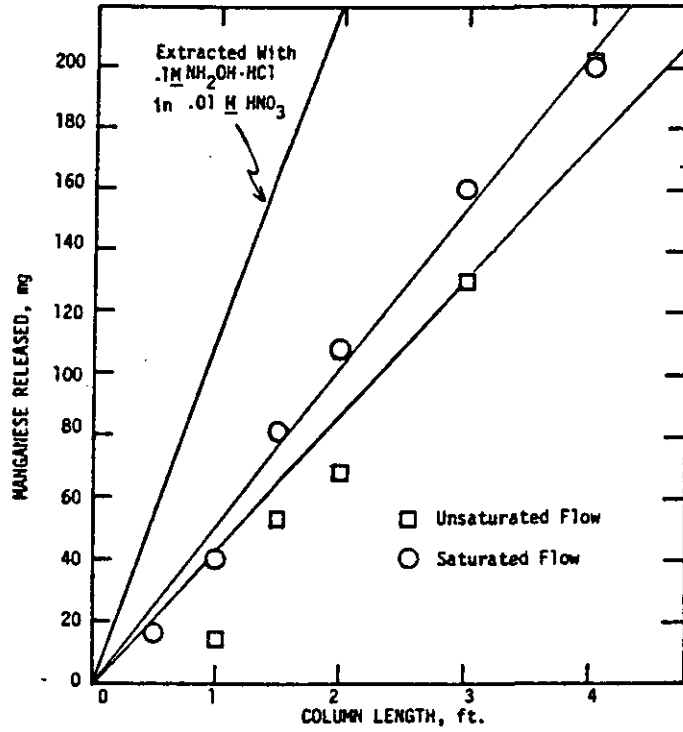


FIGURE 40. MANGANESE RELEASE IN COLUMN STUDY.

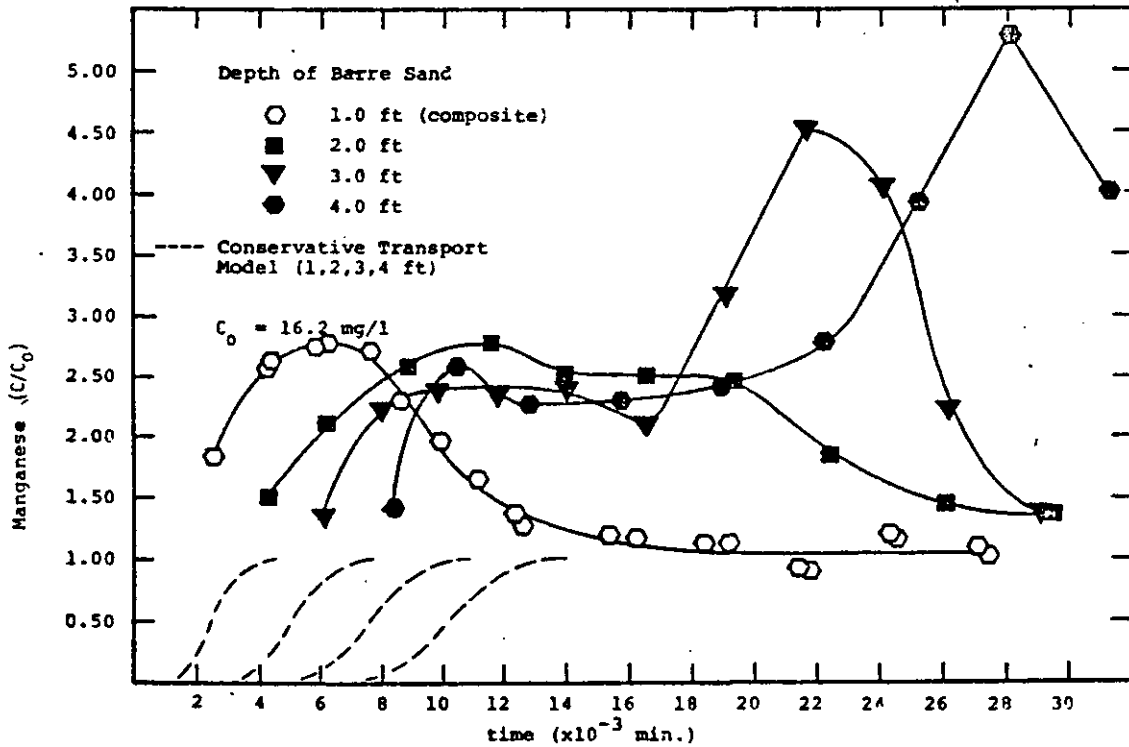


FIGURE 41. MANGANESE BREAKTHROUGH CURVES (UNSATURATED FLOW).

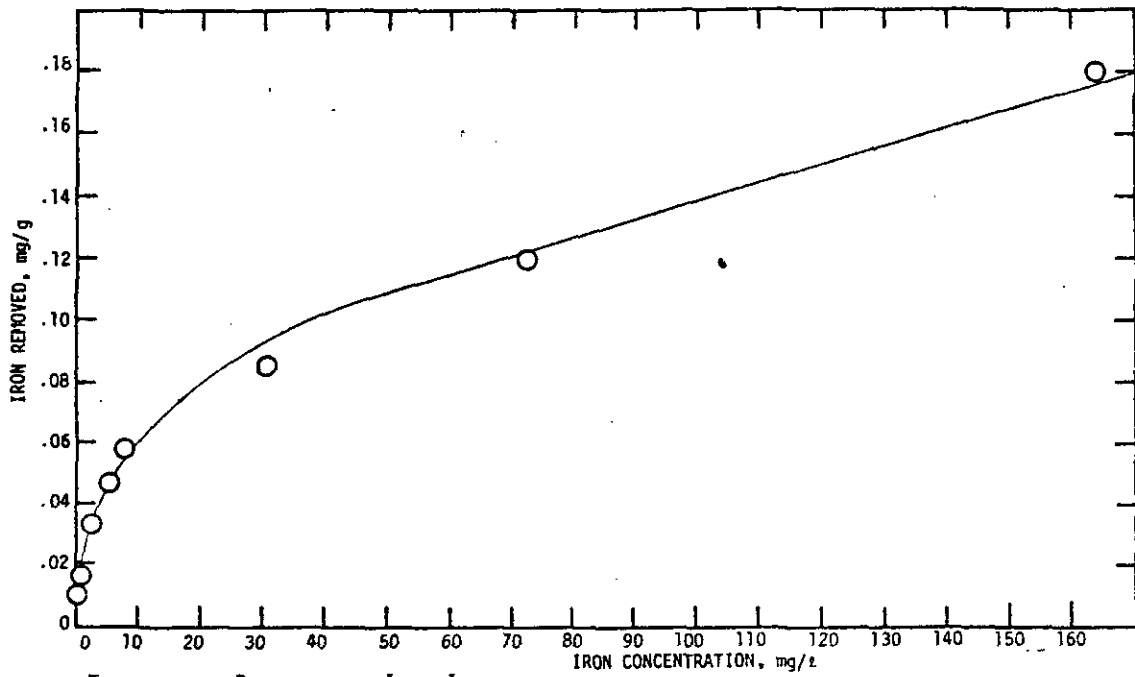


FIGURE 42. PRELIMINARY IRON ISOTHERM

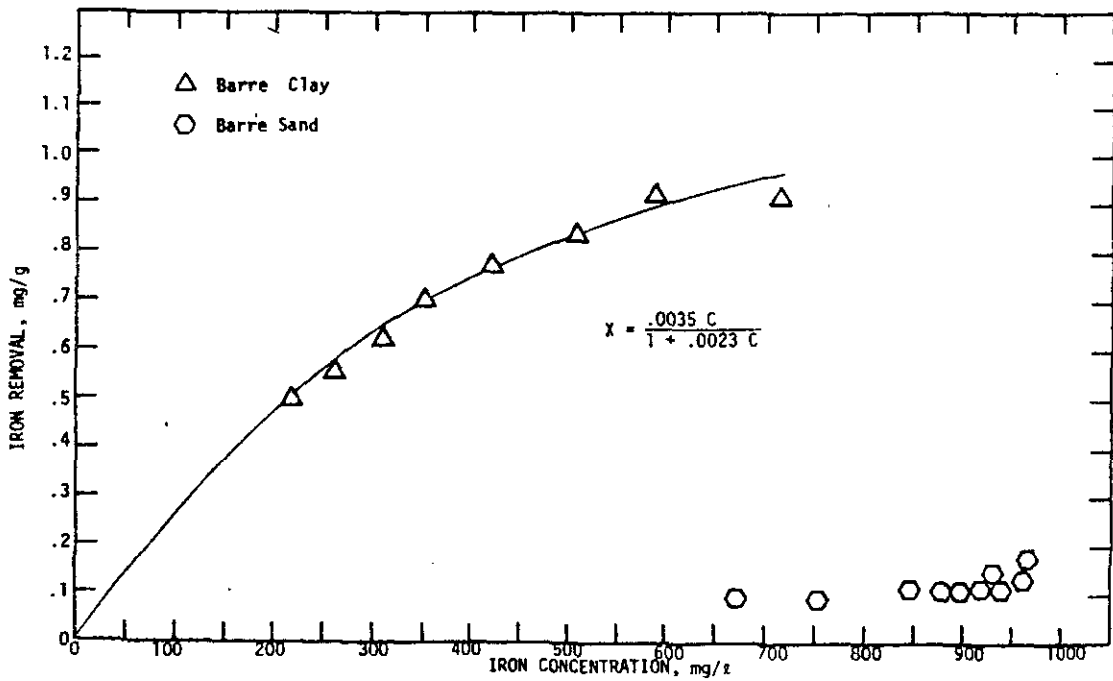


FIGURE 43. IRON REMOVAL IN BATCH EQUILIBRATIONS.

form during handling and sample preparation, Chian and DeWalle (10) and others have discussed the formation of this precipitate as a result of sample aeration during collection, storage, and handling. The solubility equilibria for ferric hydroxide were examined and, for the pH and iron concentrations of the dilution series, precipitation of $\text{Fe}(\text{OH})_3$ was indicated.

A new batch of leachate was collected and to eliminate the problems of aeration during dilution undiluted leachate was mixed with varying quantities of soil. The results are shown in Figure 43. For the Barre sand the iron removal was relatively constant at approximately 0.11 mg/g over the concentration range 650 to 1000 mg/l. For the Barre clay the equilibrium iron concentration covered the range 200 to 700 mg/l. The Langmuir equation describing this iron removal by the Barre clay takes the form

$$S = \frac{0.0035 C}{1 + 0.0023 C}$$

The saturated flow breakthrough curves for iron are shown in Figure 44. The dashed lines represent the convective dispersive prediction for a conservative substance. Each of the breakthrough curves is delayed behind the prediction indicating that iron is being attenuated. Each of the curves also approaches C/C_0 equal to 1 indicating that a finite removal capacity to remove iron is eventually exhausted. An approximate mass balance was made and iron removal was approximately 386 mg/ft or 0.09 mg/g. This compares quite well with the 0.11 mg/g observed for the Barre sand in the batch equilibrations.

The columns were maintained on line beyond the breakthroughs shown in Figure 44. During this extended run a "black layer" developed at the column surfaces and progressed downward. In their study of failed septic systems McGauhey and Winneberger (38) observed a black layer of soil extending to a depth of 5 to 10 cm. They report that the black color was the result of particulate ferrous sulfide.

