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INFLUENCE OF HIGH LEVEL WASTE SALTS ON MOVEMENT OF STRONTIUM AND CESIUM IN SAVANNAH RIVER PLANT SOIL

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Waste Disposal and Recovery
(TID 4500)

INFLUENCE OF HIGH LEVEL WASTE SALTS ON MOVEMENT OF STRONTIUM AND CESIUM IN SAVANNAH RIVER PLANT SOIL

by

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ABSTRACT

The presence of salts from high level radioactive waste reduced leaching of ^{90}Sr and ^{137}Cs in laboratory columns of sandy clay soil by groundwater and by 0.1N solutions of $Ca(NO_3)_2$, HNO_3, and KNO_3. Waste salts decreased leaching rates by reducing the permeability of waste saturated zones and by increasing ^{137}Cs fixation by mica minerals.

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INTRODUCTION

At the Savannah River Plant (SRP), liquid radioactive wastes are stored in large underground tanks.[1] Although the probability of waste leakage into the surrounding soil is minimized by tank design and operating controls, it is important to be able to predict the fate of radionuclides released to the soil in the unlikely event that the tanks should leak. Such a prediction allows the consequences of a release to be analyzed and corrective action to be planned.

Laboratory studies were made of the rate of movement of cesium and strontium through the soil surrounding the waste tanks. The feasibility of recovering these radionuclides from the soil by leaching was also studied.

SUMMARY

When the highly salted waste solution was injected into small columns of SRP soil and diluted with groundwater, the permeability of the soil was reduced due to dispersal of clay aggregates by sodium ions. As a result of the reduced permeability, strontium moved through the column at a much lower rate.

Cesium is retained by SRP soil because of fixation in mica minerals; this fixation was greatly increased by sodium ion present in the waste. Consequently, cesium was virtually immobilized even after extensive flow of groundwater through the column.

Strontium was readily leached from the waste-soil mixture by dilute solutions of acid or salts, but cesium was not readily leached by any solution tested.

These results indicate that if radioactive waste leaked from a storage tank the movement of strontium and cesium through the surrounding soil would be retarded because of reduced permeability of the soil. The movement of strontium would accelerate as the waste became diluted with groundwater, but cesium would continue to move at a low rate.

DISCUSSION

EXPERIMENTAL

Preparation of Simulated Waste

High level liquid radioactive waste is essentially an alkaline solution of sodium salts. The following table shows a representative chemical assay.[2]

Constituent	Concentration, molar
$NaNO_3$	3.5
Na_2CO_3	0.3
Na_2SO_4	0.2
NaOH	0.3
$NaAlO_2$	0.6

The waste also contains very important but chemically insignificant quantities of fission products such as ^{90}Sr, ^{95}Zr-^{95}Nb, $^{103,106}Ru$, ^{137}Cs, and $^{141,144}Ce$. Because waste from the tanks was too radioactive for convenient use in the laboratory, a simulated waste was prepared with the assay shown above; tracer amounts of ^{90}Sr or ^{137}Cs were added for the leaching studies.

Leaching Studies

The most probable way for a tank to leak would be from small stress corrosion cracks along welds on the bottom or sides of the tank. As a result, waste would flow with little dilution into a zone in the soil immediately adjacent to the leak rather than spread widely over the groundwater table. Since many of the tanks are either entirely submerged or have their lower portions submerged in groundwater, water can flow either through or around the waste zone depending upon the influence of the waste upon soil permeability.

These conditions were simulated in the laboratory with apparatus shown schematically in Figure 1. Clear plastic columns

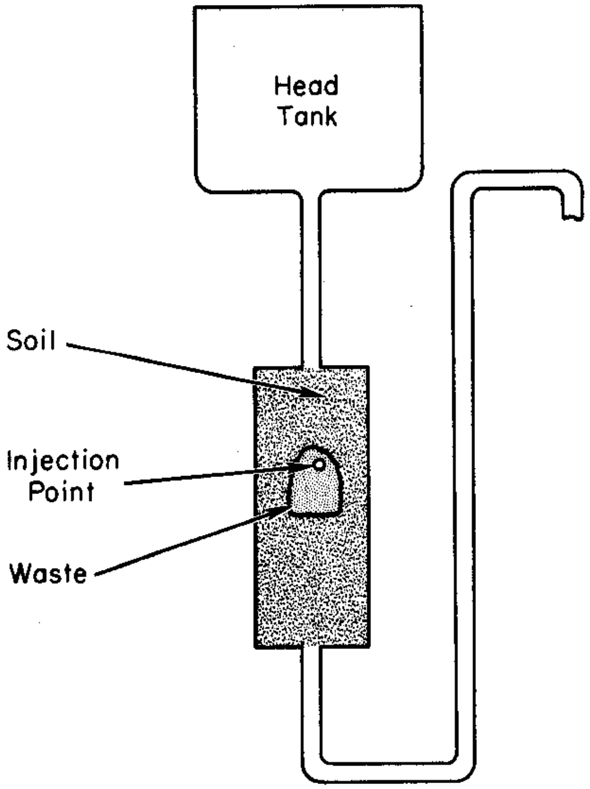

FIG. 1 LEACHING AND PERMEABILITY TEST EQUIPMENT

2 inches in diameter by 6 inches long were packed with about four hundred grams of sandy clay soil. The drip point of the column was elevated above the soil sample so that flow through the sample was under saturated conditions. Waste was injected at the center of the column with a hypodermic needle. The resulting waste-saturated zone was approximately spherical and about one inch in diameter. This provided an opportunity for leach solutions to flow either through or around the waste. Solutions used for leaching were 0.1N KNO_3, 0.1N HNO_3, 0.1N $Ca(NO_3)_2$, and untreated SRP groundwater. The various treatments in the tests are given in the following table.

