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Earth Sciences

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B. F. Hajek and K. C. Knoll

BATTELLE-NORTHWEST

INTRODUCTION

This report presents the experimental results of an investigation requested by Isochem, Inc., Richland, Washington. The research was needed to provide data for use in the evaluation of the disposal characteristics of a high salt waste (AAW) containing small amounts of plutonium and americium.

This acid aqueous waste contains saturation amounts of organic compounds generated from recovery of plutonium and americium in a plutonium reclamation facility. Occasionally slug disposal of organic compounds (principally DBBP in CCl_4) into the aqueous disposal stream occurs.

Previous research by Battelle-Northwest (1) indicated that soil can imbibe this waste (including slugs of organic) almost as readily as water; however, uptake of plutonium by soil was low and of americium negligible. The study from which these results were obtained was conducted with surface soil material (< 20') which is representative of much of the soil profile to ground water. However, strata occur between the surface and ground water which have different chemical properties and could exhibit better plutonium and americium retention characteristics. In addition, treatment of the waste prior to ground disposal could result in a solution from which plutonium and americium would be retained on soil or in which the concentration of these radionuclides would be greatly reduced.

The objectives of the present study were to: 1) determine the waste neutralization ability of soil material selected from various depths between the surface

and ground water; 2) characterize plutonium and americium sorption from AAW waste (both simulated and actual) by this soil material; 3) determine plutonium and americium soil sorption from diluted, neutralized and partially neutralized waste; 4) investigate the effect of a complexing agent on plutonium soil sorption; 5) determine the effectiveness of precipitation on scavenging plutonium and americium.

SUMMARY

This study confirmed that adsorption of plutonium and americium on soil material from the surface to ground water was minor from AAW waste and showed that soil neutralization or complexing agents would not satisfactorily improve adsorption. Gelling in soil pores could be induced by partial neutralization; however, permeability was lost. Precipitation by neutralization effectively scavenged both plutonium and americium in a waste containing only saturation amounts of organic and produced a supernate with improved soil adsorption characteristics.

METHODS

Soil material was selected from samples obtained from two wells at the Z - 1A tile field site (299-W18-6 and 299-W18-7). The soils were air dried and sieved to < 2 mm diameter.

A synthetic waste was prepared from composition data supplied by Isochem (Table I). This composition was the same as given in the interim report (1). Actual waste samples were obtained from Isochem. These composite samples were obtained by daily sampling for at least one week.

TABLE I

Aqueous Waste Composition

<u>Constituent</u>	<u>M*</u>
HNO ₃	0.30
AlF(NO ₃) ₂	0.26
Al(NO ₃) ₃	0.44
Mg(NO ₃) ₂	0.18
Ca(NO ₃) ₂	0.18
Fe(NO ₃) ₃	0.05
NaNO ₃	2.38
Total NO ₃ ⁻	5.4

*Further diluted with $\frac{1}{15}$ its own volume with water.

Equilibrium batch experiments were used to determine the soil adsorption characteristics of plutonium and americium. An equilibrium distribution coefficient (K_d) was calculated from batch data by the use of the following expression:

$$K_d = \frac{C_o - C}{C} \frac{\text{ml.}}{\text{g}}$$

in which C_o = initial concentration, C = final equilibrium concentration, ml = milliliters of solution, and g = grams of soil.

Soil columns were used to determine breakthrough characteristics of treated simulated waste and soil neutralization ability.

Precipitation treatments were performed by reverse strike neutralization of two parts waste with one part 50 percent caustic in one part water.

All experiments were made at ambient room temperature.

RESULTS AND DISCUSSION

Neutralization

The milliequivalents of acid which can be neutralized by a gram of soil at various depths to the water table are shown in Figure 1. These data were obtained by reacting an excess of HCl with soil and titration with NaOH to the phenolphthalein end point. The soil material is essentially uniform with respect to this property except for a layer 20-feet thick at 140 feet.

The waste titration curve shown in Figure 2 was obtained without complexing agents and includes titration of acidity from hydrolyzable metals present in the waste. The availability of soil bases to neutralize the waste in equilibrium soil:waste suspensions is shown in Figure 3. The measured capacity was exceeded as the waste:soil ratio was increased, indicating greater solubilization of soil minerals when suspended in the waste. This capacity was not available for waste neutralization when the same waste sample was subjected to successive equilibration with fresh soil followed by centrifugation. Colloidal iron could be formed during soil:waste neutralization but was not filtered or sorbed on soil surfaces.

