

REMOVAL OF CATIONS FROM LEACHATE BY INTERACTION WITH SUBSURFACE SOILS

By Ira W. Leighton¹ and Frederic C. Blanc²

Abstract

This investigation was conducted in order to determine the magnitude of cation removal from leachate provided by soils under a landfill. The interaction of sodium, potassium, calcium, iron, and magnesium cations in leachate with a soil was examined for eight Massachusetts soils in laboratory soil column experiments. Removal capacities for the various soil types were developed based on the soil column experiments. The removal values ranged from 3.8 milliequivalents to 31.1 milliequivalents per 100 grams of dry soil. Shaker tests were used to verify the soil column experiments.

Introduction

In recent years the expansion of suburban areas combined with increased refuse production has resulted in greater public awareness of solid waste disposal problems. One of the problems associated with solid waste disposal sites is the deterioration of groundwater quality in the vicinity of the site resulting from the entrance of highly contaminated drainage i.e. leachate, into the underlying aquifers. This problem can be controlled by: not permitting refuse to be deposited below the maximum elevation of the groundwater table, minimizing the amount of infiltration into the fill, and by collection and treatment of the leachate. Where the leachate is allowed to enter the soil below the fill, the attenuating capacity of the soil and dilution must be relied upon to protect groundwater supplies.

Data on the actual leachate treatment provided by the subsoils are scarce. This investigation (4) was conducted to collect such data and examine the interaction between the leachate and the soils underlying the fill. Leachate can add a variety of inorganic contaminants to the local groundwater in the area of a landfill. Elements existing as ions, such as chloride, calcium, magnesium, potassium, and sodium, are usually present in high concentrations. Fortunately ion exchange and adsorption in the sub-soils result in the removal of some ions from the leachate-groundwater mixture. This removal can be considerable, particularly in the case of some cations. Nitrogen can be present as the ammonium cation, as undissociated ammonia at high pH,

¹San. Engineer, Solid Waste Management Branch Environmental Protection Agency, Boston, Mass., formerly Grad. Student, Department of Civil Engineering Northeastern University, Boston, Mass.

²Assoc. Prof. of Civil Engineering, Northeastern University, Boston, Mass.

or as the nitrate. None of these is well retained by soils. Phosphorus as the phosphate anion is well retained by most soils.

Specifically, this research focused on the ability of eight different Massachusetts soil types to remove five major cations from leachate. The five cations studied were calcium, magnesium, potassium, sodium, and iron. All of the cations investigated may have a detrimental effect on groundwater uses. Calcium and magnesium cause hardness problems. Iron can cause staining problems and problems in industrial processes. Sodium is detrimental in drinking water to persons suffering from cardiac and circulatory diseases. The removal of such cations by soils is therefore of considerable interest. In addition to evaluating the removal capacity of the soils, the order of preference in removal and other factors were observed. The experiments were carried out to determine the removal which might be expected in the unsaturated subsoil zone between the refuse and the groundwater table, or an unsaturated subsoil which may be used for subsurface disposal of leachate.

Cation Removal in Soils

The capacity of a soil to remove leachate cations is due to any or a combination of the following mechanisms: ion exchange, adsorption, complexing, fixation, biological uptake, precipitation, and filtration. The relative contribution of any one mechanism to the total observed removal capacity is difficult to establish in such a complex system; however the literature suggests that in terms of orders of magnitude cation retention in soils is primarily a function of ion exchange and adsorption. Adsorption and ion exchange are surface chemical phenomena which are most pronounced in the finer sized particles within a soil mass. The importance of the colloidal-sized particles stems from the fact that although larger particles can develop the surface charges required to attract and hold ions, the larger particles do not have the tremendous surface area per unit weight which the smaller particles have. It is for this reason that fine-grained soils containing clay and silt particles have greater cation removal capacity than the coarse grained sandy soils. In addition to soil particle size, there are many other factors which determine the nature of cation removal by adsorption or ion exchange. Some of the other factors are: the composition of the exchangeable ions present in the soil, the amount of organic matter in the soil, the particular ions in solution and the concentration of the ions in solution.

It should be emphasized at this point that the term "removal capacity" as used to describe the results of this investigation, does not mean the total ion removal capacity nor is it the total cation removal capacity. The term as used here refers to the total removal of the five cations considered in the research.

Experimental Methods

Leachate Sampling and Testing

Leachate samples for this investigation were obtained from the dump fill refuse disposal site in the town of Scituate, Massachusetts. Four samples were taken by excavating a sump into the bottom of an existing cut in the fill. The Scituate disposal site is situated in an area where the groundwater table is near the surface of the fill and the refuse is in contact with the groundwater. All of the samples collected were highly colored and possessed a strong odor which indicates that the fill was undergoing active decomposition.