It is believed that the observed "black layer" was a ferrous sulfide compound. It is not clear whether this precipitate was formed in the reservoir and flowed into the columns, formed within the columns, or resulted from a combination of the above. In either case, no great

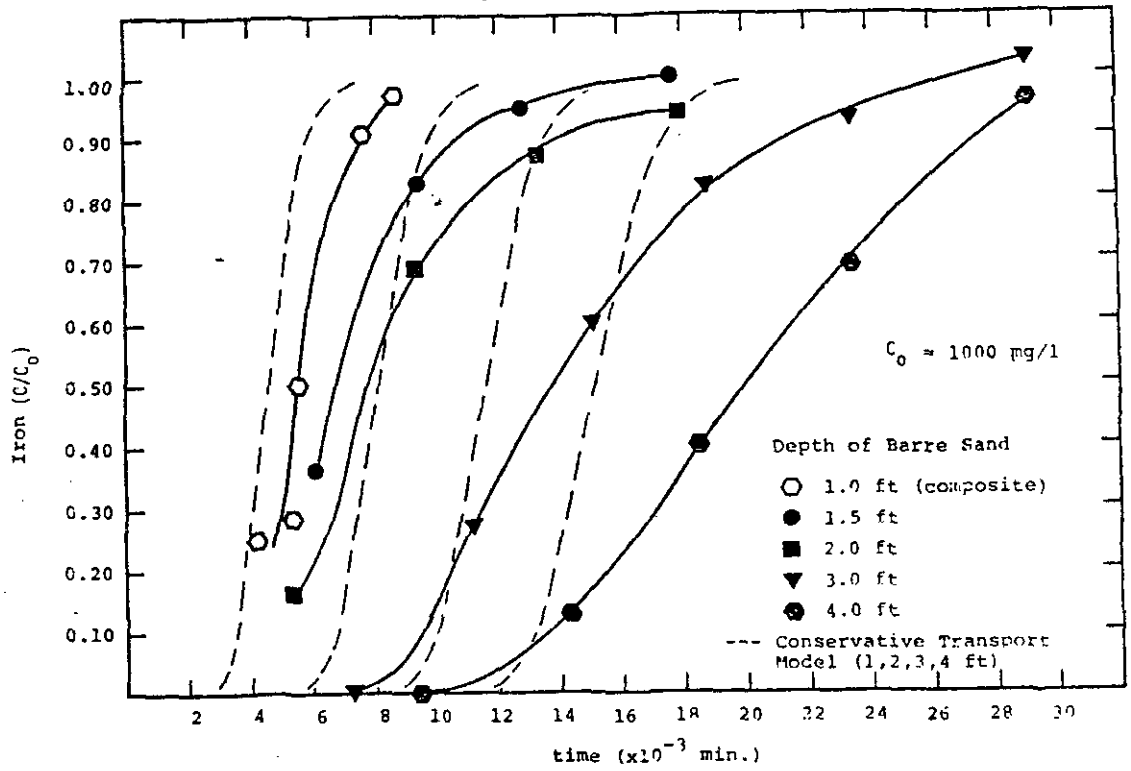


FIGURE 44. IRON BREAKTHROUGH CURVES (SATURATED FLOW)

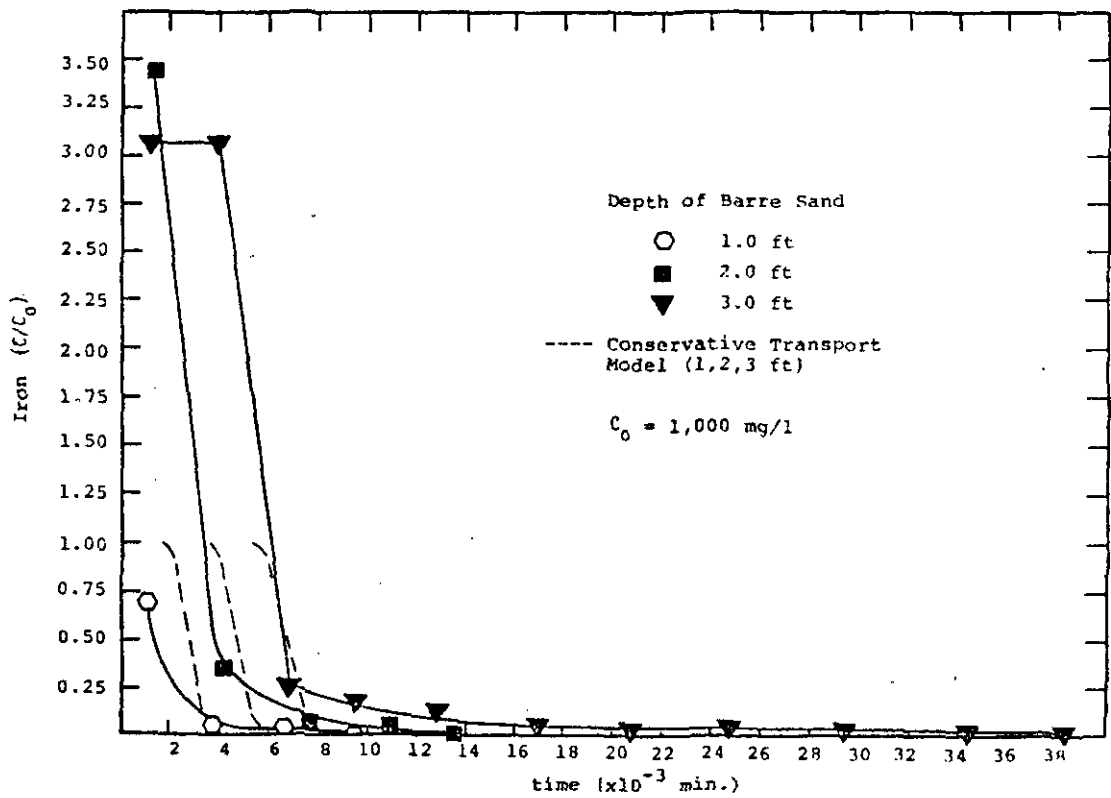


FIGURE 45. IRON BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW).

mechanical clogging as described by McGauhey and Winneberger was observed.

Once a breakthrough curve has reached C/C_0 equal to 1 the attenuation capacity is exhausted. Everything that enters the system should exit unchanged and the total amount removed should not change. When iron removals were calculated over the whole period of leachate application they were different than those calculated at breakthrough. At the time of shut down the "black layer" had penetrated approximately 2-1/2 feet. Columns 1 through 5, which had experienced breakthrough of the "black layer," had lower removals, while columns 6 and 7 had increased removals at this stage. No specific numbers are presented here and even the generalizations of "increased" or "decreased" removal must be treated with caution. The iron concentrations in the reservoir fluctuated considerably in the latter stages of the experiment. The changes in removals may be more a result of these concentration fluctuations and the use of a C_0 equal to 1000 mg/l than to actual changes in the columns.

The iron washout curves are shown in Figures 45 and 46. The area under the curves provides an indication of the amount of iron washed out. For the 1, 2, and 3 foot depths 788, 3869, and 6477 mg of iron respectively were washed out. These values indicate that more Fe was washed out than was originally removed from the leachate!

Apparently the highly reducing environment created by the leachate resulted in the reduction of ferric oxide coatings to ferrous compounds which were more readily washed off. In a discussion of leachate plumes in an aquifer, Kimmel and Braids (27) remark that iron oxide coatings on the sand grains of the aquifer had been stripped off in regions where the plume was strongly reducing in chemical character.

The stream water supplied to the columns was well aerated. With time the DO caused the oxidation of the column surfaces. The original brown color of the soil returned and slowly spread to a depth of 1/2 inch over the duration of the experiment. A similar situation was observed by McGauhey and Winneberger (38) in their investigation of septic system failure. As sewage was applied to a soil column, ferrous sulfide developed and clogged soil pores. When the DO of the sewage was increased the ferrous sulfide at the surface was dispelled.

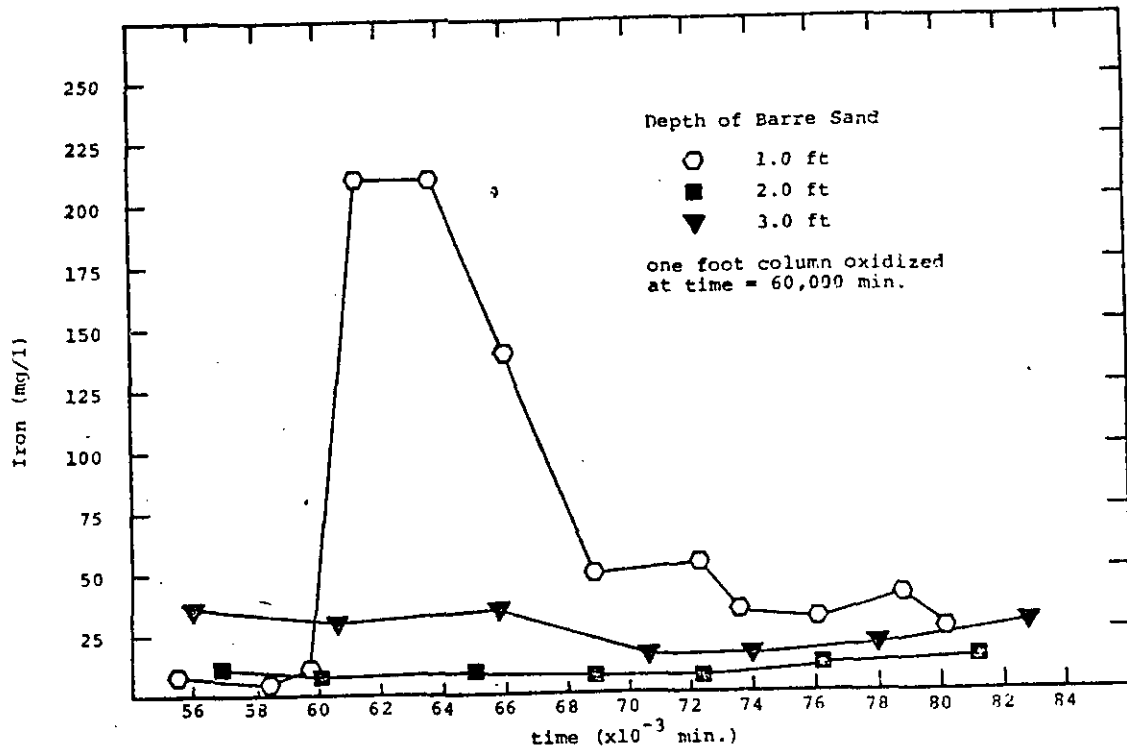


FIGURE 46. IRON BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW AFTER AERATION).

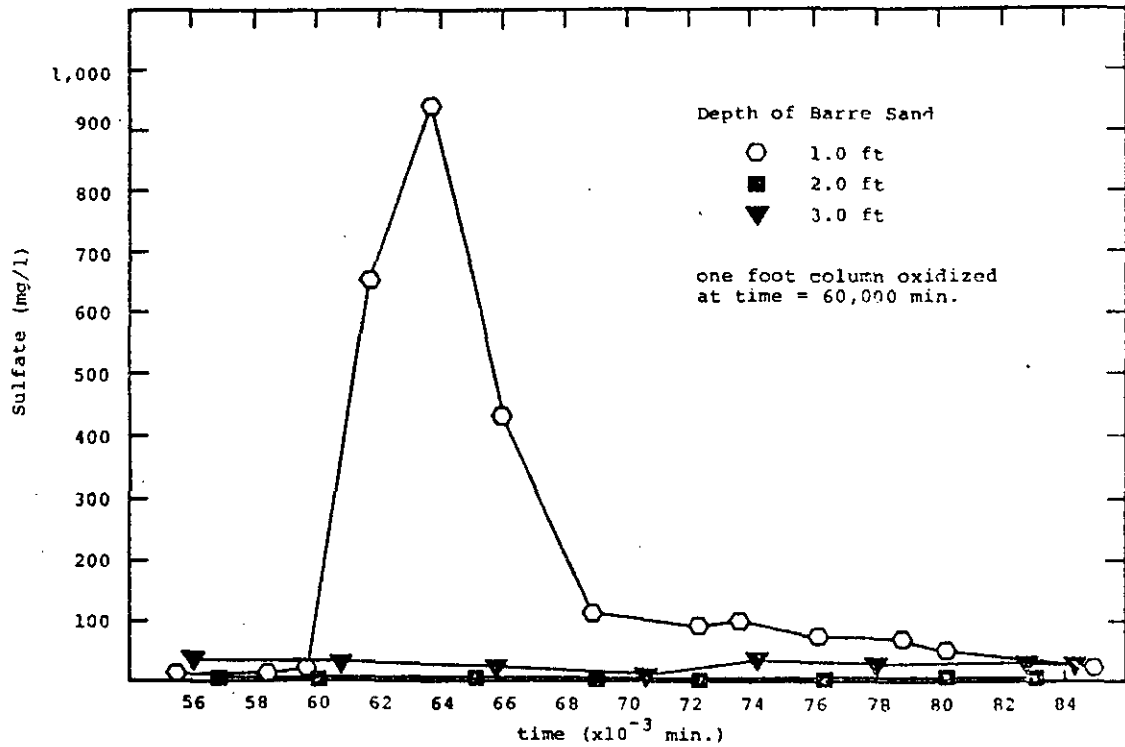
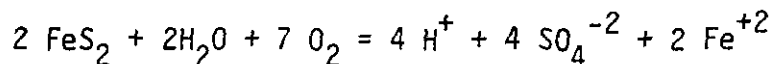


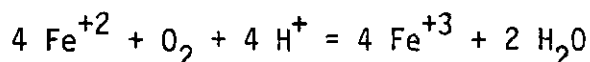
FIGURE 47. SULFATE BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW AFTER AERATION).