Leach Solution	Solution Added to Column[a]
Distilled water	^{137}Cs in waste
Groundwater	^{137}Cs in distilled water
Groundwater	^{90}Sr in waste
Groundwater	^{90}Sr in distilled water
0.1N KNO_3	^{137}Cs in waste
0.1N KNO_3	^{137}Cs in distilled water
0.1N KNO_3	^{90}Sr in waste
0.1N KNO_3	^{90}Sr in distilled water
0.1N HNO_3	^{137}Cs in waste
0.1N HNO_3	^{137}Cs in distilled water
0.1N HNO_3	^{90}Sr in waste
0.1N HNO_3	^{90}Sr in distilled water
0.1N $Ca(NO_3)_2$	^{137}Cs in waste
0.1N $Ca(NO_3)_2$	^{137}Cs in distilled water
0.1N $Ca(NO_3)_2$	^{90}Sr in waste
0.1N $Ca(NO_3)_2$	^{90}Sr in distilled water

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[a] 10.5 μCi ^{137}Cs or 8 μCi of ^{90}Sr in 5 ml of solution

Each liter of column effluent was collected separately and assayed for ^{137}Cs or ^{90}Sr. After leaching, the columns were drained, and the distribution of radioactivity on the column was determined by scanning with a single-channel pulse height analyzer. The soil was then dried and ground in a mortar and pestle, and the total residual activity was measured with a thin window proportional counter.

Permeability Studies

Clay particles normally exist in soil as aggregates, so that pores between aggregates and other particles are large and permeability is high. If the clay aggregates become dispersed into smaller particles, soil pores then fill with the smaller clay particles and permeability is reduced. Such dispersion should be visible under the microscope. SRP sandy clay saturated with groundwater was observed with a stereoscopic widefield microscope. Various concentrations of waste were then added to the soil and the result observed. Photomicrographs were made at 110X.

A second test used was a modification of the flocculation series test reported by van Olphen.[3] In this test, 1 gram of soil was placed in each of twenty-three test tubes, and 60 ml of a different concentration of waste solution was added to each. After the tubes were agitated for 20 minutes, they were allowed to stand for 24 hours. Results were determined by visual observation.

For the permeability measurements, a small diameter pipe was substituted for the head tank shown in Figure 1. A measured change in head could then be timed and the permeability calculated.[4] The effects of waste on soil permeability were determined by first measuring permeability of untreated SRP sandy clay with the four leach solutions and then repeating the measurements after the entire cross section of soil at the midpoint of the column was saturated with waste solution.

RESULTS

Permeability Studies

In SRP soil, clays normally exist as aggregates. Figure 2 is a photomicrograph of a dry sample of the sandy clay used in the leaching study. Arrows indicate clay aggregates; quartz sand grains and open pores are visible. Figure 3 shows the same sample saturated with groundwater. Clay aggregates, quartz grains, and pores remain about as they were. Figure 4 shows the sample after addition of waste diluted with water. Quartz grains remain, but a thick slurry of the dispersed clay fills all pores. Dispersion of the clay was rapid and could be observed under the microscope. Similar observations showed that undiluted waste did not disperse the clay.

The effect of waste salts upon the soil is due to the same phenomena that cause dispersion or flocculation of suspended colloids.[3] Maximum dispersion occurs in a dilute solution of monovalent cations, and the concentrations of cations required to flocculate a colloidal suspension decreases as the valence increases. In the soil wetted with groundwater, the active