Table 1 lists a reasonably thorough analysis of the Scituate Leachate. Comparison of this analysis with leachate characteristics observed in other studies (2) indicates that the Scituate Leachate can be considered as a typical strong leachate which would be produced in the years immediately after filling.

All the analyses conducted on the leachate were conducted in accordance with the procedures prescribed in Standard Methods (6), with modifications in sample pretreatment. The analyses for sodium, potassium, calcium, magnesium, iron, copper, nickel, zinc and lead were performed using an atomic absorption spectrophotometer.

Soil Sampling and Testing

The eight soil samples selected for this investigation were collected at various locations in the Boston Metropolitan area. Sieve analysis and hydrometer testing revealed that the soil types ranged from sand to silty clay. Table 2 indicates the classification of the samples based on the textural triangle nomenclature developed by the U.S. Soil Conservation Service (5). The soil samples were collected from both the A Horizon (surface soil) and the B Horizon (subsurface soil). In this case the B Horizon material was taken from the depths of 6 to 8 feet below the surface.

Soil Column Tests

In order to establish the cation removal capacities of the various soil types, a series of soil column tests were set up. The soil columns consisted of $\frac{1}{2}$ in. (1.27 cm) ID acrylic tubing, approximately 18 inches (46cm) long. Each tube was threaded and a $\frac{1}{4}$ x $\frac{1}{4}$ in. nylon tube insert placed into the end of the column. The soils were supported on a small piece of 50 mesh stainless steel screen which had been taped into the nylon insert. In addition to the screen, one gram of double-washed coarse sand was added to each column to minimize the loss of fines in the effluent.

TABLE 1
COMPOSITION OF SCITUATE LEACHATE

<u>Contaminant</u>	<u>Concentration*</u>	<u>Contaminant</u>	<u>Concentration*</u>
pH	5.5	Nickel	0.16
Hardness, as CaCO ₃	1950.0	Zinc	0.81
Alkalinity, as CaCO ₃	729.0	Copper	0.02
Calcium	632.0	Lead	0.00
Magnesium	94.8	Total Solids	6770
Sodium	298.0	Suspended Solids	460
Potassium	440.0	Conductivity	2940 mhos
Iron (Total)	280.0	BOD ₅	11700
Chloride	502	BODL	13820
Sulfate	298	K (BOD rate constant)	0.163 1/day
		COD	15000

*All results in this table with the exception of pH are reported in mg/l unless otherwise noted.

TABLE 2
CLASSIFICATION OF SOILS INVESTIGATED

Soil Sample	Soil Classification	Source of Soil Sample
1	Sand	B Horizon - Scituate, Ma.
2	Loamy Sand	A Horizon - Sudbury, Ma.
3	Loamy Sand	B Horizon - Chelmsford, Ma.
4	Sandy Loam	B Horizon - Chelmsford, Ma.
5	Sandy Loam	B Horizon - Sudbury, Ma.
6	Silt Loam	B Horizon - Sudbury, Ma.
7	Silt Loam	A Horizon - Chelmsford, Ma.
8	Silty Clay	B Horizon - Sudbury, Ma.

The soil samples were weighed and then placed in columns in small increments, with each successive increment being tamped in place with a $\frac{1}{2}$ in. (1.27 cm) glass rod. The depth of soil in the column was measured and the density of the soil computed. A blank column was prepared for the purpose of establishing how much of the observed removal was due to the column surface and supporting base i.e. the sand and 50 mesh stainless steel screen.

Leachate was added in ten milliliter increments to each column and the flow rate through the column recorded. The addition of each leachate increment was spaced so as to maintain an unsaturated condition in the column. The columns were allowed to leach freely until the ten milliliters of leachate had passed through the column or until the flow of leachate from the effluent stopped for an excessive period of time. The leaching was continued in this manner i.e. adding successive ten milliliter increments until the cationic concentrations of calcium, magnesium, sodium, potassium, and iron in the effluent were equivalent to that of the raw leachate. At this point the removal capacity of the soil was considered to have been exhausted and the leaching was discontinued.

Shaker Test Experiments

In order to determine the effects of varying contact times on the cation removal processes, it was necessary to utilize shaker tests to supplement the soil column data. The procedure utilized involved placing twenty grams of soil in a 50 ml plastic centrifuge tube and adding a 20 ml volume of leachate to the tube. A series of tubes was prepared in this manner for each of the eight soil samples. After sealing, the tubes containing the leachate and soil were placed in a variable speed shaker. The soils and the leachate were contacted for time periods of $\frac{1}{2}$ hr, 1hr, 2hrs, 3hrs, 5hrs and 7hrs. At the end of the appropriate contact time a tube containing each soil type was removed from the shaker table and centrifuged for 15 minutes at 2000 rpm to separate the soil from the leachate.