At one point the stream water feed was shut off and column 3 was drained and aerated. A pipette bulb was used to force air into the column through the side sampling ports. The black colored column converted to its original brown color and the stream water feed was resumed. The results are shown in Figure 46. Note that the ordinate scale is now simple concentration, C, rather than the ratio, C/C₀. The aeration resulted in the release of an additional 880 mg iron. The reactions taking place are easily explained given the additional information in Figures 47, 48, and 49. The aeration of the column induced an "acid mine drainage" situation. Manahan (36) summarizes the reactions in acid mine waters as follows:

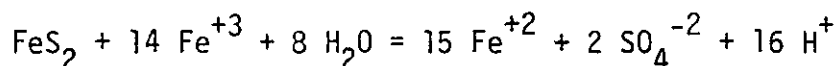
First there is the oxidation of pyrite



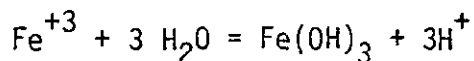
Next is the oxidation of ferrous iron to ferric iron



The ferric iron further dissolves pyrite



The ferric iron also precipitates as ferric hydroxide at pH values much above 3



Thus, the sharp rise in iron shown in Figure 46 and the sharp rise in sulfate shown in Figure 47 are the results of "acid mine drainage". Although some of the iron was oxidized to the ferric state, as evidenced by the brown color of the column, much of the iron was in the ferrous state. This is demonstrated by the sharp rise in COD shown in Figure 48. The pH history shown in Figure 49 provides evidence that H⁺ was released and the general increase of species in solution caused the peak in specific conductance shown in Figure 50.

The iron breakthrough curves for unsaturated flow conditions are shown in Figure 51. A general inspection of the shape of the curves

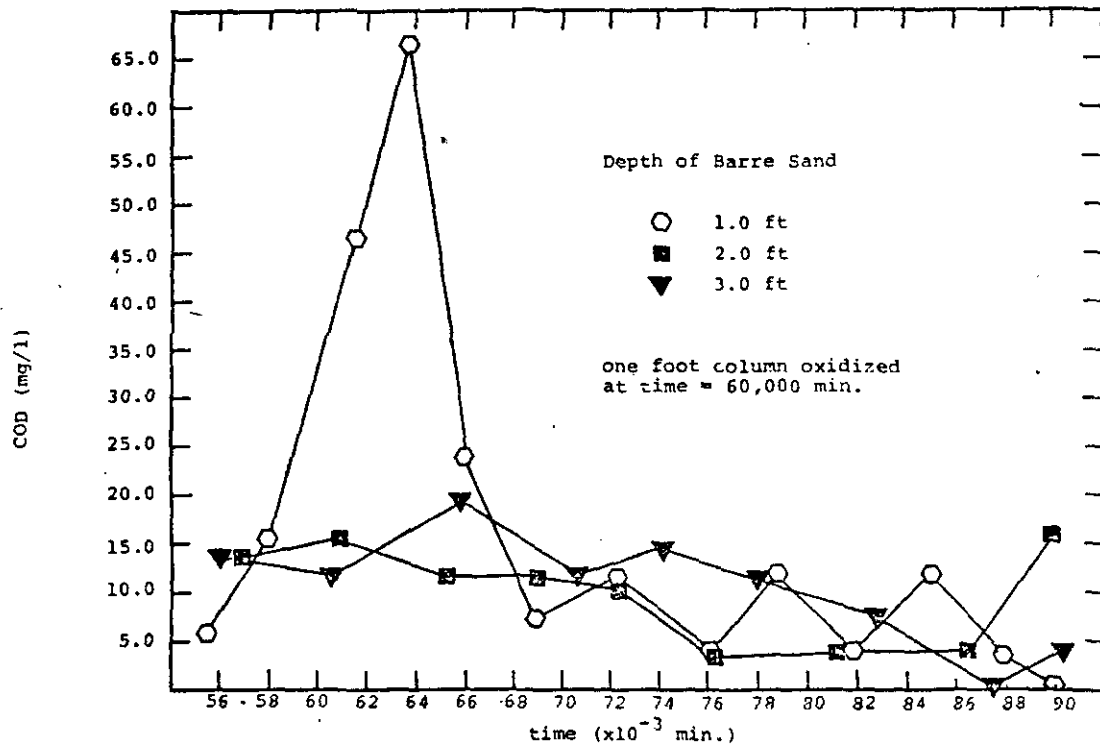


FIGURE 48. CHEMICAL OXYGEN DEMAND BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW AFTER AERATION).

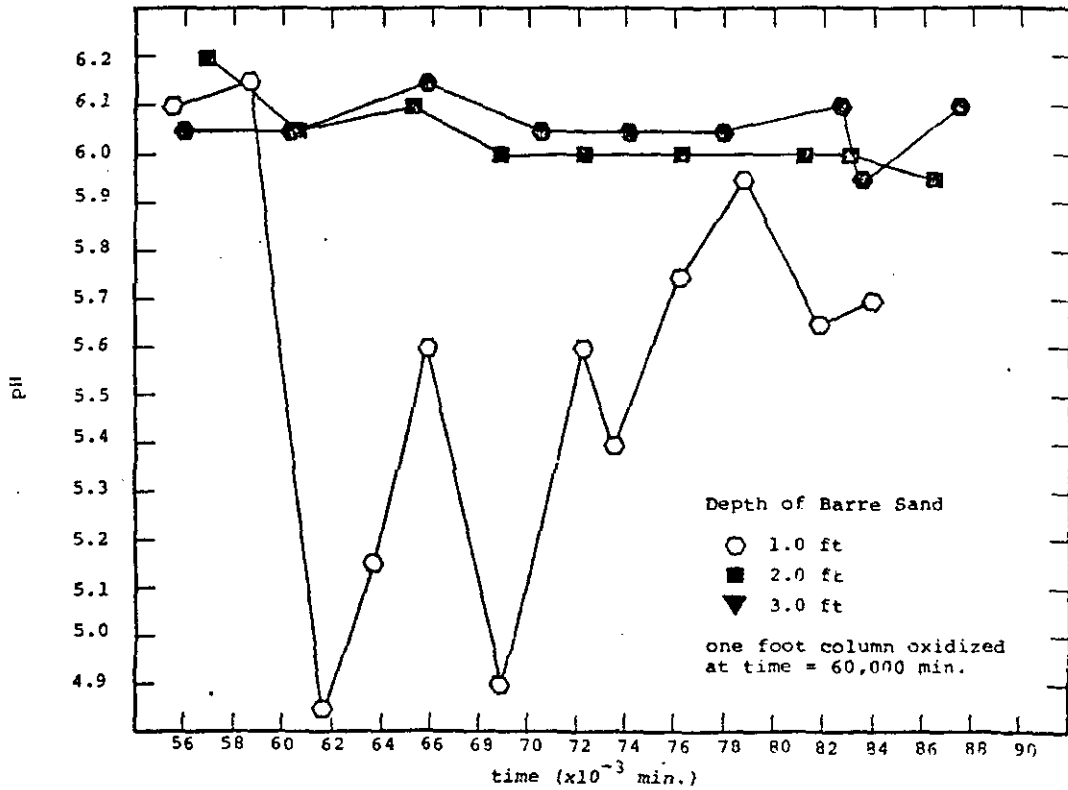


FIGURE 49. pH HISTORY FOR SATURATED "WASHOUT" FLOW AFTER AERATION.

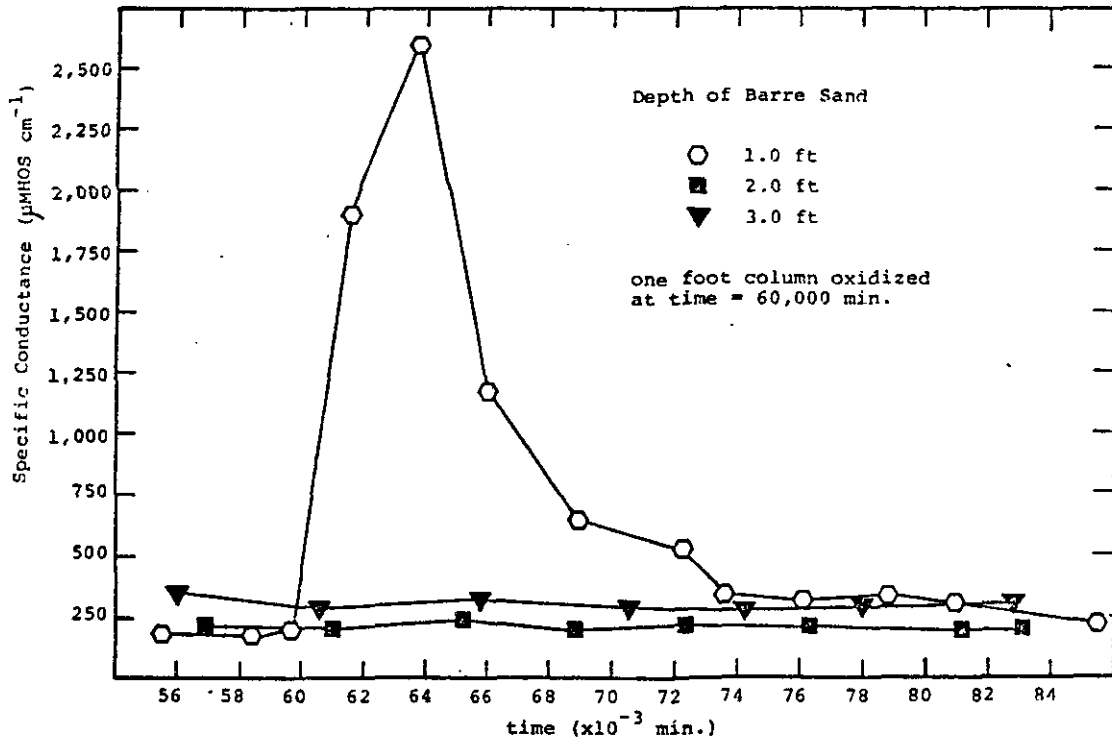


FIGURE 50. SPECIFIC CONDUCTANCE BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW AFTER AERATION).