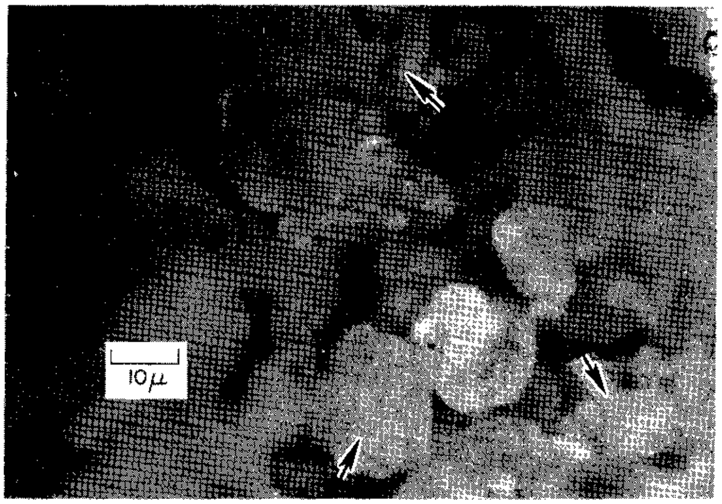


FIG. 2 DRY SRP SANDY CLAY

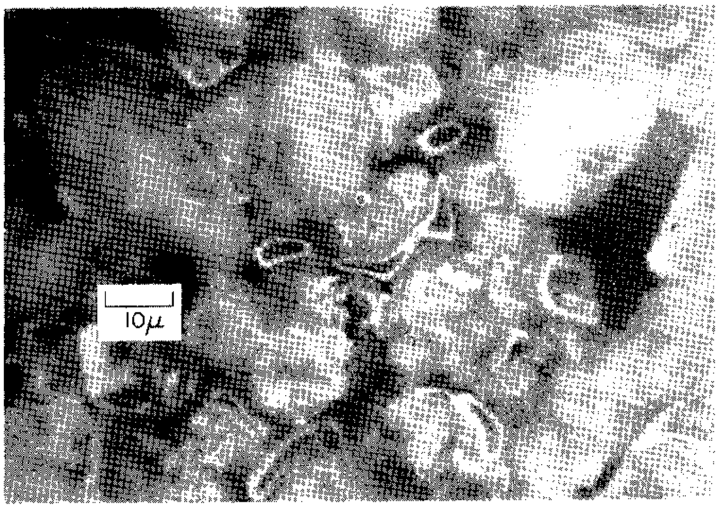


FIG. 3 SRP SANDY CLAY SATURATED WITH GROUNDWATER

cations in the soil-water system included H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}, and the concentration of divalent and trivalent cations was adequate to prevent clay dispersion. Addition of NaOH in the waste increased the pH thereby removing H^+, Fe^{3+}, Al^{3+}, and possibly Ca^{2+} and Mg^{2+} from solution and from the soil exchange sites. Dilute Na^+ was then the predominant cation in the system, and the clay aggregates dispersed.

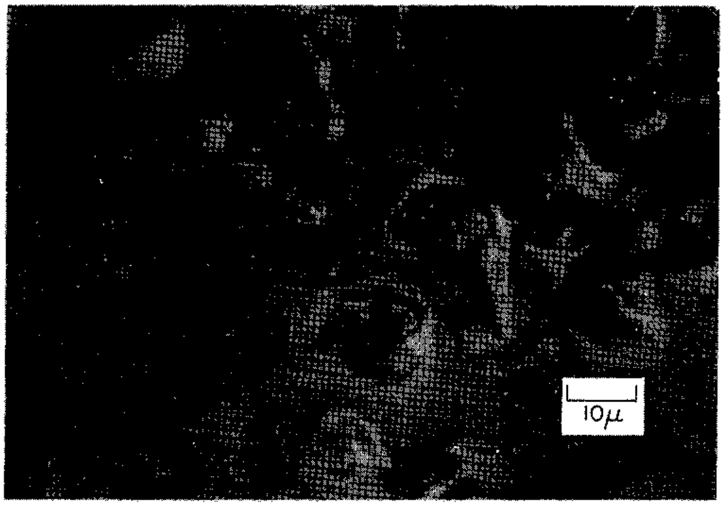


FIG. 4 SRP SANDY CLAY AFTER ADDITION OF DILUTE SRP WASTE

The effect of waste concentration upon the dispersion or flocculation of clay is demonstrated in Figure 5. Waste concentrations in the test tubes from left to right ranged in equal decrements from 6.10 to 6.02 ml of waste/liter of water. The picture was made 24 hours after the soil was suspended by shaking. From left to right, the amount of clay remaining in suspension gradually increases until near the end of the series where a slight decrease is visible.

As shown below, the effect of waste upon soil permeability to various solutions conforms to the order of clay dispersion predicted by the above observations and discussion.

	Permeability Coefficient K, cm/sec	
Solutions Tested	Sandy Clay	Sandy Clay Injected with Waste
Distilled water	1.2×10^{-2}	8.0×10^{-7}
Groundwater	1.7×10^{-2}	4.6×10^{-6}
0.1N KNO_3	9.4×10^{-3}	1.2×10^{-4}
0.1N HNO_3	9.0×10^{-3}	1.5×10^{-4}
0.1N $Ca(NO_3)_2$	5.6×10^{-3}	1.8×10^{-4}

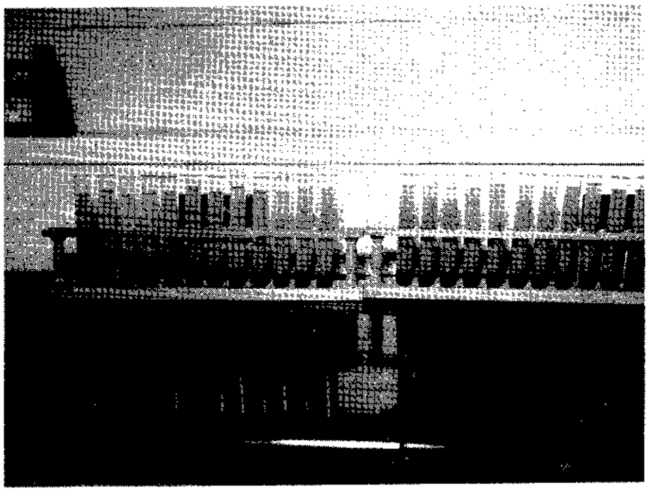


FIG. 5 CLAY IN SUSPENSION AFTER 24 HOURS IN VARIOUS WASTE CONCENTRATIONS

Leaching Studies

Figures 6 through 12 show the removal of ^{90}Sr and ^{137}Cs by leaching from both waste-free soil and soil containing a waste saturated zone. No results are given for the ^{137}Cs leached with distilled water or $Ca(NO_3)_2$. The former became impermeable after 2 liters. $Ca(NO_3)_2$ failed to remove any ^{137}Cs although the columns were leached with 167 liters.