After centrifuging the leachate was siphoned off and then analyzed for calcium, magnesium, sodium, potassium, and iron.

The removal was calculated based on flow volume and concentration relationships between the samples containing the soil and leachate and the leachate blanks which had been carried through the same procedures.

Discussion of Results

Soil Column Experiments

The selection of specific soil types utilized in the soil columns was based upon the desirability of using a fine-grained soil which would possess good removal potential and also be sufficiently permeable to allow the leachate to pass through the column. Figures 1-4 are typical plots of decrease in cation concentration, in milliequivalents per milliliter versus the cumulative volume of leachate passed through the column. Noted on each figure is the total removal capacity in milliequivalents per 100 grams of soil. As one can observe from the figures, the ability of each soil type to retain the cations in question decreases as each additional increment of leachate is passed through the columns until the removal capacity is exhausted. It is interesting to note from the figures that the soils do not approach exhaustion of removal capacity in the same manner. For the eight soil types tested the removal values ranged from a low of 3.8 milliequivalents per 100 grams of soil to a high of 31.1 milliequivalents per 100 grams of soil. Table 3 lists the removal capacities for the various soils. The removal capacities in this investigation are in the same range reported by Hill (3) for cation removal from domestic wastewater effluent for six major soil formations extensive in New England.

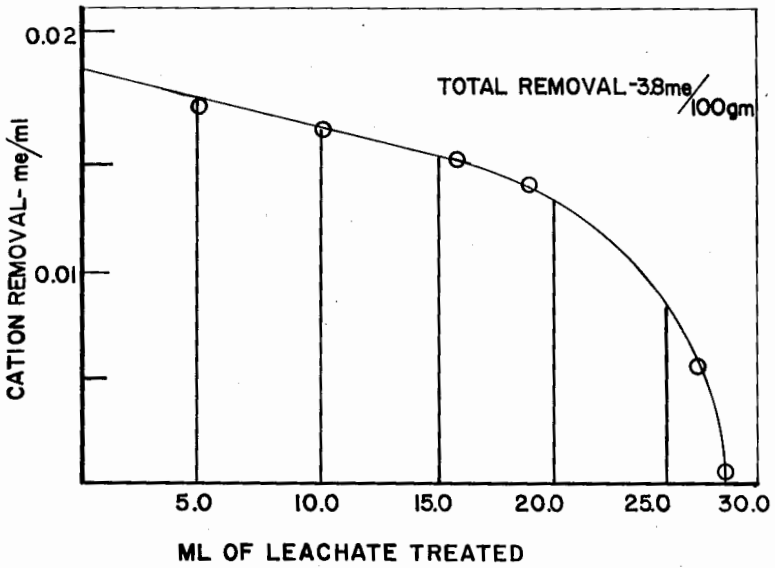


Figure 1 — Removal capacity of soil sample 1

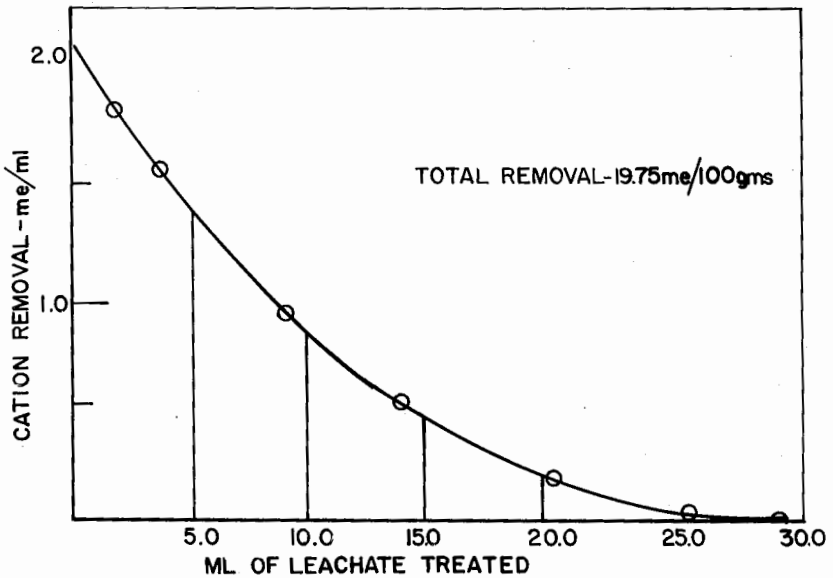


Figure 2 — Removal capacity of soil sample 3

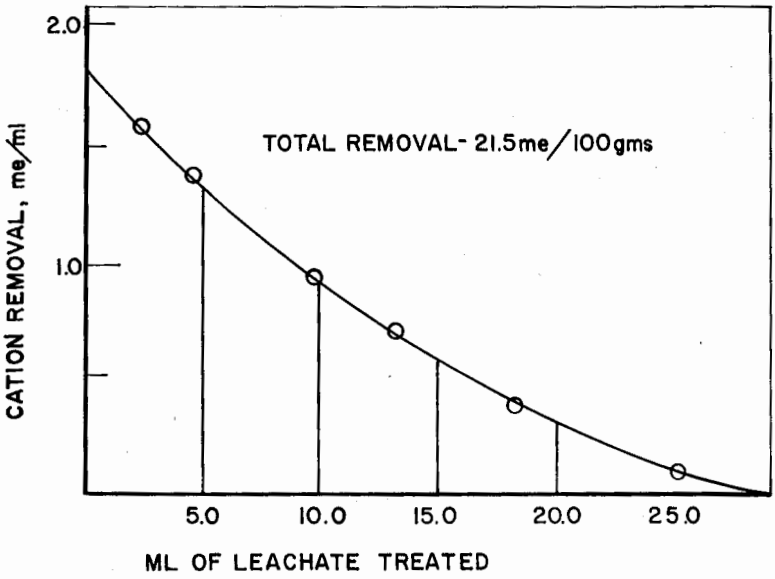


Figure 3 — Removal capacity of soil sample 6

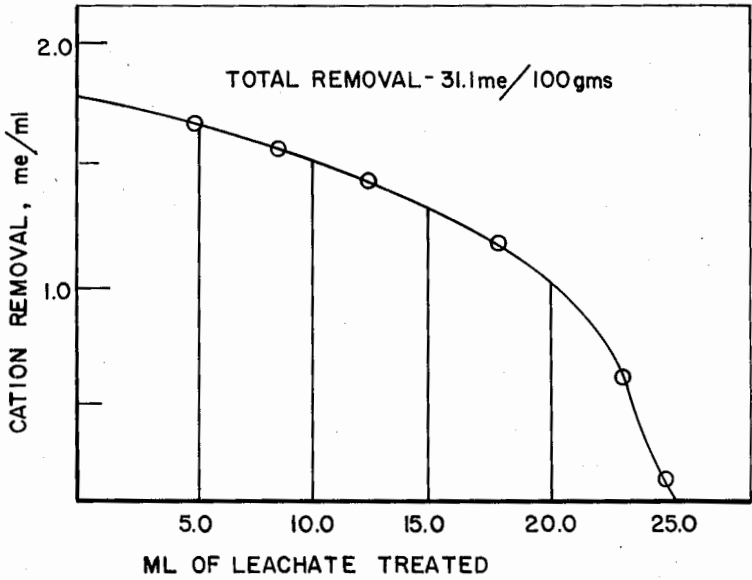