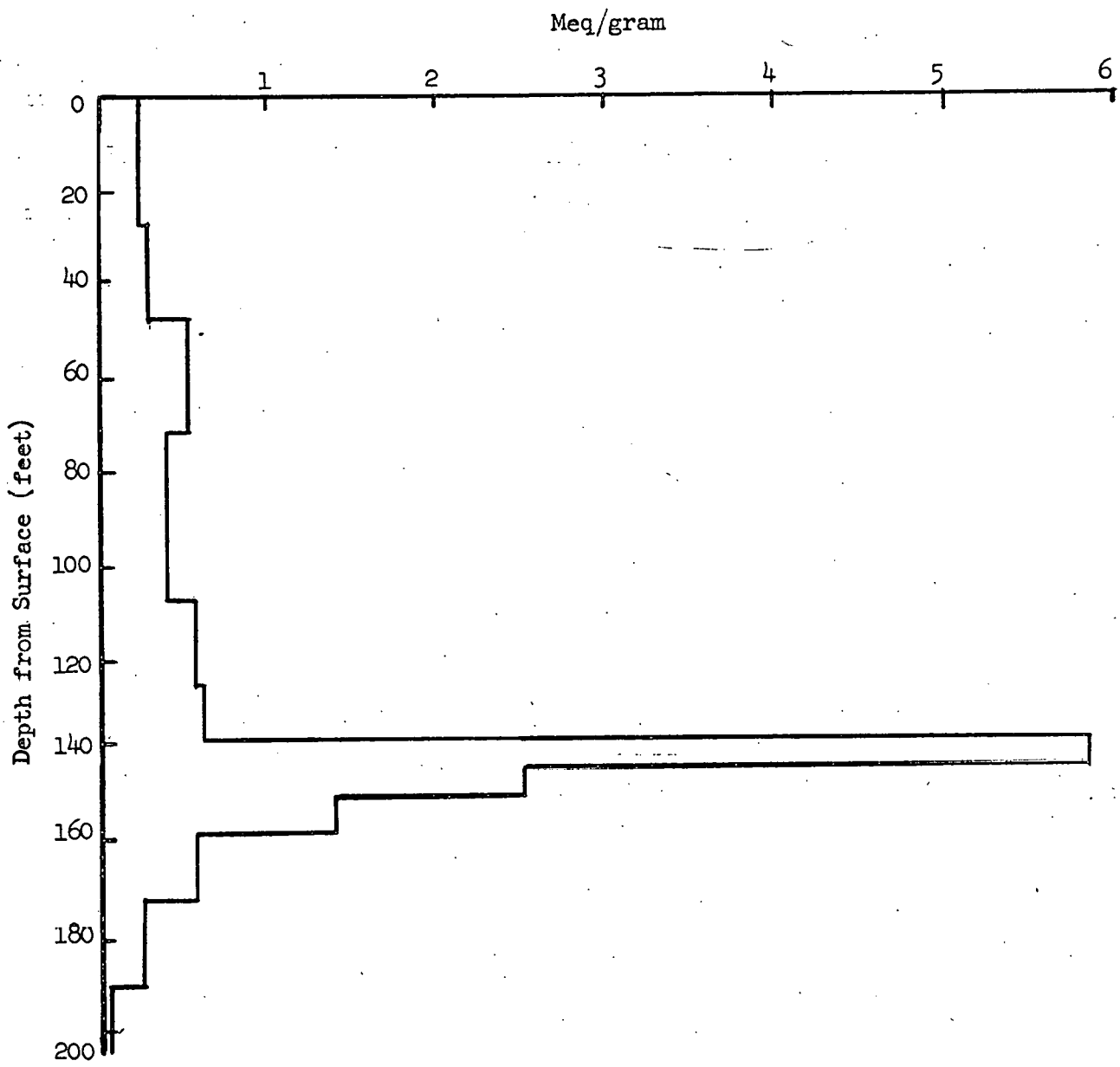
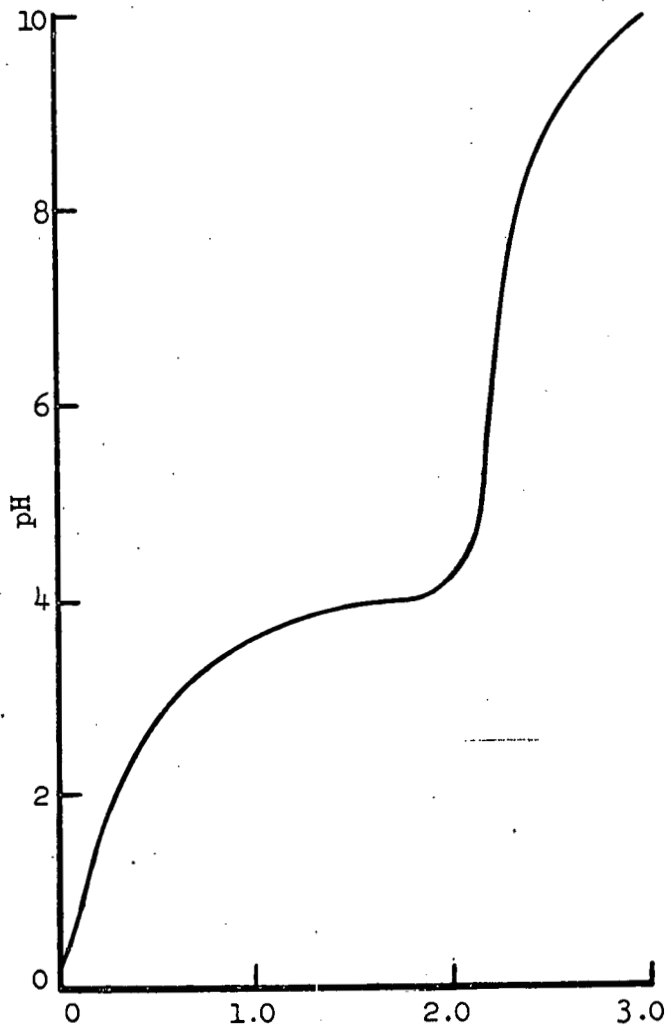