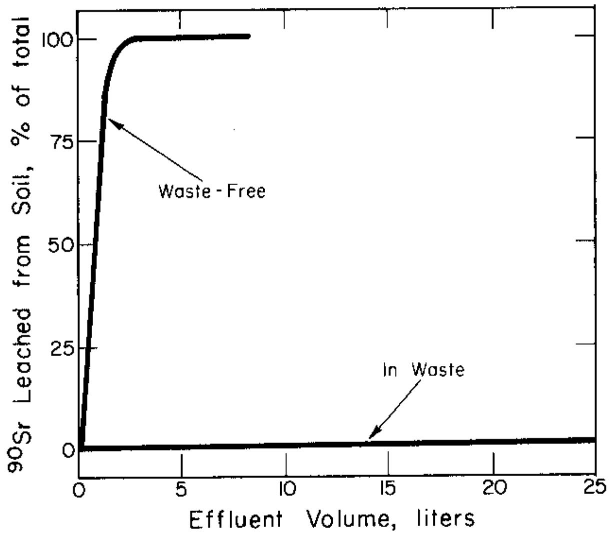


FIG. 6 ^{90}Sr LEACHED FROM SANDY CLAY SOIL BY GROUND WATER

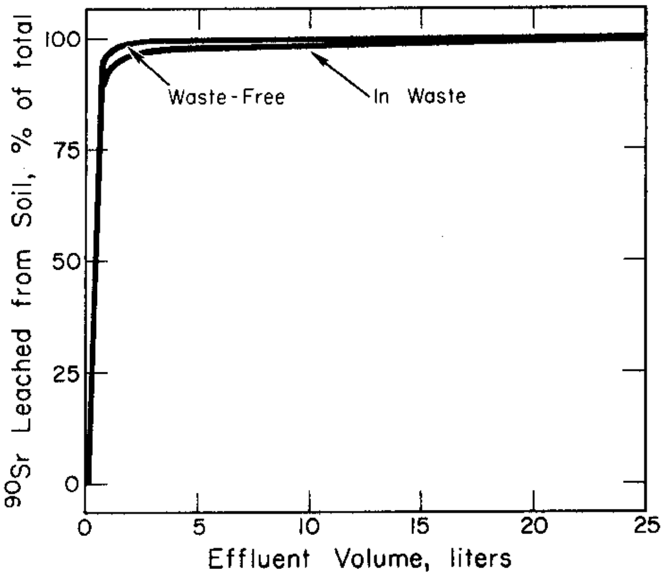


FIG. 7 ^{90}Sr LEACHED FROM SANDY CLAY SOIL BY 0.1N HNO_3

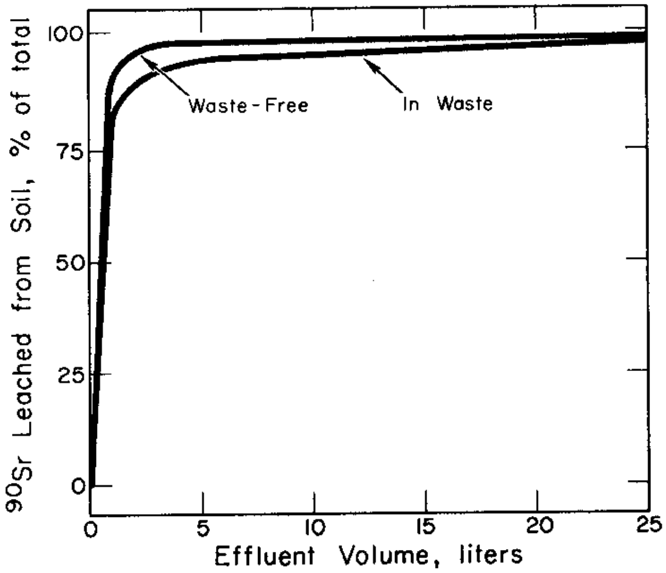


FIG. 8 ^{90}Sr LEACHED FROM SANDY CLAY SOIL BY 0.1N $Ca(NO_3)_2$

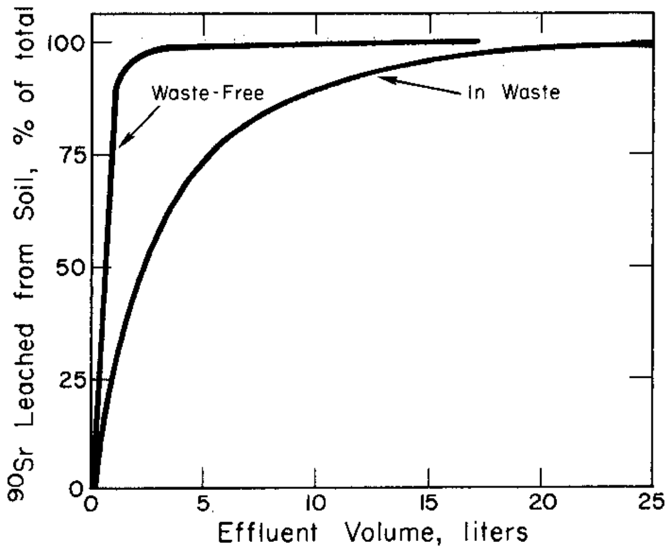


FIG. 9 ^{90}Sr LEACHED FROM SANDY CLAY SOIL BY 0.1N KNO_3

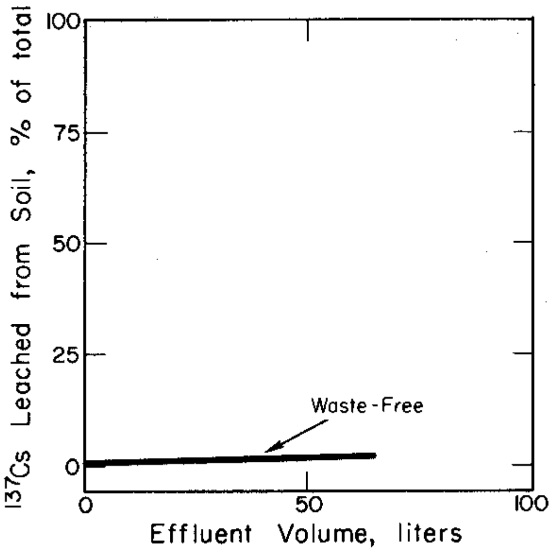


FIG. 10 ^{137}Cs LEACHED FROM SANDY CLAY SOIL BY GROUNDWATER

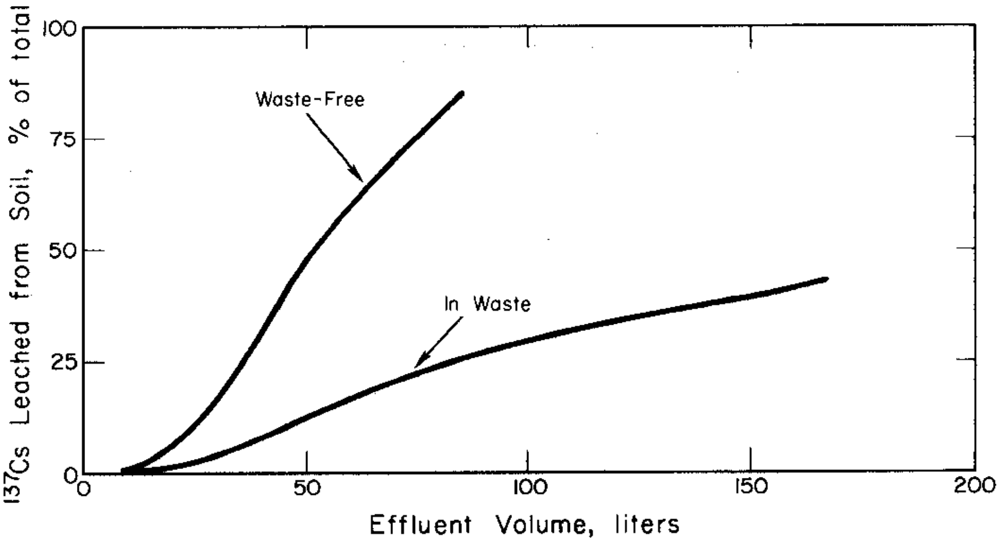


FIG. 11 ^{137}Cs LEACHED FROM SANDY CLAY SOIL BY 0.1N HNO_3