Figure 4 — Removal capacity of soil sample 8

TABLE 3

CATION REMOVAL CAPACITIES OF SOILS TESTED

<u>Soil Sample</u>	<u>Soil Classification</u>	<u>% Weight Passing #200 Sieve</u>	<u>Removal Capacity Milliequivalents Per 100 Grams</u>
1	Sand	2.44%	3.8
2	Loamy Sand	12.28%	17.1
3	Loamy Sand	18.66%	19.7
4	Sandy Loam	30.84%	18.1
5	Sandy Loam	32.54%	23.1
6	Silty Loam	55.0 %	21.5
7	Silt Loam	65.11%	29.8
8	Silty Clay	87.84%	31.1

The effect of particle size on the cation removal capacity is illustrated in part by Table 3. Comparing the percentage of the soil which passes a number 200 sieve (.075 mm in diameter) with the removal capacity of the sample shows the increasing removal capacity with decreasing particle size. It should be noted that there are other factors such as the nature and origin of the particles and the humus content which may also affect the removal capacity.

The selectivity ion exchange and adsorptive reactions taking place in the soil is well documented. Certain cations are adsorbed to a greater or lesser extent as a result of the following factors: 1. pH of the leachate, 2. Valence of the cations in solution. 3. Degree of hydration of the ions present, 4. The relative concentrations of the ions, 5. The nature of the anions associated with the cations.

Bear (1) points out that there is no one order of cation removal which consistently applies to all soil types, instead each soil develops an order of removal in response to the above-mentioned factors. There is, however, a definitive pattern of removal expressed with reference to each specific factor.

The relative quantities of calcium, magnesium, sodium, potassium and iron removed by the different soils tested are a function of any or all of the above-mentioned parameters. The relative order in which each ion was removed also varied with respect to each soil type. It becomes quite apparent that the mechanisms involved in this removal process are extremely complex.