FIGURE 1
Soil Neutralization Capacity



Meq. NaOH/ml Waste

FIGURE 2

Waste Titration with NaOH.

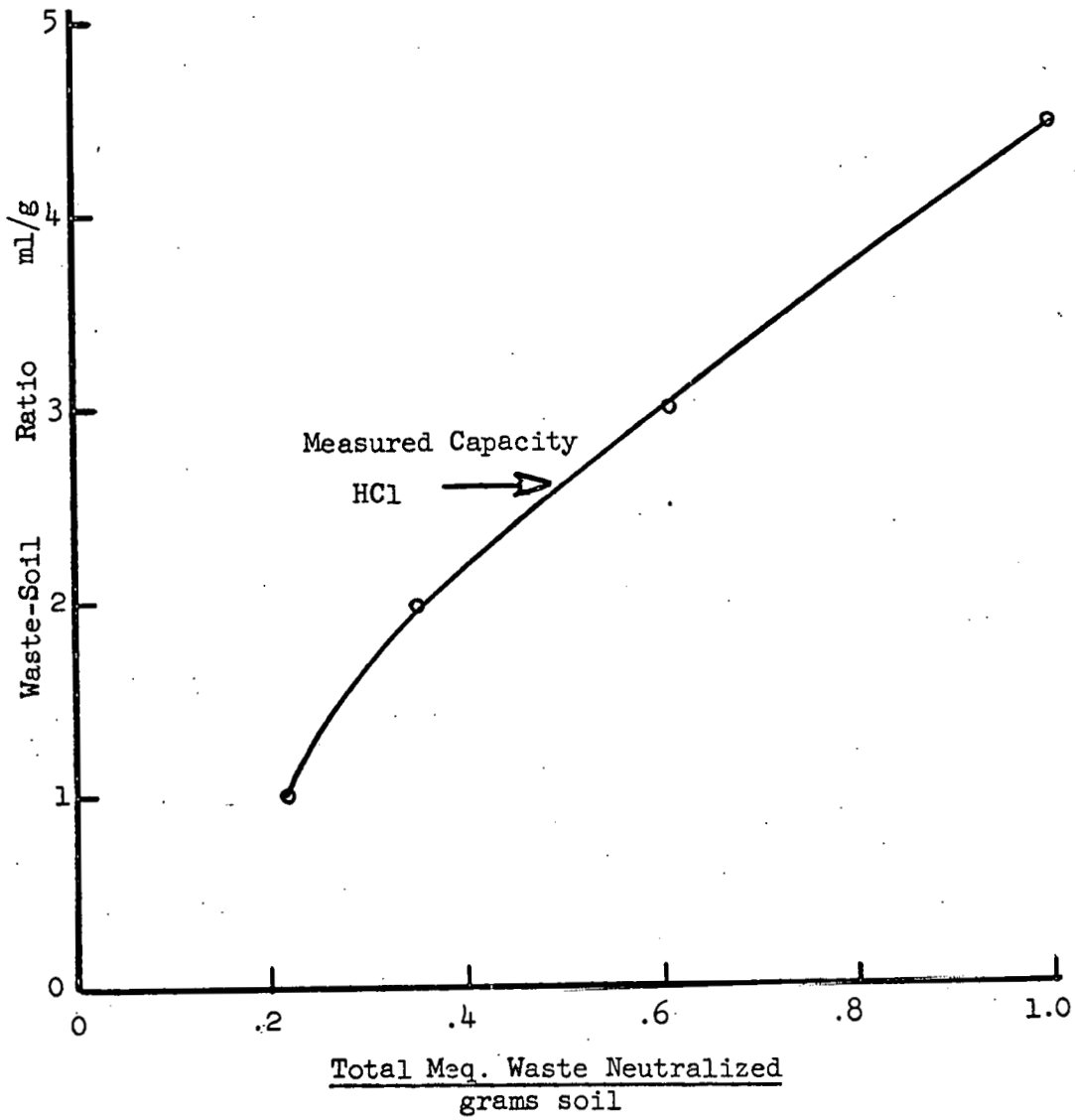


FIGURE 3
Equilibrium Soil Neutralization Capacity

Figure 4 clearly shows the inability of soil to completely neutralize this waste in a soil column. The initial pH breakthrough at column volumes less than 0.1 represents displacement of resident soil solution added to the soil before packing. Infiltration of waste through successive dry soil columns and analysis of initial breakthrough pH showed that the pH became constant at about pH 2.5. This constancy was maintained regardless of the fact that an excess of soil was contacted which should have been adequate to overcome buffering and cause precipitation.

Soil Adsorption

Adsorption of plutonium and americium by soil was studied by a batch equilibration technique. The data in Table II show that adsorption from strongly acid or partially neutralized waste is minor. Dilution and partial neutralization did not improve adsorption.

Adsorption on soil was high (Table II) from alkaline supernate generated from precipitation-scavenging treatment, if only saturation amounts of organic were present.

Introduction of a slug of organic (20% by volume) reduced the K_d of both plutonium and americium.

The precipitated sludge was washed with water and analysis of the leachate showed that small amounts of both plutonium and americium could be leached; however, both are adsorbed on soil from this solution.

Addition of citric acid on a ratio of slightly less than mole to mole metal allows the waste to be neutralized without precipitation. Solutions of the complexed synthetic waste were spiked with plutonium and neutralized with