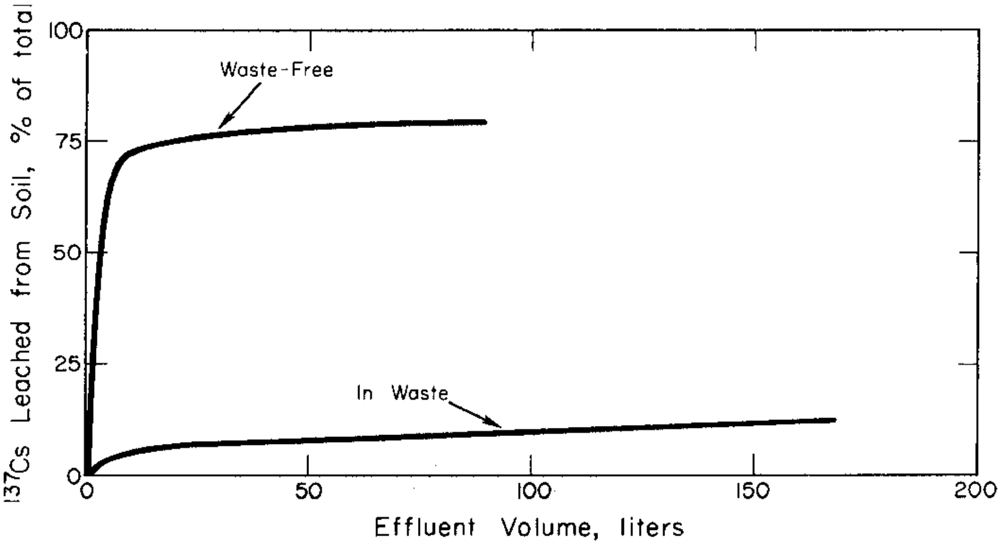


FIG. 12 ^{137}Cs LEACHED FROM SANDY CLAY SOIL BY 0.1N KNO_3

The location of ^{137}Cs remaining in the columns after leaching is shown in Figures 13 through 16. Highest concentrations were at or near the injection point in all columns except those in which waste-free ^{137}Cs was leached with HNO_3. In these columns, the distribution was uniform from the injection point to the bottom of the column. Figure 17 shows the location of ^{90}Sr remaining in the columns leached with groundwater. Essentially all of the ^{90}Sr was leached from the columns by the other solutions.