An indication of how the removal order varies for the various soil types may be obtained from an examination of Table 4. This table shows results for two leachate samples of normal and low cation concentration. Leachate Sample A represents the normal concentrated leachate used in this investigation, while Leachate Sample B is a more dilute sample selected in an effort to ascertain the effects of concentration on the removal order. Table 5 lists the concentrations of the five cations tested in samples A and B. From the analyses it is apparent that, except for iron content, Sample A was approximately four times as concentrated as Sample B. This can be considered to be representative of the wide variation in leachate concentration which may be experienced by the soils under landfills. It should be noted that the results reported for leachate Sample A in Table 5 represent the percent of each cation contributing to the ultimate "removal capacity" i.e. leaching of the soil column to the point of exhaustion, whereas the percent of "removal" values for Leachate Sample B represent the "removal" from the first five milliliter slug of leachate passing through each soil column. The soil samples handling the dilute leachate could not pass the volume of leachate required to exhaust the cation removal capacity of the columns because solids caused a clogging of the columns before the exhaustion point was attained.

The results indicate a variation in removal order with respect to at least two factors: 1. A variation in removal with respect to soil type and 2. A variation with respect to the concentration of the leachate. The results indicated that cation concentration and valence appear to be at least equally important in establishing the removal pattern, or order of removal for the different cations. The concentration of magnesium in the effluent from the columns increased above that of the raw leachate with Sample B. This indicated that magnesium was being released from the soil into the leachate. Magnesium is one of the most common exchangeable cations found in the soils of this region; therefore, the increase in magnesium concentration is evidence that exchange reactions are taking place in the soils.

Shaker Tests

In order to determine the influence of contact time on the cation removal process and removal capacity as determined by the soil column experimental procedures, a series of shaker test experiments were performed.

TABLE 4
CATION REMOVAL PATTERNS FOR CONCENTRATED AND
DILUTE LEACHATE SAMPLES

	Concentrated Leachate Sample A					Dilute Leachate Sample B				
Raw Leachate Constituents Expressed as % of Total Milli- equiv.	Fe	Ca	Mg	Na	K	Fe	Ca	Mg	Na	K
	5.0	38.0	6.0	21.0	30.0	27.0	41.0	7.0	10.0	15.0
Soil Sample	Removal of Cations as expressed as a % of "Total Removal"*									
1	4	25	6	23	42	67	6	0	10	17
2	8	39	0	13	40	82	17	0	0	1
3	4	67	6	6	17	65	28	0	0	7
4	11	50	10	9	20	80	13	0	2	5
5	10	60	9	11	10	78	17	0	0	5
6	12	13	0	21	54	88	8	0	1	3
7	4	38	6	16	36	67	26	0	3	4
8	9	42	6	13	30	75	18	0	3	4
Average	8	42	5	14	31	75	16	0	3	6

*Total Removal = total milliequivalents of the Fe, Ca, Mg, Na, K cations removed by the soil column in this experiment.

Initial shaker tests performed on two soil types produced an interesting result, namely an increase in removal with contact time up to a maximum followed by a decrease in removal. The results of this experiment are presented in Figures 5 and 6. The plot of removal versus contact time gives the impression that material which is adsorbed during a specific time interval is later placed back into solution. The soil's inability to reach an equilibrium with respect to the quantity of cations removed is of particular importance in that it has a direct bearing upon the soil's ultimate removal capacity.

TABLE 5
CATION CONCENTRATION ANALYSES OF SAMPLES A AND B

<u>Cation</u>	<u>Sample A</u>	<u>Sample B</u>
Calcium	110.0 Me/l	28.0 Me/l
Magnesium	17.8 Me/l	5.0 Me/l
Sodium	62.2 Me/l	7.8 Me/l
Potassium	90.0 Me/l	10.0 Me/l
Iron	14.2 Me/l	18.8 Me/l
Totals	294.2 Me/l	69.6 Me/l

In the interest of determining whether this phenomenon of an increase to a maximum removal value followed by a decrease was a function of the testing procedure or a function of a soil-leachate interaction, the experiment was repeated. The second experiment consisted of contacting the remaining six soil types with the leachate as well as a synthetic ion exchange resin.