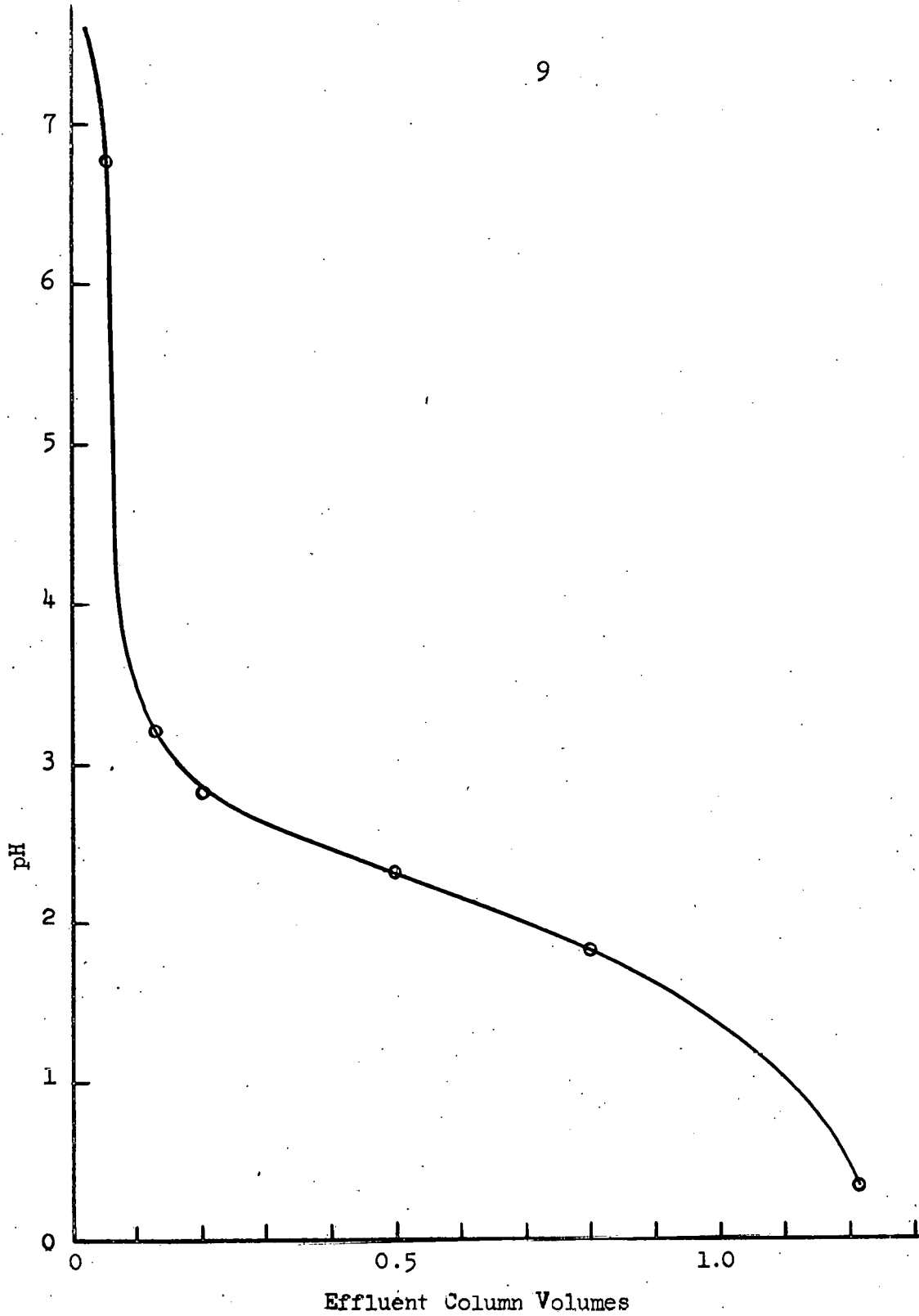


FIGURE 4

Soil Waste Neutralization Breakthrough

TABLE IIAdsorption of Plutonium and Americium by Soil

<u>Solution</u>	<u>Equilibrium Distribution Coefficient (ml/g)</u>	
	<u>Plutonium</u>	<u>Americium</u>
Acid Waste (AAW) untreated	2.4	< 1
pH 2 (soil neutralized)	2.7	< 1
pH 3 (NaOH neutralized)	2.9	< 1
Alkaline Waste from Precipitation		
Supernate -		
aqueous	*	212
aqueous + organic	1.4	42
Sludge leachate	1540	500

* Initial plutonium concentration and equilibrium concentration were too low for confident analysis.

different amounts of NaOH. These solutions were then put through soil columns and removal of plutonium was measured by analyses of the effluent. Results showed that soil removed most of the plutonium but there was a "leakage" through the soil that remained constant for the passage of at least 290 column volumes. The least leakage was associated with the higher pH (5% at 6.3 effluent pH). Precipitates tend to form if neutralization is carried further. Plutonium equilibrium distribution coefficients were about twice that for uncomplexed waste.

Precipitation-Scavenging

Two composite waste samples were used in precipitation-scavenging studies. Plutonium and americium scavenging was not as effective from the sample containing an excess of organics (Table III). Decantation of the aqueous part only and scavenging improved decontamination; however, the DF for plutonium was about 7.5 times less than for composite 1, which contained only saturation amounts of organics.