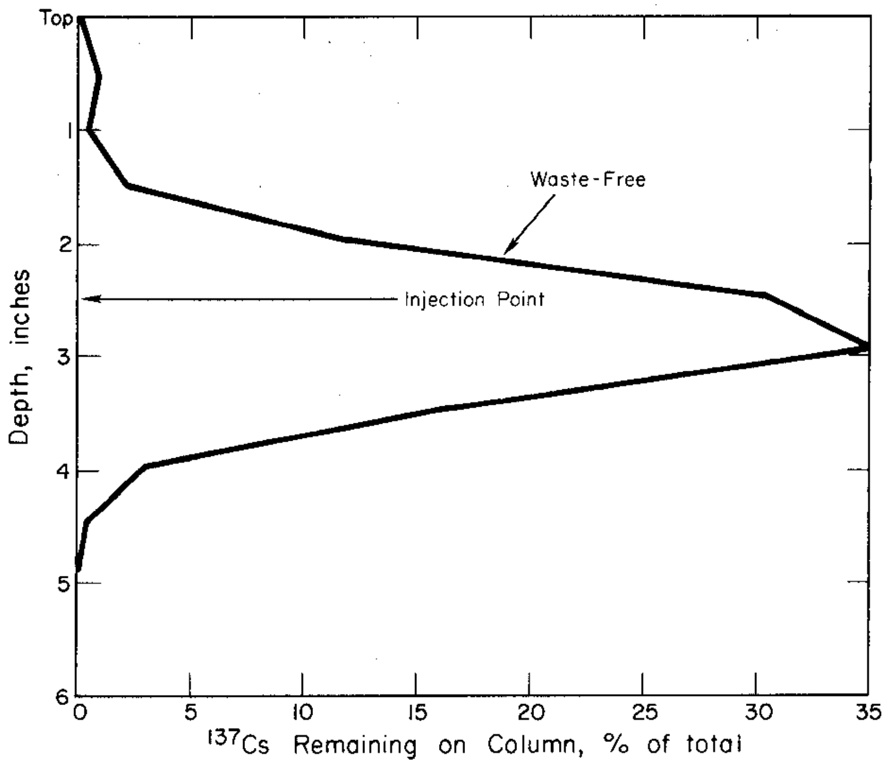


FIG. 13 DISTRIBUTION OF ^{137}Cs AFTER LEACHING WITH GROUNDWATER

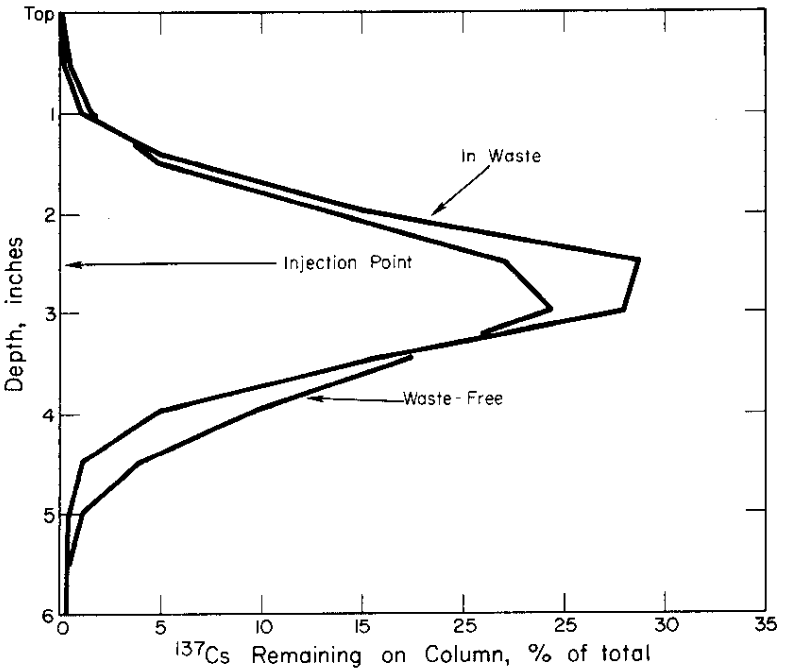


FIG. 14 DISTRIBUTION OF ^{137}Cs AFTER LEACHING WITH 0.1N $Ca(NO_3)_2$

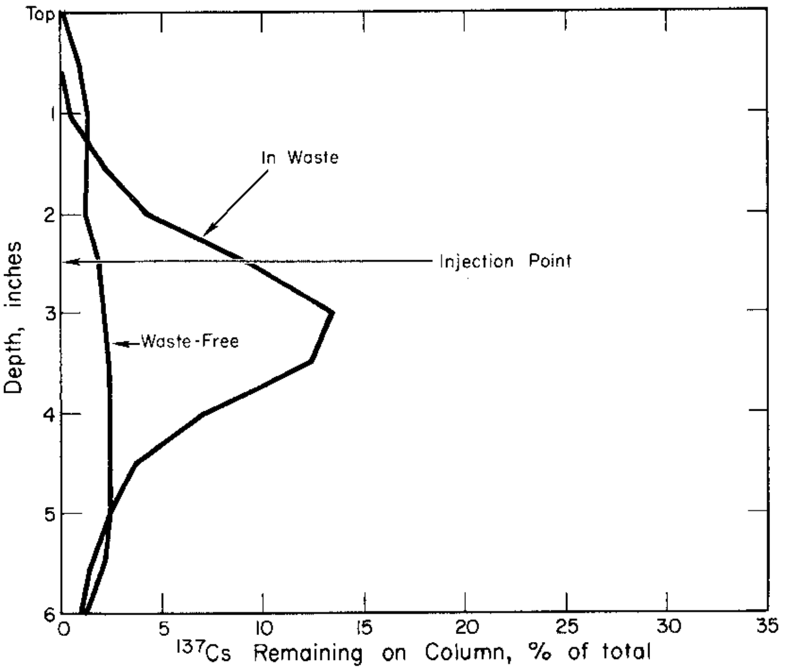


FIG. 15 DISTRIBUTION OF ^{137}Cs AFTER LEACHING WITH 0.1N HNO_3

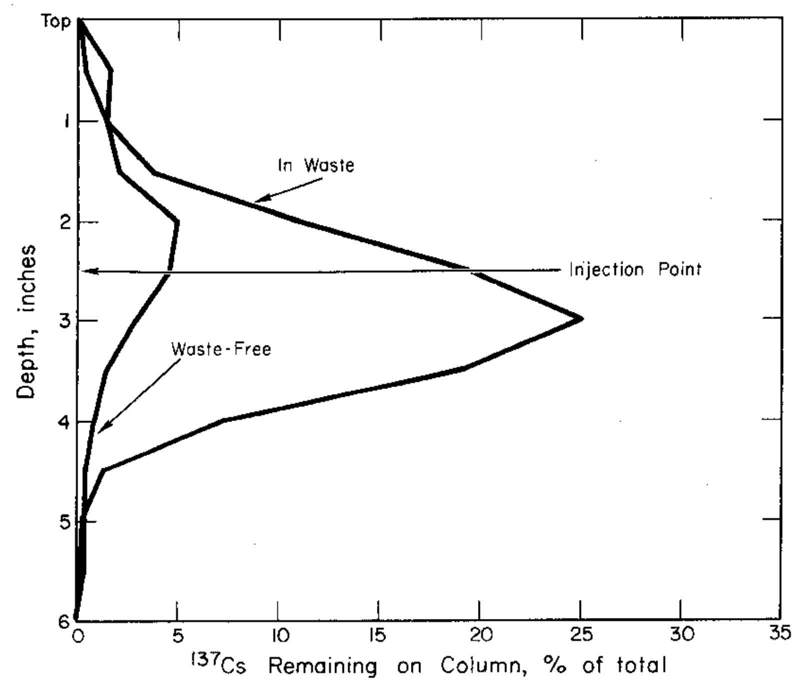


FIG. 16 DISTRIBUTION OF ^{137}Cs AFTER LEACHING WITH 0.1N KNO_3

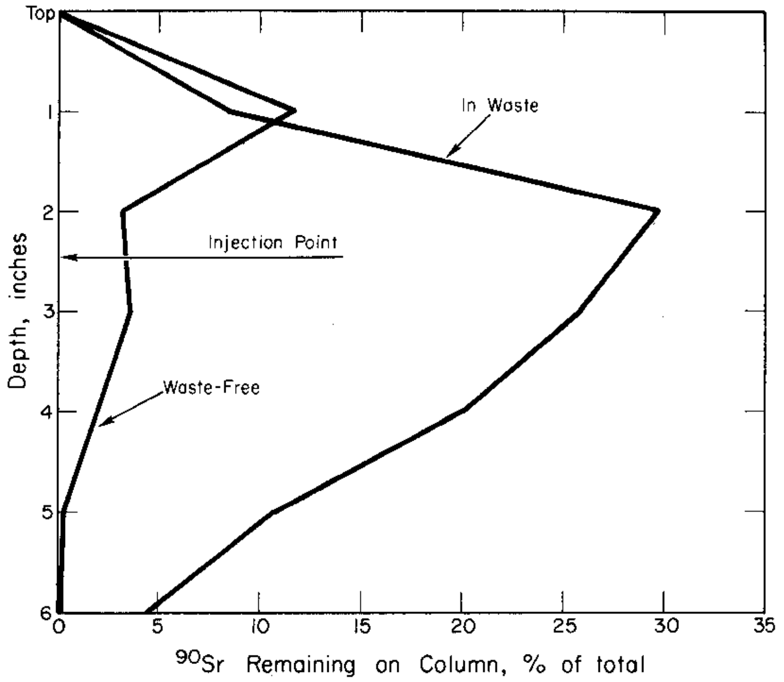


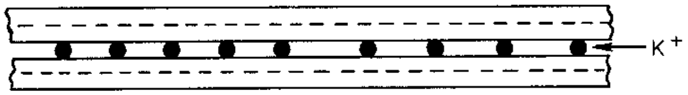
FIG. 17 DISTRIBUTION OF ^{90}Sr AFTER LEACHING WITH GROUNDWATER

The primary influence of waste upon the leaching rate of ^{90}Sr is attributed to reduced soil permeability in the waste saturated zone. The effect was negligible when leaching with $Ca(NO_3)_2$ and HNO_3, small with KNO_3, and quite large with groundwater. Although the leaching rate with groundwater was quite small, it is of concern since the results imply that continued leaching would eventually remove all ^{90}Sr. In SRP high level waste, this slow elution rate would result in the transfer of hazardous amounts of ^{90}Sr from a waste saturated zone to surrounding soil. Simultaneously Na^+ would also leach out of the waste zone and move with the ^{90}Sr. As they moved with the groundwater, Na would become too dilute to disperse clay. ^{90}Sr would then migrate at the much faster rate shown by the waste-free curve in Figure 6.

