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ON MIGRATION IN THE TERRESTRIAL ENVIRONMENT OF  
LONG-LIVED RADIONUCLIDES FROM THE NUCLEAR FUEL CYCLE

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SATURATED-COLUMN LEACH STUDIES: HANFORD 216-Z-1A SEDIMENT

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## INTRODUCTION

Chemical process wastes containing low concentrations of transuranic radionuclides (TRU) were discharged to the unsaturated sediments at the U.S.D.O.E. Hanford Site from the start-up of operations in 1944 to 1973. Studies are being conducted to determine the distribution of TRU in the sediments beneath the retired facilities which received the waste and evaluate the potential mobility of the TRU in order to provide data for evaluating long-term options for TRU waste management. This paper reports results of experiments to evaluate environmental factors that could change the present distribution beneath a retired underground liquid waste disposal facility (216-Z-1A crib).

The Z-1A crib received  $6.2 \times 10^6$  liters of waste containing an estimated inventory of 57 kilograms of plutonium and 1 kg of americium. The waste was primarily derived from solvent extraction processes in which Pu and Am were purified from a variety of scrap materials. The bulk of the waste was the nitric acid solution used to dissolve TRU from the scrap. The nominal composition of this waste was: 0.15 M  $\text{HNO}_3$ ; 0.24 M  $\text{AlF}(\text{NO}_3)_2$ ; 0.40 M  $\text{Al}(\text{NO}_3)_3$ ; 0.16 M  $\text{Mg}(\text{NO}_3)_2$ ; 0.16 M  $\text{Ca}(\text{NO}_3)_2$ ; 0.05 M  $\text{Fe}(\text{NO}_3)_3$ ; 2.4 M  $\text{NaNO}_3$ . In addition to the aqueous phase, the organic phases used for the solvent extraction were also discarded when degradation products built up to the point where they interfered with the extraction. The bulk of the organics consisted of  $\text{CCl}_4$ , TBP and DBBP. Less than 5% of the volume discharged to the crib consisted of organic waste.

A laboratory study [1] investigating the sorption properties of this waste type indicated that Pu sorption was limited ( $K_d \sim 2.5$ ) and Am sorption was negligible ( $K_d < 1$ ). The conclusion of the study was that the TRU in the waste would not be sorbed on the sediment but migrate with the waste solution. Distribution of TRU beneath the crib was determined by a previous field study [2]. Waste-sediment interactions resulted in the bulk of the TRU being retained in the sediments within a few meters of the point of discharge, but TRU activity up to  $1 \mu\text{Ci/g}$  is present 30 meters below the crib, supporting the conclusion of the laboratory study regarding the low sorption of TRU for this waste type. The volume of liquid discharged to the crib was limited to retard breakthrough of the aqueous phase to the groundwater, but a study of the environmental factors which could remobilize the TRU was needed due to the low sorption properties of the TRU.

## EXPERIMENTAL

A 5 kg sample of contaminated sediment was obtained from the center of the crib at a depth of nine meters below the crib bottom. The sample as received from the field was handled in a glove box where it was air dried and blended by tumbling. The Pu-239 activity was  $107 \pm 10$  ( $1\sigma$ ) nCi/g; Am-241 activity was  $100 \pm 2$  ( $1\sigma$ ) nCi/g. Particle size analysis of the material indicated the sediment was a slightly silty fine sand. TRU analysis of the size fractions indicated there was little segregation of Pu or Am activity with particle size. The pH of the sediment was 3.9.

Both column and batch experiments were used to study the leaching behavior of the sediment. Column leaching studies were conducted at  $23^\circ\text{C}$  using a single-pass, continuous flow, saturated column configuration. The experimental arrangement, in the direction of leachant flow, consisted of a leachant reservoir, followed by a positive displacement syringe pump, the sediment column, a pH electrode and a fraction collector. The pH electrode gave continuous reading of the leachate pH as the solution left the sediment column. Five-ml fractions were collected and composited as required. In a saturated column configuration, the leachant solution is pumped upward through the column, allowing few unwetted surfaces, flow channels or air pockets to exist. The saturated column configuration approximates environmental leaching conditions corresponding to groundwater intrusion or massive surface flooding. The sediment column was 2.5 cm in diameter, 22 cm long and contained 180 g of packed sediment. Volumetric throughput was set at approximately 5.1 ml/hr, corresponding to a linear flow rate through the sediment of about 2.6 cm/hr, or a water column linear flow rate of about 1.0 cm/hr. Columns were leached for a maximum of 60 days, corresponding to about 210 pore volumes of leachant. Both synthetic groundwater and a 0.01 M  $\text{CaCl}_2$  solution were used as leachants in the column studies. The synthetic groundwater had a composition of approximately 1.0 mM  $\text{Na}^+$ , 0.17 mM  $\text{K}^+$ , 0.5 mM  $\text{Mg}^{+2}$ , 0.5 mM  $\text{Ca}^{+2}$ , 1.1 mM  $\text{H}_4\text{SiO}_4$ , 0.7 mM  $\text{NO}_3^-$ , 0.3 mM  $\text{Cl}^-$ , 0.4 mM  $\text{SO}_4^{-2}$ , and 1.3 mM  $\text{HCO}_3^-$  (mM=millimolar). The ionic strength of the groundwater solution was approximately 4.5 mM with a pH of 8.1. The 0.01 M  $\text{CaCl}_2$  solution had an ionic strength of ~30 mM and a pH of 6.2.