Precipitation treatment formed a precipitate which settled to a sludge volume 50 percent of the initial waste volume in 140 hours. Settling to 75 percent occurs in 48 hours. Vacuum filtration or centrifugation (approximately 1500g) reduced the sludge volume to 20 percent. Additional caustic did not reduce the final settled volume; however, less caustic (0.5 caustic: 2 water: 2 waste) resulted in final settled sludge volumes 1.5 times the initial waste volume.

TABLE IIIDecontamination by Precipitation Scavenging

	DF	
	<u>Plutonium</u>	<u>Americium</u>
Composite 1	230	> 6000
Composite 2		
aqueous	37	> 10000
Aqueous + slug organic	10	2090

CONCLUSIONS

Laboratory studies show that disposal of AAW waste to ground will result in plutonium and americium contamination of all soil material wetted by the waste. Both column and batch equilibrium data show that soil adsorption of plutonium and americium is low between the surface and ground water. Thus, any assumption that plutonium and americium is confined to the upper layers of soil beneath the Z-1A tile field is invalid for this type waste.

Alternate disposal methods which would safely confine both plutonium and americium in a small well-defined volume should be considered. Neutralization of AAW waste by reverse strike, as reported above, provides an alternate method for safe ground disposal of the alkaline supernate. The sludge containing the plutonium and americium could be stored in tanks for maximum confinement, or could be stored with a high degree of safety in covered cribs.

ACKNOWLEDGMENT

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REFERENCE

1. Knoll, K. C. Reaction of High Salt Aqueous Plus Organic Waste with Soil, Interim Report- BNWL-CC-313. September 17, 1965.