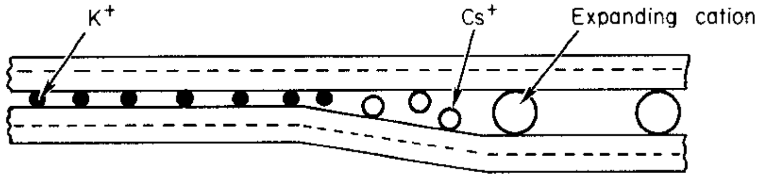
The influence of waste upon leaching of ^{137}Cs was more pronounced than with ^{90}Sr. The same permeability effects were present but minor compared with the effect of waste upon cesium fixation by mica minerals. Potassium, cesium, and other cations having similar ionic radii are adsorbed between the sheets of mica type minerals so that they are not easily replaced by other cations.[5-8] This reaction is influenced by the other cations in solution.

Horton[9] proposed a mechanism based on the "lattice-hole theory" of Page and Baver[6] and the degree of mica lattice expansion by various cations as measured by Barshad[10,11] to explain the influence of various cations on potassium fixation and release. Other investigations[12-14] have substantiated parts if not all of this theory. The same reasoning can be used to explain our ^{137}Cs leaching results.

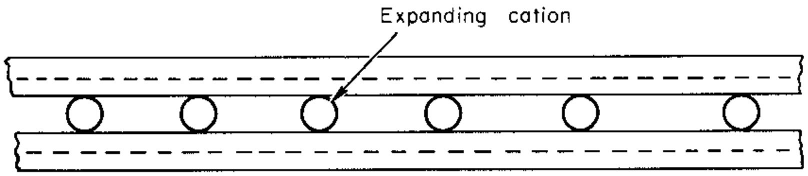
Mica minerals in the columns of sandy clay are in various stages of weathering so that the interlayer planar surfaces are occupied by all of the various cations in soil. The distance between unit layers is determined by the cations adsorbed between the layers. For the cations added in our experiment the distances between unit layers were Ca(15.07)*, H(14.33)*, Na(12.56)*, Cs(11.97)*, and K(10.42)*. Three possible configurations of the crystal lattice of mica minerals depending upon the interlayer cations are shown in Figure 18. The contracted lattice (Figure 18A) contains only potassium ions and exchange is restricted on interlayer sites. The expanded lattice (Figure 18C) permits easy access to the interlayer exchange sites by any cation smaller than the lattice-expanding cation. Around the edge of the mica sheet, along the front where weathering is in progress, there is



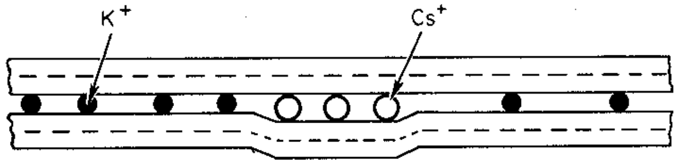
A. Unweathered, contracted lattice



B. Weathering in progress, partially expanded lattice



C. Weathered, fully expanded lattice



D. Fixed cesium

FIG. 18 POSSIBLE CONFIGURATIONS OF THE CRYSTAL LATTICE OF MICA MATERIALS

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* Basal reflection d(002) in Å as obtained with vermiculite.[11] These are due to differences in the hydrated radii of the cations when adsorbed in the interlayer space and are quite different from those of the cations in solution.

a diminishing gradation in the space between layers. This gradation in spacing extends from the weathered area inward to the unweathered mineral. This results in a wedge-shaped space as seen in cross section (Figure 18B). Exchange of the larger hydrated cations for Cs^+ is hindered in this area because the larger ions can enter this space only with difficulty. Cs^+ exchange will progress along this front only as the lattice expands. This is one phase of Cs^+ fixation. If K^+ ions replace the expanding cations in the weathered area, the lattice will collapse and trap Cs^+ within the interlayer area (Figure 18D). Fixation is now complete and the mineral will have to be reweathered from the edge of the sheet to the former weathering front before Cs^+ exchange will resume.

Cs^+ fixation was apparent with all leaching solutions. Consider the waste-free columns first. Groundwater contains many different cations but in such small amounts that it was almost completely ineffective in leaching Cs^+ from the soil (Figure 10). In the columns leached with $Ca(NO_3)_2$, the Ca^{2+} could not displace Cs^+ from interlayer exchange sites since no cation can expand the lattice beyond the hydrated radius of Ca^{2+}. Ca^{2+} did exchange for Cs^+ on external sites, but as exchange progressed down the column eventually all of the Cs^+ was adsorbed between layers and the leaching rate became so slow that no Cs^+ was eluted during the test. In the columns leached with HNO_3 (Figure 11), H^+ exchanged for Cs^+ on sites where the weathering ion was larger than H^+. Where H^+ was the expanding ion, Cs^+ was not easily exchanged. In the columns leached with KNO_3, both K^+ and Cs^+ could compete about equally for all exchange sites because of their similar size. Since the number of K^+ ions greatly exceeded the number of Cs^+, mass action favored K^+ adsorption. After about 5 liters, the expanding ions had been exchanged for K^+ or Cs^+, which collapsed the mineral and fixed the ^{137}Cs. The leaching rate then became very slow.

Addition of waste salts tended to increase the amount of expanded or partially expanded mica in the soil because of the very high concentration of Na^+ in the waste. Thus with waste salts present, ^{137}Cs exchange on interlayer sites was increased with subsequent increase in Cs^+ fixation (Figures 11 and 12).

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