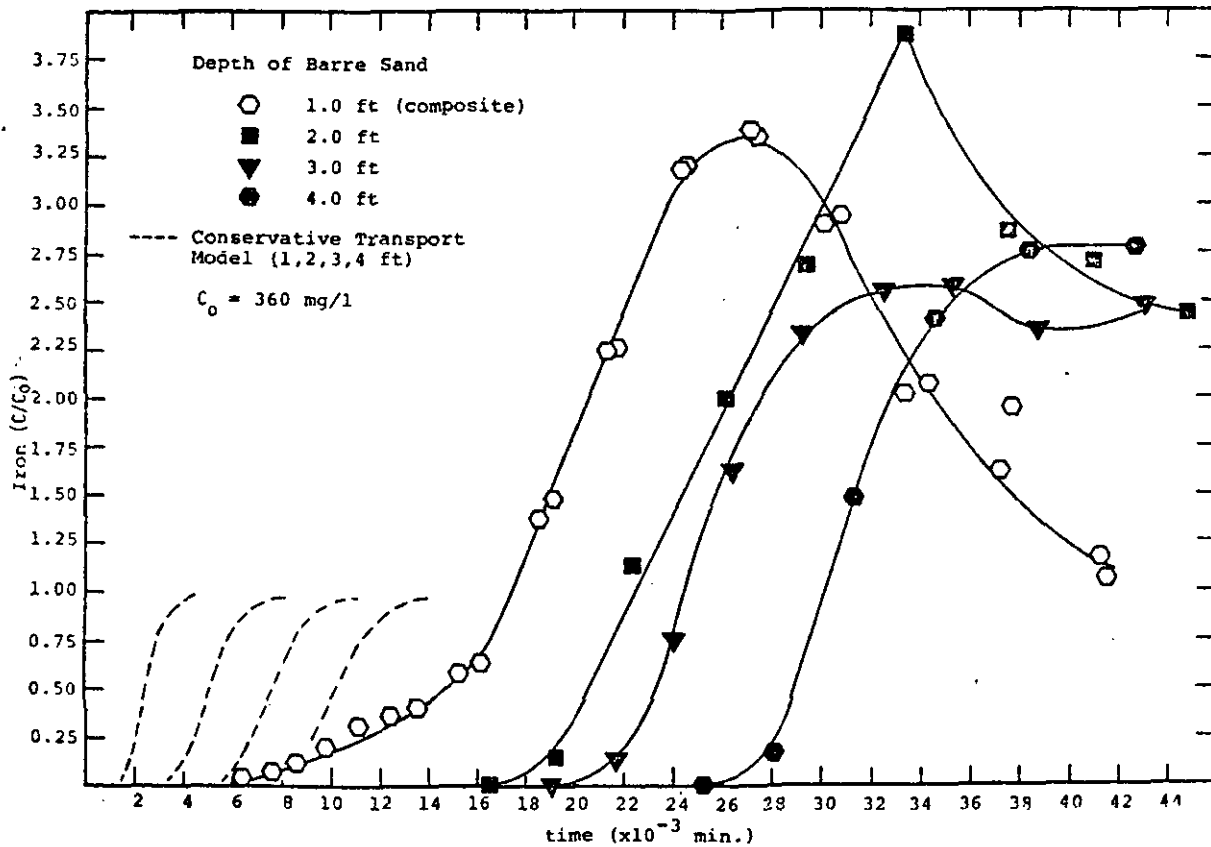


FIGURE 51. IRON BREAKTHROUGH CURVES (UNSATURATED FLOW).

indicates that two events take place. Firstly, the curves are greatly delayed behind the prediction for a conservative material indicating that iron is being removed. Secondly, after this initial removal, the C/C_0 values are greater than 1 and iron is released from the columns. The net balance over the whole run shows that more iron exited from the columns than was applied to the columns. The net release in milligrams was as follows:

Depth, ft	1.0	1.0	1.5	2.0	3.0	4.0
Column No	2	3	4	5	6	7
Fe, mg	1450	1530	1590	2110	800	810

As was the case in saturated flow, a "black layer" developed at the soil surfaces and progressed downwards. The strong reducing conditions associated with the "black layer" caused the reduction of ferric oxide coatings on the soil particles and the ferrous iron was eventually washed out. Columns 6 and 7 had lower values for iron release. This is because the "black layer" had not penetrated the full length of each column.

The iron breakthrough curve for the 1/2 foot of Barre clay is included in Figure 57. The curve is greatly delayed behind that of a conservative substance such as Cl^- . Approximately 2465 mg of iron were removed over the duration of the run. Assuming uniform removal with depth this corresponds to 1.12 mg/g which is higher than the .69 mg/g predicted using the Langmuir model based on the isotherm results.

Sulfate

Brady (6) reported that most soils will retain sulfate but that the quantity held is generally small. The mechanism is thought to involve hydroxyl groups in the hydrous oxides and silicate clays. Hydroxyl groups held by aluminum ions in the oxides or silicates are replaced by sulfate or acid sulfate ions.

There was no indication of sulfate removal by the Barre sand or Barre clay soils. In fact, there was significant $SO_4^{=}$ formation during the course of the investigation. Figures 52, 53, and 54 represent the saturated, washout, and unsaturated flow situations respectively. The organic matter in leachate could serve as the source of the sulfur.

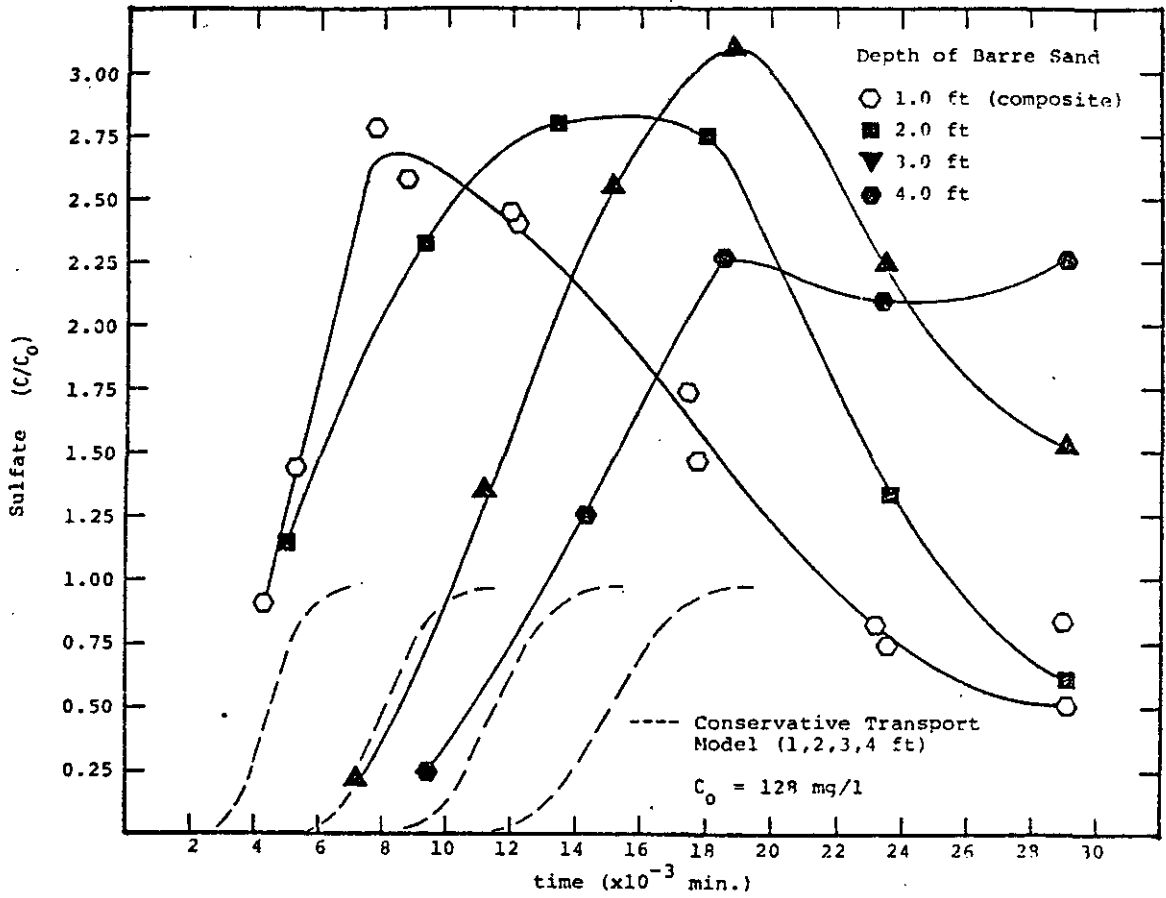


FIGURE 52. SULFATE BREAKTHROUGH CURVES (SATURATED FLOW).

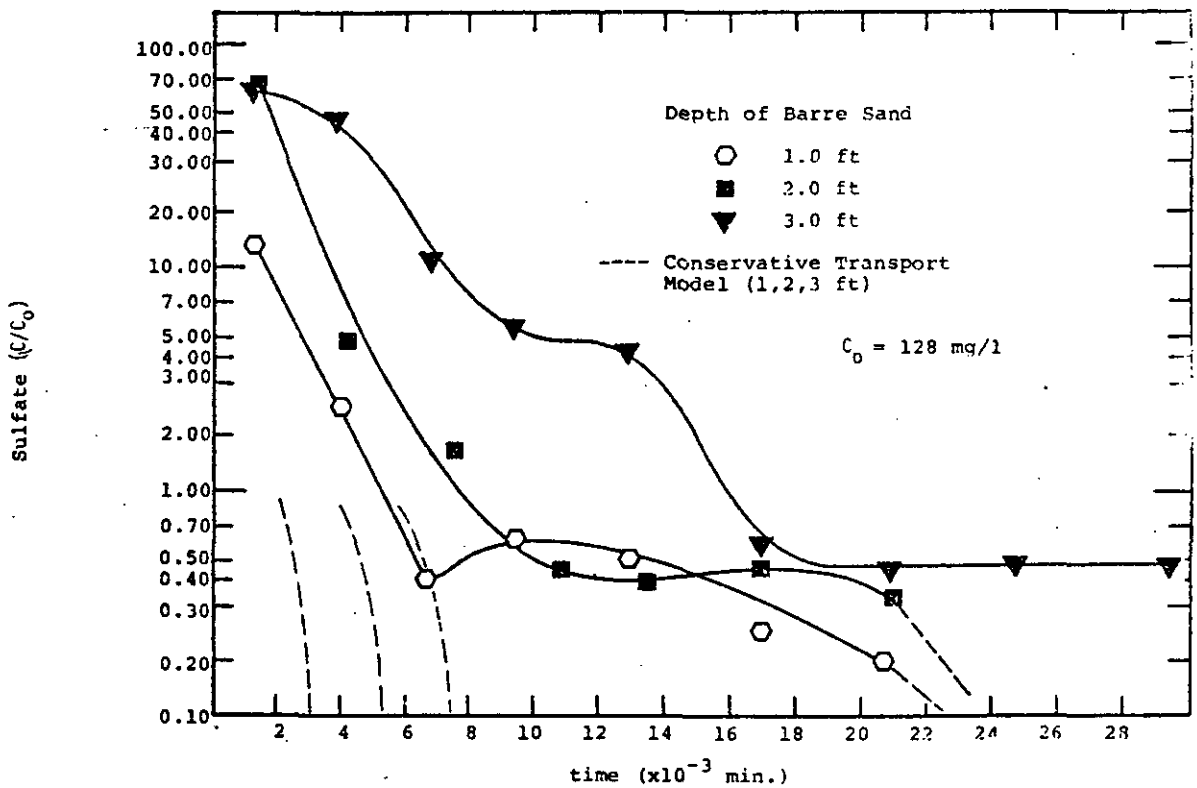


FIGURE 53. SULFATE BREAKTHROUGH CURVES (SATURATED "WASHOUT" FLOW).