The second experiment produced the same results as the original test in the case of the six soil samples, as typified by Figures 7 and 8. However, the synthetic ion exchange resin (Rexyn H, a hydrogen regenerated cationic resin marketed by Fischer Scientific) did not exhibit a decrease in removal, as is illustrated in Figure 9. The removal pattern of the resin with respect to time resulted in a gradual increase in removal up to a maximum value which was near the exchange capacity of the resin, followed by a leveling off at this point. This result indicated that the inability of the soil samples to retain the cations after initial removal probably was the result of a soil-leachate interaction and not a function of the testing procedure. A specific contact time requirement for a soil to reach its maximum removal capacity is an understandable phenomenon. However, the apparent release of cations in the shaker experiments with longer contact time is a phenomenon which was not expected. Establishment of the exact mechanisms responsible for such behavior would have required an effort beyond the time limits of this investigation.

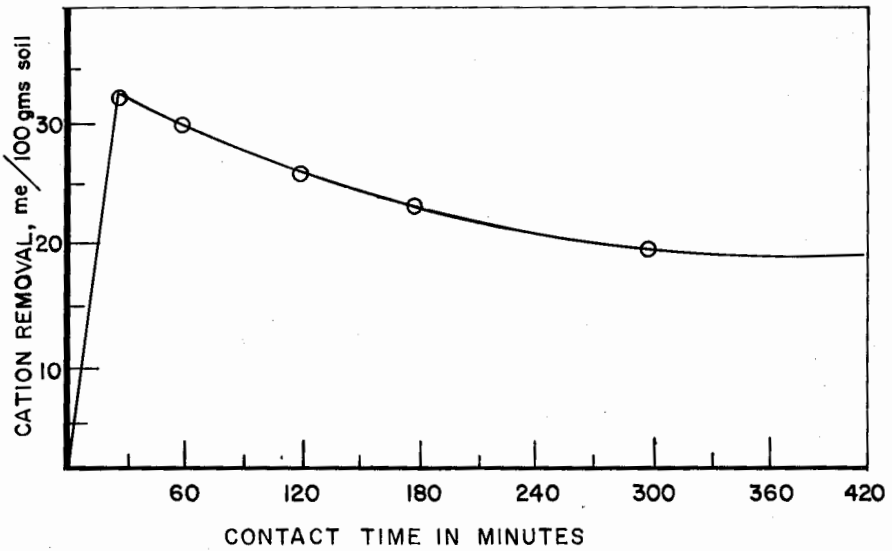


Figure 5 — Shaker test results on soil sample 5

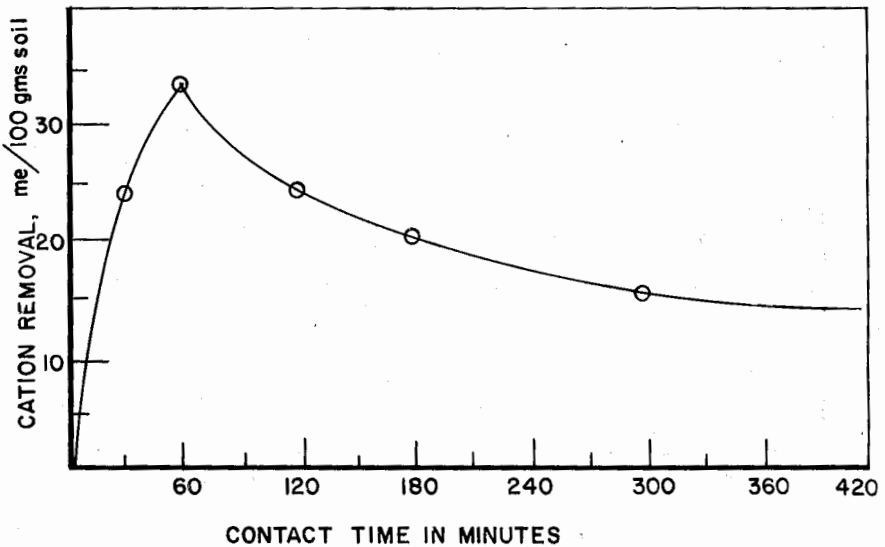


Figure 6 — Shaker test results on soil sample 4

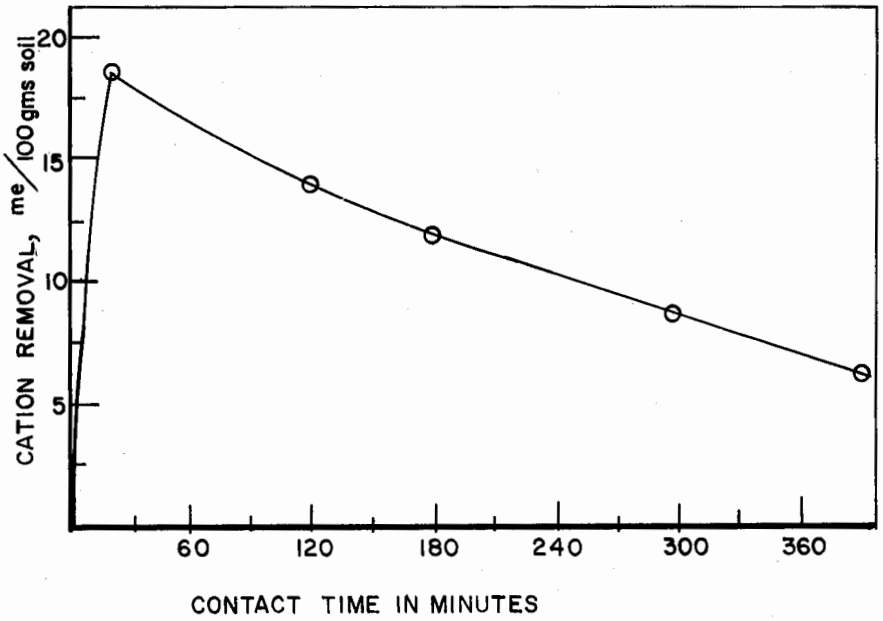


Figure 7 — Shaker test results on soil sample 3

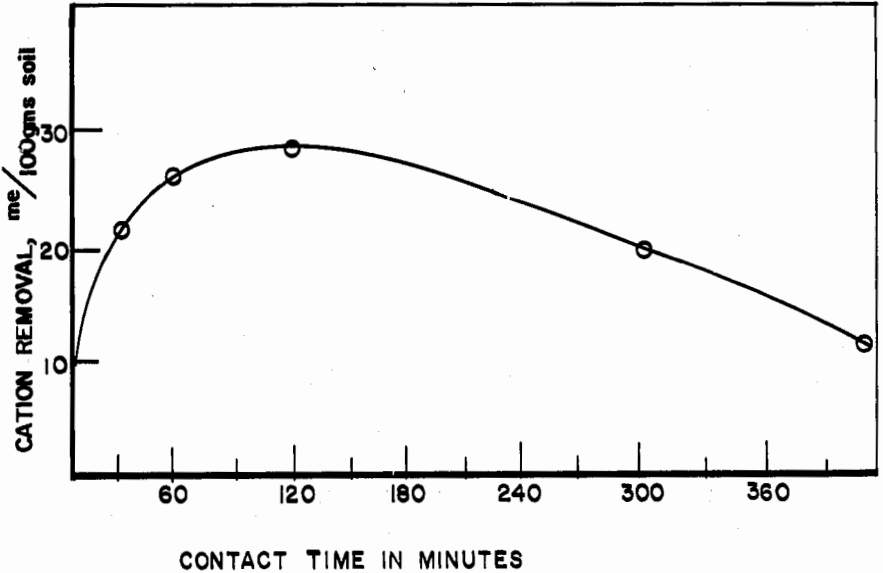


Figure 8 — Shaker test results on soil sample 8

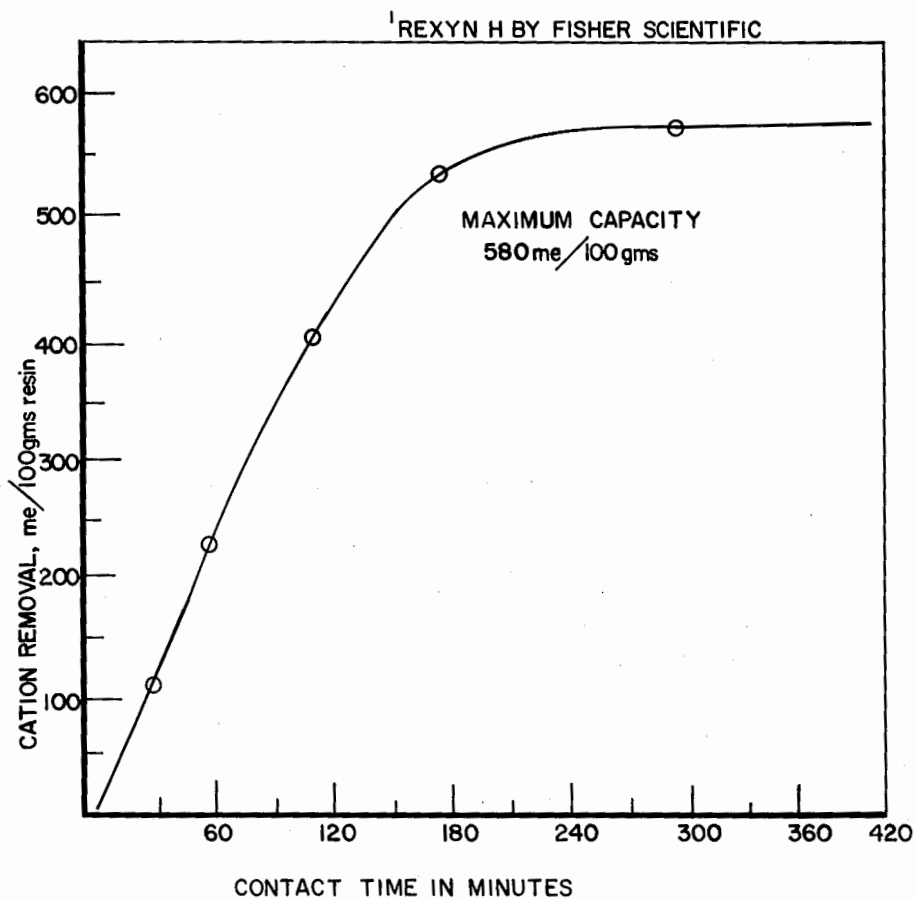


Figure 9 — Shaker test results on the synthetic ion exchange resin¹

The results of the soil column experiments cannot be directly compared with those in the shaker test experiments due to the difference in the testing methods. However, the shaker tests indicate that a potential may exist for the soil to release previously adsorbed material. The fact that the quantity of material adsorbed by the soils was lower in the shaker tests after prolonged contact times than that observed in the soil column experiments at the time of breakthrough also suggests that the soil may reach equilibrium with respect to permanently adsorbed ions. It appears that this equilibrium may be lower than the total quantity of material initially removed by the soil.