Batch studies were used to supplement the column studies. Sediment/leachant ratios ranged from 0.3 to 4 g/ml, and contact times from two minutes to three weeks. In addition to the synthetic groundwater and 0.01 M  $\text{CaCl}_2$ , distilled water, 0.001 to 1 M  $\text{CaCl}_2$ , 0.01 to 0.3 M  $\text{Al}(\text{NO}_3)_3$ , and 0.01 to 0.1 M NaF were used as leachants. Leachate solutions were analyzed for  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Si}^{+4}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{-2}$ , and  $\text{PO}_4^{-3}$ , in addition to Pu and Am.

## RESULTS AND DISCUSSION

For the column studies, increased concentrations of  $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Mg^{+2}$ ,  $Ca^{+2}$ ,  $Al^{+3}$ ,  $NO_3^-$ , and  $F^-$ , in addition to Pu and Am, was observed in the initial fractions collected for both the groundwater and 0.01 M  $CaCl_2$  leachants. Pu and Am had similar elution patterns but Pu activity in solution was two orders of magnitude less than that of Am. Pu activity in later fractions was generally below the detection limit of the analytical technique (alpha spectrometry) and discussion of the results is limited primarily to Am. Figure 1 shows Am activity versus pH for both groundwater and 0.01 M  $CaCl_2$ . Am was leached in two steps. The first step was characterized by rapid leaching of Am and low initial solution pH (~3.5). Of the 210 pore volumes of leachants passed through the columns, over 80% of the Am ultimately leached is removed in the first pore volume of leachant through the column. Continued leaching results in an increase in pH although the sediment has interacted with the acid waste sufficiently to have a buffering capacity below that normally found in Hanford sediment (pH=8). After the initial rapid leaching step, Am concentration is reduced with increasing pH. Both  $H^+$  and Am concentration however increase with total cation concentration, suggesting their concentrations are controlled by ion exchange reactions in the second step. Approximately 30% of the Am and less than 1% of the Pu were removed from the sediment with each solution after leaching with 210 pore volumes.

Slight retardation of chloride, fluoride and nitrate migration in the column experiments showed that the sediment acted as a weak anion exchanger. The anion behavior could be due to the low pH of the waste which through protonation gives some soil mineral surfaces a net positive charge. Precipitation of iron oxides or extensive loading of amphoteric aluminum ion on the soil exchange sites could also explain the anion exchange behavior of the sediment.

Batch leaching studies of a sediment sample obtained from another waste crib which received a similar waste type, showed a linear pH to log (Am concentration) relationship [3]. The report indicated that Am concentration was probably controlled by an Am compound, present as a solid phase. The line defining the Am compound's solubility is given in Figure 1. Am concentrations observed for initial fractions from the column studies were approximately an order of magnitude higher than that indicated by the solubility line.

Batch leaching of the sediment used in the column studies was used to supplement the column studies, and to investigate leaching mechanisms for the high concentration of Am in the initial fractions of leachate collected from the columns. The Am concentrations found in the batch studies were within 0.4 log (Am) units of the Am solubility line in Figure 1. The Am

concentrations found did not significantly exceed the solubility line with varied soil/solution ratio (varied from 0.3 to 4 g/ml), concentration of a competing cation in solution (0 to 1 M  $\text{CaCl}_2$ ; 0 to 0.3 M  $\text{Al}(\text{NO}_3)_3$ ), contact times (varied from two minutes to three weeks), or fluoride concentration (0.01 to 0.1 M  $\text{NaF}$ ). Filtration of all leachates through 0.003  $\mu\text{m}$  filters did not affect the Am concentration indicating that Am was not present as a colloid. The Am species in solution was found to be cationic using ion exchange resin techniques. It is believed the enhanced Am concentrations shown in the column experiments are due to accumulation of a trace complexant species, originating in the waste liquid, at the solution front in the column which then increased Am solubility.