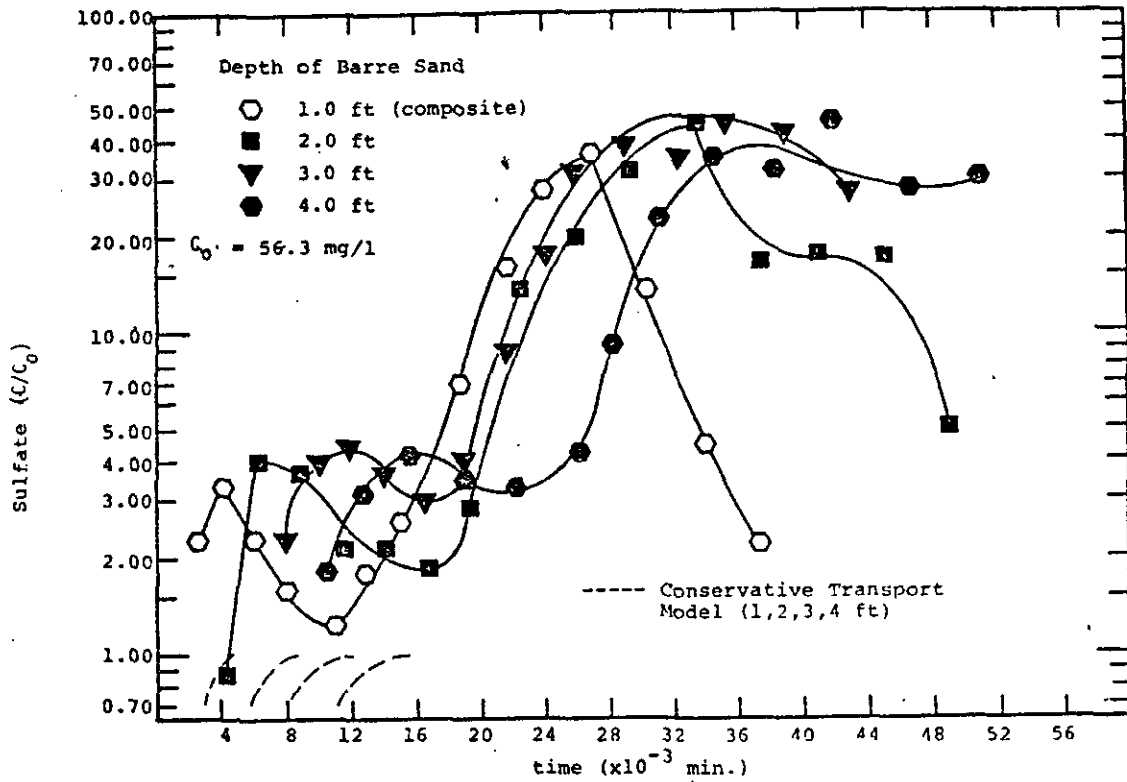


FIGURE 54. SULFATE BREAKTHROUGH CURVES (UNSATURATED FLOW),

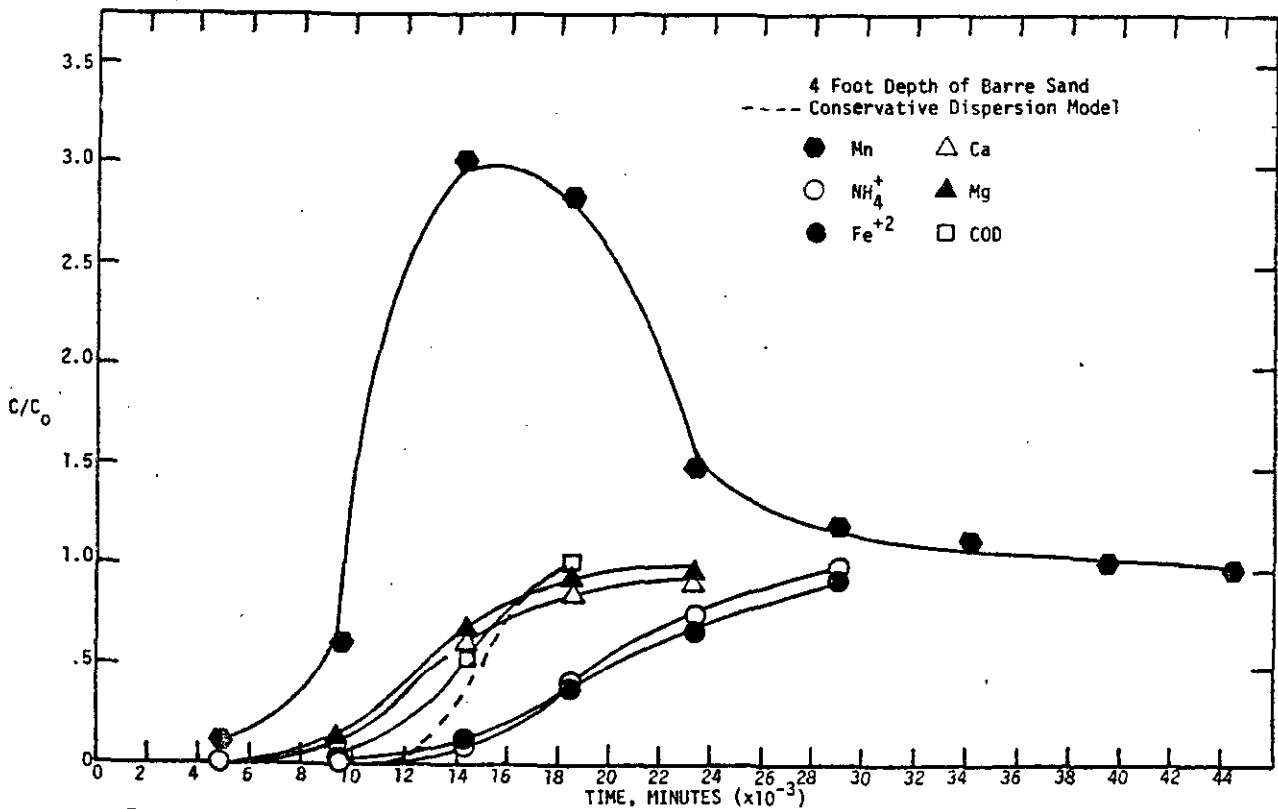


FIGURE 55. RELATIVE ATTENUATIONS BY BARRE SAND IN SATURATED FLOW.

Among the common sulfur-containing functional groups found in organic compounds are hydrosulfide (-SH), disulfide (-S-S-), sulfide (-S-), sulfoxide (-S-), sulfonate (-SO₂OH), thioketone (-C-), and thiazole(a

heterocyclic sulfur group) . Transformations of these sulfur containing compounds are discussed in detail by Starkey (43).

With the anaerobic conditions in the reservoir and columns, sulfate would not be expected to form. This leads one to believe that the sulfate was formed during the collection and analysis steps. As discussed earlier in the section on pH, there was sufficient aeration during sample collection for the iron to be oxidized to the ferric form and precipitate as ferric hydroxide. At the same time it is plausible that reduced sulfur forms were oxidized to sulfate.

Thus, given the breakdown of organics and the availability of reduced sulfur forms the apparent formation of sulfate in the columns is the result of oxidation of the samples during collection. The fact that the curves in Figure 52 show little depth dependence lends strength to the argument.

The curves for the washout case show tremendously high sulfate values (note the use of the log scale for the C/C₀ axis). Before the washout began the columns stood for a while with full strength leachate occupying the pore spaces. Continued breakdown of sulfur containing organics could have occurred. The columns were black indicating the presence of ferrous sulfide. When the columns were drained they were briefly exposed to atmospheric oxygen. In addition, the stream water used in the washout was well aerated. These oxidations coupled with the oxidation during sample collection account for the extremely high initial values. The gradual decrease corresponds to the gradual release of material from the soil.

The explanation for the unsaturated flow case shown in Figure 54 follows the same line. The C/C₀ values greater than 1 are the result of oxidation during sample collection and analysis. The sharp rise at approximately 20,000 minutes may simply correspond to increased availability of reduced sulfur species resulting from increased micro-biological breakdown of organics.

This entire analysis has been based on the assumptions that since the system was anaerobic the sulfur in the organics was released in a reduced form and that all oxidation took place during collection and analysis. Unfortunately there is a conflict with the iron data. At these sulfur concentrations, the iron sulfide equilibrium calls for extremely low iron concentrations. The iron concentrations were as high as 1000 mg/l and FeS precipitates were not observed until late in the run.

Microbial Activity

The question of biological activity during leachate transport is of importance since it represents a potentially powerful attenuation mechanism. Unfortunately, doubts are often expressed as to how much of this potential will actually be fulfilled due to leachate's toxicity. Serious questions may be raised about the ability of native, unacclimated organisms to adapt to a leachate flow. Also, it has been hypothesized that as physical attenuations proceed, toxic materials will build up in the soil, making it hostile even to acclimated organisms.

To investigate these effects, direct measures of microbial activity were attempted. Tests were conducted to quantitatively enumerate organisms present in the liquid phase and on the soil. By repeating the tests for different stages of column operation, it was hoped that the population trends could be uncovered.

Almost immediately, the leachate itself frustrated these attempts. It was rapidly discovered that standard membrane analysis techniques could not be used. When leachate is passed through a membrane filter, the solids formed by sample oxidation accumulate on the filter face. This accumulation proved to be a serious inhibitor when the filters were incubated. In addition to concentrating potentially toxic metal precipitates around the organisms, this accumulation also isolated them from the nutrient medium. It was observed that on gridded plates, growth occurred along the grid lines. Microscopic inspection of the plates showed that solids did not build up along the grid lines since the ink formed an impermeable barrier. Medium from the nutrient pad

was then able to wick up along the edges of the grid lines and the medium initiated colony formation.

Due to this inhibition only agar plate techniques proved to be successful. If the organisms are "frozen" in agar, they are held away from the hostile leachate elements and nutrient contact is insured. The preparation of plates did, however, force limitations on the amount of analysis which could be done and on the species which could be enumerated.

In deference to this, the total plate count was selected as the best indication of gross biological activity. Counts were carried out using both standard plate count agar and soil extract agar. The best results were achieved with lower temperature, extended duration incubations, since the organisms appeared to be under stress conditions and rapid colony growth was rare. Counts were taken at 48, 96, 168, and 336 hours, and the maximum counts were used. Reinnoculation of the plates during these long incubation periods was not found to be a problem.

The results of total plate counts for all phases of column operation are presented in Tables 5 and 6. The liquid phase determinations were performed during actual column operation while soil counts were taken only at the ends of runs. For these soil counts, selected columns were removed from the apparatus and sectioned to yield samples at the various depths.

The scatter of the data attests to the difficulty with which it was gathered and the significance of absolute values must be de-emphasized. Analyzed as trends only, the counts still propound some very interesting trends.

Comparisons of reservoir activity between leachate Batches "A" and "B" show that even when refrigerated, the lower strength leachate supported more life. This is a clear indication that at the strength of Batch "A", leachate was inhibitory and may have been pushing the toxicity limits.

This effect is also evidenced in the column study done with the stronger leachate. The initial liquid phase profiles (counts dated 5/4) show a rapid decline in population with depth. This is taken as indicating organisms native to the soil were not adapting well to the leachate

TABLE 5
LIQUID-PHASE MICROORGANISM POPULATIONS
(organisms per ml x 10⁻³)

Operation		Saturated Leachate Flow		Saturated Groundwater Flow		Unsaturated Leachate Flow	
Date		5/4	5/28	7/14	8/18	10/15	10/26
Reservoir		71	54	5.9	8.2	240	210
Column Depth (ft)	0.00	70	55	18	42	-	-
	0.125	-	-	148	92	-	-
	0.375	5.3	34	208	133	-	-
	0.625	8.4	-	21	570	-	-
	1.00	2.9	59	53	21	90	160
	1.50	2.6	240	-	-	81	23
	2.00	.08	1050	920	81	9.8	2.34
	3.00	-	184	238	244	.04	43
	4.00	-	-	-	-	.62	92

TABLE 6
SOLID-PHASE MICROORGANISM POPULATIONS
(organisms per gm soil x 10⁻⁴)

Operation		Saturated Leachate Flow		Saturated Groundwater Flow		Unsaturated Leachate Flow		
Dry Soil		20 x 10 ⁴ gm ⁻¹		20 x 10 ⁴ gm ⁻¹		14 x 10 ⁴ gm ⁻¹		
Feed		5.4 x 10 ⁴ ml ⁻¹		0.84 x 10 ⁴ ml ⁻¹		22 x 10 ⁴ ml ⁻¹		
Date		7/1	7/1	9/3	9/3	11/13	11/13	11/15
Column No.		#2	#7	#3	#6	#2	#6	#7
Depth (ft)	0.00	-	19	150	49	650	690	3200
	0.50	630	-	59	-	320	138	132
	1.00	40	2.4	75	40	8.5	23	63
	2.00	-	91	-	15.1	-	7.8	470
	3.00	-	2.3	-	19.6	-	9.0	22
	4.00	-	2.6	-	-	-	-	8200

and that the acclimated reservoir population was not able to penetrate to depth due to filtration.