Significance of Results

In order to evaluate the significance of the soil "removal capacities" for the five cations determined in this investigation, the results must be related to a typical sanitary landfill operation. Comparing the shaker test results with the soil column experiments it seems reasonable to select removal capacities which are more conservative than the values obtained in the soil column experiments. For this comparison the following values were assumed based on the experimental data and typical soil densities:

<u>Soil Type</u>	<u>Five Cation Removal Values</u>		<u>Density of Soil Lbs/ ft³</u>	<u>Gram Equivalents of Cations Removed per ft³</u>
	<u>Me/100gms</u>	<u>Me/lb</u>		
Sand	3.8	17.2	110	1.893
Sandy Loam	10.0	43.5	105	4.756
Silt Loam	20.0	90.6	105	9.513

An estimate of the quantity of the five leachable cations coming from a typical landfill can be made based on values reported in the literature. In this case the values in Table 6 were assumed as total quantities released from an acre-ft of compacted refuse during the critical leachate generation period when contaminant concentrations are at the highest levels. Based on the values in Table 6 and the conservative removal values selected for the soil types, the following soil to landfill refuse volume ratios may be calculated to provide total removal:

<u>Soil Type</u>	<u>Acre-ft of soil/acre-ft of refuse</u>
Sand	1.72
Sandy Loam	.69
Silt Loam	.34

TABLE 6
TOTAL QUANTITIES OF LEACHABLE CATIONS RELEASED
FROM REFUSE

<u>Ion</u>	<u>Gram Equivalents/acre-ft</u>
Sodium	29,500
Potassium	27,500
Calcium	46,900
Magnesium	14,000
Iron	24,300
Total	142,200