Plutonium concentrations in all batch and column leachates were below the concentration dictated by the solubility of  $\text{PuO}_2$ . Batch leaching experiments showed that Pu concentrations in the leachates were increased with increasing ionic strength of the leachant. Hence, the mechanism of Pu solution was ion exchange desorption and not failure to obtain equilibrium in solution with  $\text{PuO}_2$ .

#### CONCLUSIONS

A previous laboratory study indicated that Pu and Am in the waste discharged to the crib would not be sorbed on the sediment but migrate with the waste solution [1]. Field study of the TRU distribution beneath the crib [2] support the conclusions of the laboratory study. The current laboratory study indicates that waste-sediment interactions have altered the waste, resulting in the retention of almost all of the Pu and most of the Am on the sediment tested. Batch leaching study results, in agreement with results of an earlier study [3], show Am concentrations are determined by an Am compound having pH dependent solubility. Batch studies also show that Pu is not present in the sediment sample as  $\text{PuO}_2$ . The mechanism of Pu solution is ion exchange desorption. The solubility of TRU can be enhanced under column leaching conditions which favor concentration of complexing agents at the wetting front. Plausible environmental leaching conditions might be expected to mobilize less than 1% of the Pu present in the sediment and approximately 30% of the Am.

#### REFERENCES

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FIG. 1. Saturated column leaching of Am from 216-Z-1A sediment using: A, 0.01 M  $\text{CaCl}_2$  and B, synthetic groundwater. Numbers given on column leaching curves are throughput column pore volumes.