The organism profile taken near the end of this run (5/28) shows that, with time, this condition abates. This is believed to be the result of the eventual transport of acclimated organisms rather than the revival of natives. This postulate is supported by the results of the soil counts done at the end of the run (7/1) since counts were generally lower than for the dry soil.

The column studies done with the weaker Batch "B" leachate show this same initial pattern. The liquid phase organism population decline is attributable to filtration. The subsequent liquid phase profile (10/26) shows increased activity, but again this probably is the result of organism transport. Unlike the first run, however, for the weaker leachate, soil counts at equilibrium greatly exceed those of the dry soil. This indicates the development of a viable soil community, a conclusion supported by the results of the chemical analysis.

The results of the washout studies yield no obvious trends other than to indicate that conditions did not significantly change from those observed at the end of the first run. It appears that the surface water did little to revive organisms stressed by the high strength leachate.

Soil Analysis of Sectioned Columns

At the end of the saturated flow, washout, and unsaturated flow runs the columns were drained and soil samples were collected at different depths. Each sample was analyzed for pH, CEC, Fe, Ca, Mg, Al, exchangeable acidity, and organic matter using the methods previously described. The results are summarized in Tables 7 and 8.

One of the most striking changes in soil properties involved exchangeable calcium and magnesium. Exchangeable calcium and magnesium increased significantly after interaction with the leachate. This result is in excellent agreement with field observations of Apgar and Langmuir (4).

TABLE 7

Soil Analysis for Columns Sectioned After
Saturated Flow and Washout Flow

Column	Depth ft.	Color	pH 10g Soil + 30 ml .01M CaCl ₂		CEC meq/100 g	Ca ⁺² meq/100 g	Mg ⁺² meq/100 g	Al ⁺³ meq/100 g	Organic Matter %	Fe ⁺² meq/100 g	Acidity meq/100 g
			5.70	.01M							
Sand	-	Brown	5.70		1.692	.069	.023	.038	.107	-	.088
1	1/2	Black	5.55		1.964	.363	.190	.012	.084	.237	.106
4	0	Black	5.45		1.768	.736	.258	-	.110	.085	.098
4	1	Black	5.15		2.161	.279	.159	.029	.097	.223	.120
7	0	Black	5.10		2.036	.747	.279	-	.114	.060	.094
7	1	Black	5.95		2.143	.165	.072	-	.094	.062	.052
7	2	Black	5.25		2.161	.208	.110	.037	.114	.187	.114
7	3	Brown- Black	4.35		2.071	.232	.133	.126	.127	.021	.243
7	4	Brown	4.35		1.964	.338	.174	.108	.058	.008	.669
3	1/2	Brown- Black	5.26		1.161	.200	.026	.145	.083	.127	.299
5	0	Black	5.29		1.393	.218	.038	.119	.117	.212	.190
5	1	Gray- Black	5.38		1.192	.222	.023	.140	.032	.137	.242
5	2	Gray	5.46		1.768	.165	.024	.159	.084	.279	.280
6	0	Gray	4.78		1.237	.159	.033	.103	.134	.114	.172
6	1	Gray	5.35		1.072	.174	.026	.139	.089	.150	.236
6	2	Gray	5.52		1.210	.135	.017	.157	.083	.033	.287
6	3	Gray- Brown	5.50		.955	.072	.024	.122	.072	.002	.203

Columns 1, 4, and 7 sectioned after saturated leachate flow.

Columns 3, 5, and 6 sectioned after saturated stream water flow.

TABLE 8

Soil Analysis for Columns Sectioned After Unsaturated Flow

Column	Depth ft.	Color	pH 10g Soil + 30 ml .01M CaCl ₂		CEC meq/100 g	Ca ⁺² meq/100 g	Mg ⁺² meq/100 g	Al ⁺³ meq/100 g	Organic Matter %	Fe ⁺² meq/100 g	Acidity meq/100 g
			4.83	.01M							
Sand	-	Brown	4.83		1.478	.070	.016	.042	.109	-	.103
2	0	Black	7.18		2.089	1.460	.239	-	.285	.509	.052
2	.5	Black	6.84		1.50	.620	.217	-	.178	.349	.158
5	0	Black	7.10		1.714	1.416	.223	-	.331	.554	.054
5	.5	Black	6.98		2.187	.739	.187	-	.165	.498	.073
5	1	Black	6.88		1.411	.632	.178	-	.168	.406	.054
5	2	Black W/Brown	6.63		1.214	.525	.218	-	.142	.355	.166
6	0	Black	7.09		2.804	1.510	.227	-	.264	.724	.049
6	.5	Black	6.80		1.464	.673	.160	-	.185	.448	.056
6	1	Black	6.61		1.482	.543	.151	-	.180	.469	.062
6	2	Black	6.11		2.375	.382	.136	.114	.132	.586	.291
6	3	Brown	5.95		2.196	.307	.169	.217	.118	.371	.726
7	0	Black	6.93		1.375	1.003	.186	-	.235	.445	.056
7	.5	Black	6.62		1.464	.720	.145	-	.144	.406	.075
7	1	Black	6.49		1.161	.606	.134	-	.182	.512	.036
7	2	Black	6.32		1.321	.470	.132	.028	.149	.471	.135
7	3	Brown W/Black	6.00		1.429	.449	.156	.145	.129	.066	.319
7	4	Brown	5.91		1.196	.287	.136	.209	.103	.012	.547
Clay			4.82		4.714	1.644	.666	.064	.103	-	.082
1	0	Black	7.0		4.107	1.387	.623	-	.215	1.827	.104
1	.5	Gray- Black	6.37		4.054	.991	.520	.043	.177	1.277	.257

The surface samples showed especially higher calcium concentrations. As discussed earlier, this was most likely due to precipitation of calcium carbonate. The crust that developed at the surfaces, especially in the unsaturated flow case, supports this premise.

After the washout the calcium and magnesium values were generally lower due to ion exchange reactions. The surface values for calcium were also on par with deeper samples. The change in pH and carbon dioxide concentration accompanying the switch from leachate to stream water probably led to the dissolution of any calcium carbonate that might have developed.

In the test for CEC the 1 N neutral NH_4Ac extract was used to determine exchangeable cations. The Barre sand control had negligible exchangeable iron at this pH. After the different column samples were filtered an orange precipitate developed in the filtrate. Apparently ferrous iron in the black coating on the soil particles dissolved in the ammonium acetate, and it is also possible that exchangeable ferrous iron was released. When the samples were oxidized during filtration the ferrous iron converted to ferric iron which then precipitated as ferric hydroxide. Hydroxylamine hydrochloride was added to dissolve this precipitate so that the iron could be measured.

The two surface samples in the saturated flow case had an average iron concentration of 0.073 meq/100 g. The iron concentration first increases with depth and then decreases. The sharp decrease with the 3 and 4 foot samples which had values of 0.02 and 0.008 meq/100 g was linked to the "black layer". These samples were from parts of the column where the "black layer" had not developed.

The washout experiment showed that more iron washed out than was originally removed. The samples from the columns sectioned after washout still had available iron. Only the samples from the bottom of column 6 where the "black layer" had not penetrated had low iron concentrations in the ammonium acetate.

Recall that in the unsaturated flow case iron was removed at first and then released. Significant amounts of iron were removed in ammonium acetate extraction of these samples. Except for the samples from the bottom of Column 7 the iron concentrations were much higher

than those from the saturated flow samples. The samples from the 3 and 4 foot depths of column 7 had very low values, and, again, were from sections where the "black layer" had not penetrated.

When manganese was extracted using 0.1 N hydroxylamine hydrochloride in 0.01 N nitric acid, iron was also removed from the soil. Approximately 1.235 and 3.866 mg/g were removed from the Barre sand and clay soils respectively. The highest amount of iron in the sectioned samples from the surface of column 7 in unsaturated flow, was 0.724 meq/100 g or 0.2 mg/g.

The organic matter content was very low and hardly changed at all within the limits of the test. The only interesting values are from the unsaturated flow surface samples. Each of these is slightly higher than the rest. The soil organic matter test is similar to the COD test and ferrous iron produces a positive interference. The iron values for these surface samples were higher than the rest.

Soil pH, exchangeable Al, and exchangeable acidity are all interrelated, and the unsaturated flow results show these relations best. The soil pH values were all higher than for the original sand. This is to be expected with the increase in exchangeable calcium and magnesium, otherwise known as "exchangeable bases." Aluminum is associated with exchangeable acidity. As the aluminum concentration increases the pH drops and the exchangeable acidity increases. Some of the values for exchangeable acidity are quite high. The analyst noted that an orange precipitate developed during the titration. Apparently, ferrous iron from some of the samples oxidized during the KCl extraction and titration. As discussed earlier in the sections on pH and alkalinity, the oxidation of ferrous iron to ferric iron and the precipitation of ferric iron as ferric hydroxide produces H^+ which would lead to erroneously high values for soil acidity. The oxidation of sulfides to sulfates also produces H^+ that would affect the determination of soil acidity.

The soil cation exchange capacity was variable. After saturated flow the sample CEC values were slightly higher than the blank. After the washout they were slightly lower. After the unsaturated flow some

were higher and some were lower. Since CEC is dependent on many factors including pH, organic content, and amorphous coatings these results are difficult to interpret.

SUMMARY

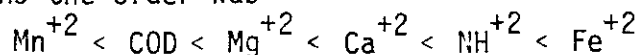
A summary of the saturated leachate flow through four feet of Barre sand is presented in Figure 55. The dashed line represents the convective-dispersive transport prediction for a conservative substance. The chemical oxygen demand curve is close to this prediction indicating that organics are essentially not attenuated and may be treated as conservative substances.

The curves for calcium and magnesium are nearly the same. Initially both appear ahead of the prediction indicating that there is a release of calcium and magnesium. However, both curves eventually cross over the prediction and level off at C/C_0 values less than 1 indicating that removal is taking place. The analysis of soil from the sectioned columns showed that exchangeable calcium and magnesium increased markedly.

The manganese curve is the most striking feature in the figure. The C/C_0 values greater than 1 with a peak as high as 3 indicate that manganese is being released from the soil. In fact, the three leachate samples had high manganese values most likely because they were collected after some passage through soil.

Iron and ammonia were both well attenuated as evidenced by the lag behind the conservative prediction. Since C/C_0 values for both approach 1.0, it appears that a certain finite removal capacity is gradually satisfied.

Overall, the parameters may be ranked in order of removal from low removal (or release) to high removal. For the Barre sand and saturated flow conditions the order was



The unsaturated flow results for four feet of Barre sand are shown in Figure 56. Recall that the unsaturated flow experiment started with dry columns. A truly conservative substance would exit at C/C_0 equal to 1.0. The chlorides come closest to this with a first value at C/C_0 equal to 0.88 and all the rest at 1.