Thus the results indicate that the unsaturated subsoil layer directly under a landfill can provide a considerable degree of leachate treatment with respect to cation retention. The possibility of using selected subsurface unsaturated soil deposits in the vicinity of a landfill for treating the collected leachate from the fill also appears to be promising based on these data. There is a definite economic advantage to this approach in many areas.

Conclusions

1. Results obtained from the soil column experiments confirm that the adsorptive capacity of a soil for the five cations tested is a function of the particle size distribution of the soil i.e. the percent weight passing a #200 sieve. The range of the removal values was as follows: 3.8 me/100 grams of sand to 31.1 Me/100 grams of silt loam (air dry weight of soil).

2. The shaker test experiments indicated that contact time is a parameter which should be investigated when determining ion removal capacities by soil column testing.

3. Comparison of the shaker test and flow test results for comparable contact times suggest that the equilibrium conditions observed in the shaker tests may be expected to occur in a flow-through system.

4. The order of removal of leachate cations is generally a function of at least two factors, namely, the relative concentrations of the various cations present in the leachate and the valence of the cations. Based on this investigation the concentration and valence appear to be equally important in establishing the removal pattern.

5. Application of the soil removal values to a typical landfill operation on a unit volume basis demonstrated the desirability of locating landfills in areas where the underlying soil is fine grained. The data suggest that collected leachate from landfills could be pumped to a separate site in the vicinity with suitable soil conditions for economical subsurface land disposal and treatment.

Acknowledgements

This investigation was supported in part by Training Grant No. EH-72-649-B from the Health Manpower Grants Branch, United States Public Health Service.

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