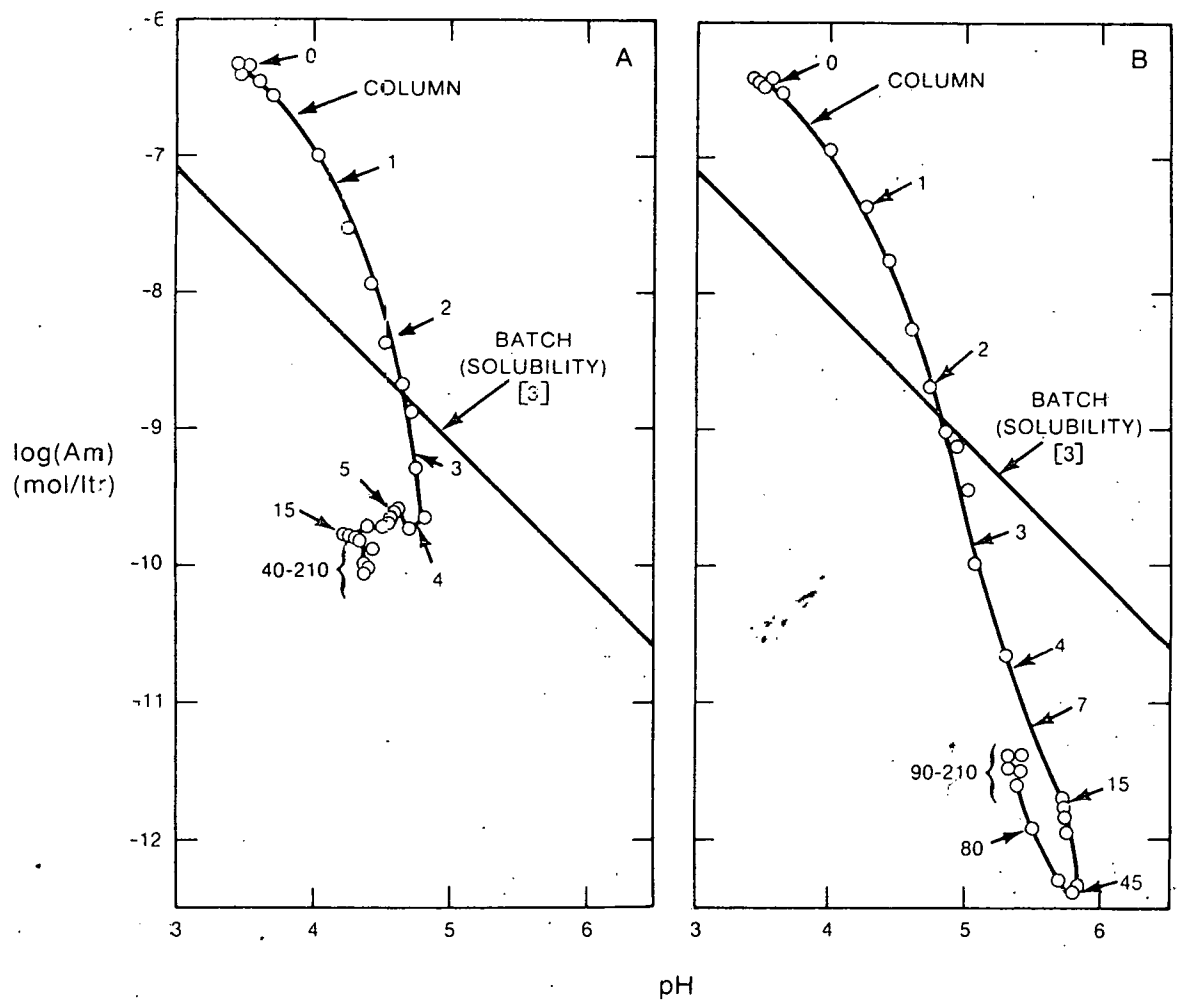


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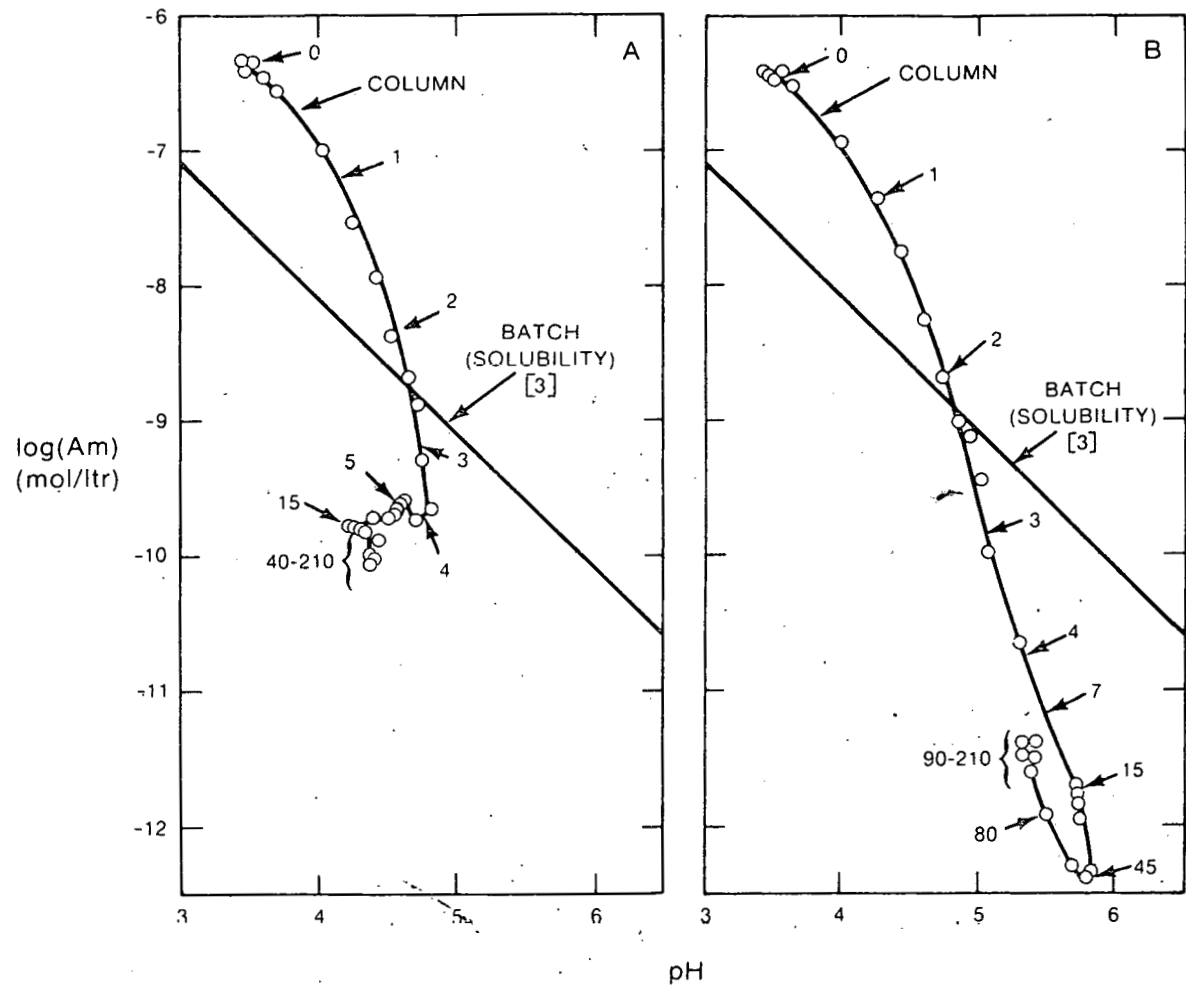


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