In the saturated flow case, COD was used as a general measure for organic materials, while in the unsaturated flow case the more accurate

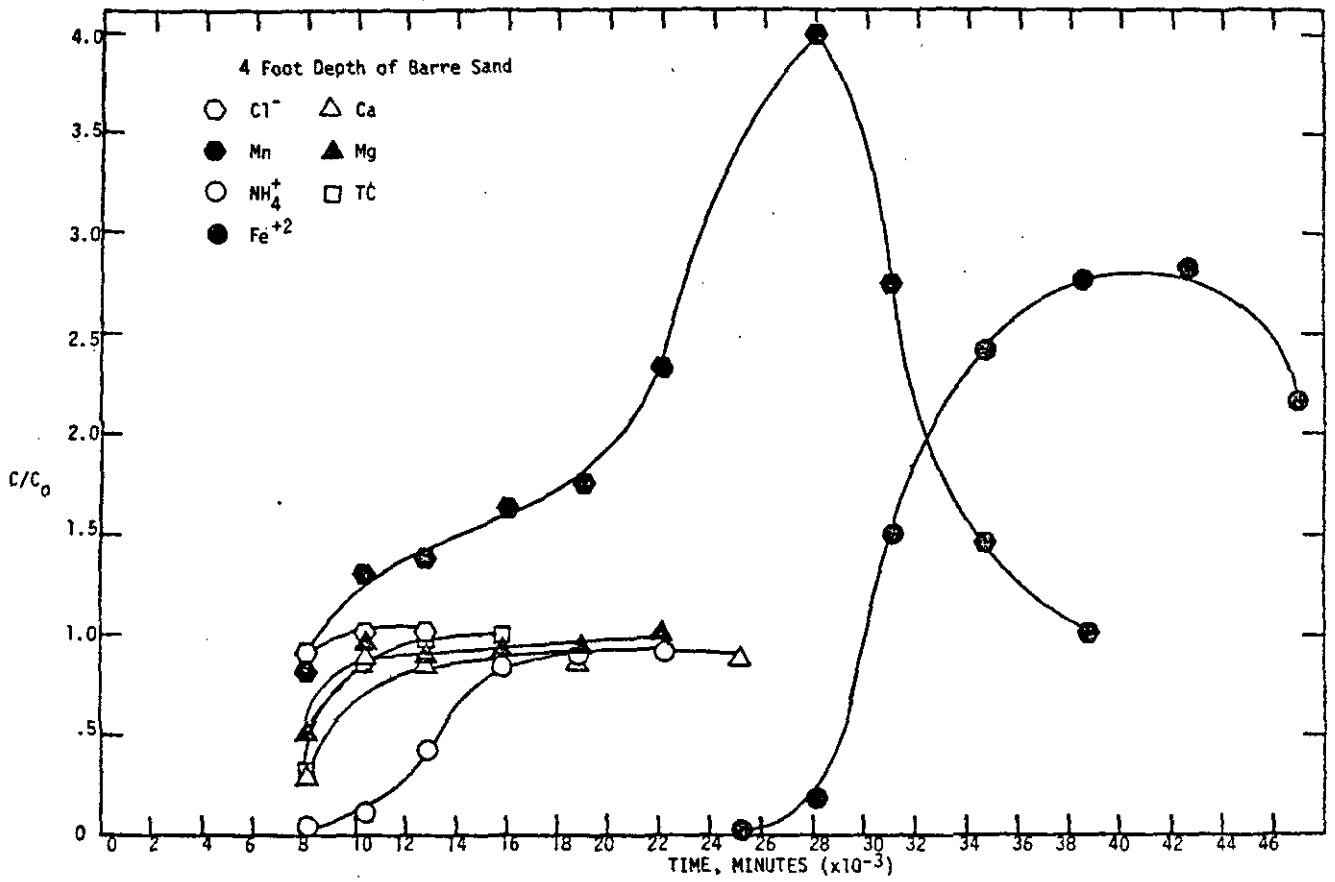


FIGURE 56. RELATIVE ATTENUATION BY BARRE SAND IN UNSATURATED FLOW.

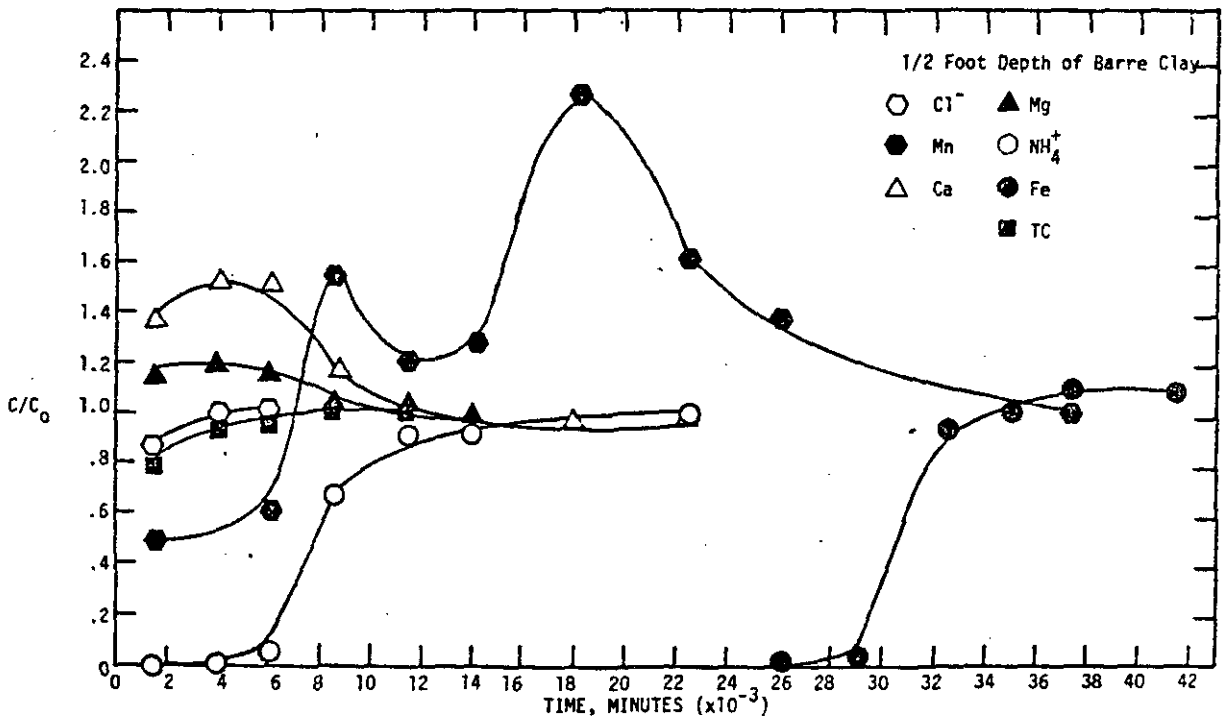


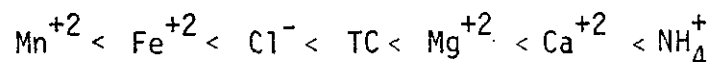
FIGURE 57. RELATIVE ATTENUATIONS BY BARRE CLAY IN UNSATURATED FLOW.

total carbon measurement was made. The breakthrough curve for TC indicates that some organics were removed.

Calcium and magnesium were nearly the same again with a moderate amount of attenuation. Ammonia was significantly removed and manganese was significantly released just as was the case for saturated flow.

The results for iron were quite different than for the saturated flow case. Initially iron is attenuated to a great degree, and then there is a very large release. The release may have been associated with changes in the reducing conditions of the reservoir and the columns.

Overall, for the unsaturated flow case, the sequence of removal follows the order

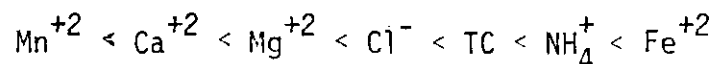


Figures 56 and 57 may be used in order to compare the Barre sand and Barre clay soils. For the Barre clay the slight removals of chloride and total carbon, the significant removal of ammonia, and the striking release of manganese are all essentially the same as observed for the Barre sand.

The breakthrough curves for calcium and magnesium indicate that these elements were released by the Barre clay. Soil analysis of the sectioned column revealed correspondingly reduced values for exchangeable calcium and magnesium.

Iron was significantly attenuated by the Barre clay. In addition, there was no sharp release of iron late in the run as there was with the Barre sand.

Overall, for the Barre clay, the sequence of removal follows the order



A summary of the significant leachate-soil interactions observed in this study is presented in Table 9. Each parameter is considered in terms of the batch equilibrations, the column studies, and the soil analysis of sectioned columns. Some brief remarks concerning the degree of removal or release, the models fitted to the data, and the most probable mechanisms are presented. All statements refer to the Barre sand unless otherwise noted.

TABLE 9

Summary of Leachate-Soil Interactions

Parameter	Experiment	Remarks
COD	Saturated Column	There was no indication of any significant COD attenuation.
	Unsaturated Column	Depth independent removal, due to surficial filtration or biological activity, amounted to 1645 mg. Depth dependent removal was approximately .112 mg/g.
TC	Batch (Undiluted)	Approximately 300mg/l of the total carbon were removed by filtration and approximately .10 mg/g were removed by contact with the soil.
	Unsaturated Column	Depth independent removal, due to surficial filtration or biological activity, amounted to 200 mg. Depth dependent removal was approximately .07 mg/g.
Cl ⁻	Unsaturated Column	Chloride removals were in the range .001 to .006 mg/g and were probably due to interaction at anion exchange sites on the soil.
NH ₄ ⁺	Batch (Diluted)	Over the equilibrium concentration range of 0 to 300 mg/l NH ₄ ⁺ removal was probably due to sorption reactions with the soil. The removal was described by the Langmuir equation. $X = \frac{.0095 C}{1 + .009 C}$ or the Freundlich model $X = .0014 C^{.71}$
	Batch (Undiluted)	At equilibrium concentrations around 300 mg/l approximately .02-.03 mg/g NH ₄ ⁺ were removed. Barre Clay - at equilibrium concentrations around 300 mg/l approximately .08-.11 mg/g were removed.
	Saturated Column	Depth independent removal, due to surficial microbiological activity, amounted to 94 mg. Depth dependent removal was approximately .016 mg/g.

Table 9, Continued

Parameter	Experiment	Remarks
NH ₄ ⁺ , cont.	Unsaturated Column	Depth independent removal amounted to 190 mg and depth dependent removal was approximately .026 mg/g. Barre Clay - Depth dependent removal was approximately .23 mg/g.
	Batch (Diluted)	Calcium removal was described by the Langmuir equation $X = \frac{.0041 C}{1 + .0867 C}$
Ca	Batch (Undiluted)	Barre clay - Calcium was released by the soil.
	Saturated Column	Depth independent removal was probably due to calcium carbonate precipitation.
	Unsaturated Column	Depth independent removal was probably due to calcium carbonate precipitation. Depth dependent removal was due to ion exchange reactions. Soil exchangeable calcium increased markedly and a crust developed at the column surfaces. Barre clay - Calcium was released in the range of .15 mg/g. Soil exchangeable calcium decreased.
	Batch (Diluted)	Magnesium removal was described by the Langmuir equations $X = \frac{.0010 C}{1 + .018 C} \quad \text{and} \quad X = \frac{.0013 C}{1 + .017 C}$
Mg	Batch (Undiluted)	Barre clay - Magnesium was released.
	Saturated Column	Magnesium was removed. Soil exchangeable magnesium increased.
	Unsaturated Column	Depth dependent removal was due to ion exchange. Soil exchangeable magnesium increased. Barre clay - Magnesium was released. Soil exchangeable magnesium decreased.

TABLE 9, Continued

Parameter	Experiment	Remarks
Mn	Batch (Diluted)	Manganese release was described by the Langmuir equation $X = \frac{.0051 C}{1 + .2879 C}$
	Batch (Undiluted)	Manganese was released at approximately .011 mg/g. Barre clay - manganese release was concentration dependent.
	Saturated Column	Manganese release was approximately .012 mg/g.
	Unsaturated Column	Manganese release was approximately .010 mg/g.
Fe	Batch (Undiluted)	Over the solution concentration range 650 to 1000 mg/l approximately .11 mg/g was removed. Barre clay - Iron removal was described by the Langmuir equation $X = \frac{.0035 C}{1 + .0023 C}$
	Saturated Column	Iron removal was approximately .09 mg/g.
	Unsaturated Column	Iron removal was followed by significant release. Barre clay - iron removal was approximately 1.12 mg/g.

DISCUSSION - LEACHATE TRANSPORT MODELING

Based on the results of these column studies, it appears that there are several different approaches by which leachate transport models might be developed. Models might be constructed to describe the transport of a single solute of particular interest, of groups or families of solutes, or of "leachate" in general, independent of any of its particular solutes. These approaches represent different levels of sophistication and require varying degrees of complexity to be successful.

General Transport Models

A crude leachate transport model may be accomplished simply by modeling the groundwater flow pattern in the neighborhood of a landfill. A three-dimensional steady-state mass balance on an aquifer control volume yields

$$-\frac{\partial}{\partial X} (\rho_w V_X) - \frac{\partial}{\partial Y} (\rho_w V_Y) - \frac{\partial}{\partial Z} (\rho_w V_Z) = 0 \quad (7)$$

where: $V_{X,Y,Z}$ = interstitial velocities (LT^{-1})
 ρ_w = fluid density (ML^{-3})

By assuming that the fluid density will remain constant and by employing Darcy's Law for Porous Medium Flow to provide the velocity components,

$$V_i = -K'_i \frac{\partial h}{\partial i} \quad (8)$$

where: K'_i = coefficient of hydraulic conductivity
in i^{th} dimension (LT^{-1})
 h = piezometric head (L)

Equation (7) may be written as

$$\frac{\partial}{\partial X} (K'_X \frac{\partial h}{\partial X}) + \frac{\partial}{\partial Y} (K'_Y \frac{\partial h}{\partial Y}) + \frac{\partial}{\partial Z} (K'_Z \frac{\partial h}{\partial Z}) = 0 \quad (9)$$

By applying appropriate initial and boundary conditions and with knowledge of subsurface soil conditions, this equation may be solved to yield the three-dimensional groundwater flow net. Often assumptions of the Laplace Equation can be simplified by assuming that the coefficient

is independent of space, but for this application the simplification is not particularly useful. Subsurface domains are often both anisotropic and non-homogeneous so it is desirable to retain K' as a function of space. In this way, soil property discontinuities may be accommodated. This probably eliminates analytical solutions of Equation (9) but its resolution may be accomplished numerically with little difficulty. A solution of this equation yielding $h=f(X,Y,Z)$ would allow for the construction of the groundwater flow net within the domain. It also could supply components of velocity for any point (X,Y,Z) via Darcy's Law (a feature important to higher orders of modeling).

Alone, this solution would provide a first approximation of the leachate transport potential of a landfill site. The results of the saturated flow experiments demonstrated that many of leachate's elements undergo no soil attenuation. Therefore, if the solution of Equation (9) showed that groundwater flow was possible between the landfill site and some point of interest at (X,Y,Z) , then its eventual degradation should be expected. For this initial approximation, it matters little whether the degradation will be due to the arrival of foreign organics, toxins, or simply to increased hardness or chloride concentrations. The fact that it will eventually occur is the first piece of essential information.

Among the problems with relying on this approximation is that it is based on a steady-state groundwater flow and yields little information about the time variable. The next step in sophistication would be to couple the groundwater transport model with a non-steady-state solute transport model. This would allow for the simulation of a pollution load imposed on the groundwater system at (X_0, Y_0, Z_0, t_0) and would produce information on its concentration as a function of space and time. It also allows for the accommodation of dispersion as well as convective transport.

Three-dimensional solute transport is described by the equation

$$-V_X \frac{\partial C}{\partial X} - V_Y \frac{\partial C}{\partial Y} - V_Z \frac{\partial C}{\partial Z} + D_X \frac{\partial^2 C}{\partial X^2} + D_Y \frac{\partial^2 C}{\partial Y^2} + D_Z \frac{\partial^2 C}{\partial Z^2} = \frac{\partial C}{\partial t} \quad (10)$$

where: $D_{X,Y,Z}$ = dispersion coefficient (L^2T^{-1})

C = solute concentration (ML^{-3})

Martel (37) and others have found that mechanical dispersion in a porous medium is directly proportional to the interstitial velocity with the proportionality constant being a property of the media composition. Using this relationship, the overall dispersion coefficient may be expressed as

$$D = D(\text{mech}) + D(\text{mol}) \quad (11)$$

$$D(\text{mech}) = kV^n \quad (12)$$

$$D_i = kV_i^n + D(\text{mol}) \quad (13)$$

where: D_i = dispersion coefficient in i^{th} dimension (L^2T^{-1})

k = proportionality constant (L)

$D(\text{mech})$ = coefficient of mechanical dispersion (L^2T^{-1})

$D(\text{mol})$ = coefficient of molecular diffusion (L^2T^{-1})

n = exponent

Refined Transport Models

The results of the unsaturated flow experiments demonstrated that for weaker leachates and special flow conditions, the conservative convective-dispersive-diffusive mass transport assumption will overestimate leachate transport. The specific conductance breakthrough curves clearly show that under these conditions, the Barre sand accomplished a modest attenuation of ionic strength. In fact, no parameter measured in the unsaturated flow experiments could be identified as absolutely conservative. This indicates that for cases where a weaker leachate may be expected (as with preliminary treatment), or when it is anticipated that the soil will be highly attenuative, an active attenuation term should be incorporated into the transport model. Therefore, the next step in sophistication is accomplished by incorporating a sorption, reaction, or constant sink term into Equation (10).

Reaction terms must be used only with a great deal of care. Reactions that proceed for the first few feet of soil may not persist over hundreds or thousands of feet or vice versa. If this term was included without restricting the domain over which it operated, it would

soon drive the solute concentration to zero. The constant sink term seems to hold some promise for modeling effects such as filtration but this could also be accomplished by altering the model inputs. It is the sorptive term which appears to hold the most promise in refining the transport model.

From the results of the washout studies it can be seen that reversibility of the attenuation process would also be a useful refinement. If a leachate enclave is to be modeled past the termination of its source, reversible attenuations would become new sources adding mass to the liquid phase.

Detailed Transport Modeling

For the modeling of many of leachate's solutes far more sophistication will be required than can be accomplished by adding general attenuation terms to Equation (10). The sulfate data, as a particularly noteworthy example, is probably the result of many competitive pH and p_e -dependent chemical reactions as well as the product of a delicately-balanced biological population. It can change forms rapidly with only minor changes in leachate's tenuous equilibria and it exerts massive effects on the transport of other solutes. Its accurate modeling will require the incorporation of chemical kinetics, thermodynamics, and a good deal of theory.

The role of column studies in this type of modeling is limited. Simply too much occurs and too few degrees of freedom are controllable when the natural system is simulated. Advances in detailed transport modeling must await far more carefully controlled experimental procedures.

CONCLUSIONS

The net effectiveness of the Barre sand must be considered very low. Although chemical distributions might shift slightly, leachate should be expected to traverse 4.0 ft (1.22 M) of this soil virtually unaltered with respect to gross ionic strength and pollution hazard. Other conclusions reached during these experiments include the following:

- 1) Organics seem to be unattenuated by the Barre soil. This result is of considerable importance to leachate modeling since it implies that a conservative transport model may be used to establish the bounds of the contamination potential. The work of Griffin, et al (19-23), also showed little attenuation of organics. This fact alone makes a strong case for allowing no leachate to migrate from a landfill site.
- 2) Indications were that "strong" leachate is toxic to unacclimated soil organisms and that significant biological activity must await the reinoculation of the soil by leachate-acclimated organisms. After reinoculation, no additional toxicity was observed, implying that the buildup of metallic cations on the soil may not promote further inhibition.
- 3) Under anaerobic conditions, no biological slimes formed at the soil surface and no noticeable decline in permeability resulted. This is contrary to the observations of Ham (25) for aerobic conditions.
- 4) Under anaerobic conditions, leachate solutes were found to be very mobile in the soil. Surface and depth filtrations did not accomplish significant strength reductions, again in contrast to the results of Ham (25) for the aerobic case. Of the active attenuation mechanisms, positive sorption seemed to be the most significant, but overall, all effects were minimal.
- 5) Leachate solutes were found to be more mobile under conditions of saturated flow. Unsaturated flow may force greater soil contact accounting for the better attenuation.

- 6) Leachate equilibrated soil was found to release much of its load back to solution as the liquid phase concentrations declined. The attenuation of Fe, NH_4^+ , $\text{SO}_4^{=}$, and specific conductance was found to be reversible. This observation that attenuation may be only temporary makes a second strong case for allowing no leachate discharge from landfill sites.
- 7) Under anaerobic conditions the dissolution of solutes undergoing reversible attenuation was found to reach a quasi-equilibrium. In this quasi-equilibrium effluent concentrations were found to reach very nearly constant values which were significantly higher than background levels. Subsequent oxidation disturbed this equilibrium and resulted in a slug release from the solid phase. This indicates that soils may have more than one attenuative capacity for a solute depending on the ORP of the liquid phase.

RECOMMENDATIONS FOR FUTURE RESEARCH

As with most studies, prior knowledge of the results would have altered some procedures. At the time this research was conceived leachate literature on soils conveyed the impression that any soil would accomplish considerable attenuation. It was not realized that the Barre sand was so inept until after the first run was well in progress. In retrospect, the first run should have been made with a weaker leachate; a fault that was corrected in the unsaturated flow experiments. This emphasizes the necessity for estimating attenuative capacity and balancing soil mass with liquid phase ionic strengths before a full-scale column study is initiated. Also, the method of *leachate application to the unsaturated columns proved difficult to model*. Application to dry columns is recommended only when attenuative capacity is very low. Otherwise, it is recommended that leachate be "stepped in" after steady flow is accomplished. Finally, the sampling interval dictated by required sample volume should be reduced. Analysis could probably be completed on 300 ml of sample if frugal procedures are followed. Reduced sample volume (and frequency) will be rewarded by more detailed breakthrough curves. Other recommendations are as follows:

A) Leachate Handling and Storage

Most researchers working with leachate have reported difficulties with its collection and storage. These problems become acute for attenuation column studies because a large volume of leachate must be collected and held stable for long periods of time. If leachate is either oxidized or reduced, insoluble metallic compounds form and precipitate from solution. Researchers have attempted to hold leachate stable by refrigeration and by storage under carbon dioxide, nitrogen, or argon gas but none of these have proved entirely successful. This has led to the suggestion that leachate be stored only under the natural landfill gases with which it was in equilibrium (a procedure both difficult and dangerous to accomplish). A generally applicable method of leachate collection and storage must be developed.

B) Standardization of Analytical Methods

The compilation of methodology by Chian and DeWalle (9) should not be ignored when chemical parameters and analytical methods are selected. There are, however, parameters such as nitrate and phosphate for which dependable methods have not yet been developed. It would also be desirable to develop methods for the quantification of reduced chemical species.

The importance of general strength parameters should not be overlooked. Measurements such as pH, ORP, conductivity, and total solids are easily done and may provide information essential to data interpretation.

The development of functional biological procedures has lagged behind chemical analysis methodology. Much study remains to be done on the biological populations which develop during the leaching process, and the effects of leachate on unacclimated organisms. Sound methods by which to accomplish these still have to be developed.

The characterization of soils used in attenuation studies should be standardized. It would be of considerable benefit if reported attenuative capacities could be correlated with work done on other soils.

C) Attenuation Studies

The attenuative properties of more naturally-occurring soils must be investigated. These properties should include capacities for the major components of leachate as well as specific trace elements. To date, research has concentrated on soils of particularly good attenuative properties (with the obvious exception of this work) but the capacities of less fortunate soils must also be quantified. An essential component of any study should be an evaluation of reversibility.

In this role, column studies serve some very useful purposes but are difficult to accomplish and yield results slowly. It would be desirable to standardize some dispersed soil experiments to yield attenuative capacity approximations more rapidly. If column studies are selected, dispersion must be carefully evaluated.

The batch equilibrations were useful in examining leachate-soil interactions. If isotherms are prepared using a series of leachate dilutions there is an increased problem of aeration and oxidation

during handling. Even if this problem is overcome the results must be treated with caution. Leachate is a complex mixture of many species and the interactions between these species may be affected by dilution.

It is recommended that future isotherms be prepared using undiluted leachate equilibrated with varying amounts of soil. This technique minimizes chances for aeration and the problems associated with the use of dilutions. However, there are some drawbacks to the method. Only a limited range for the soil/leachate ratio may be covered. Also, a certain quantity of leachate is taken up in wetting the soil and it may be difficult to obtain sample sizes large enough for all analyses, especially at high soil/leachate ratios.

D) Equilibrium Investigations

Research should be done on the distribution of chemical species in leachate for its various oxidation states. The composition, stability, and formation kinetics of the various precipitates should be known. This information will be required to accomplish higher orders of modeling. It must also be known if disposal alternatives for leachate solids are to be evaluated.

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