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Interactions of Radioactive Wastes with Soils - A Review

October 1976 through May 1979

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Prepared by E. B. Fowler, E. H. Essington, W. L. Polzer

Los Alamos Scientific Laboratory
University of California

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INTERACTIONS OF RADIOACTIVE WASTES WITH SOILS—A REVIEW
October 1976 through May 1979

by

Eric B. Fowler, Edward H. Essington, and Wilfred L. Polzer

ABSTRACT

Four soils of different physical and chemical characteristics have been reacted in both the batch and column mode with two different radioactive wastes to determine the soil's degree of retention for waste radionuclides. Two of the soils are of the same type found at two commercial waste burial grounds. The raw and treated liquid wastes were obtained from the waste stream at a large laboratory complex.

Three fractions were demonstrated in each waste as (1) insoluble, (2) soluble and sorbable by the soil, and (3) soluble but nonsorbable by the soil. Although the soluble fraction (<0.05 μm) in both wastes increased with storage time, that increase did not directly relate to the degree of retention by the soil.

Differences in degrees of retention for the same radionuclide were demonstrated among the soils. Retention of the same radionuclide from different wastes, but by the same soil, also differed.

Ninety-five to one hundred per cent of raw waste ^{137}Cs was retained by all soils. Plutonium isotopes and ^{241}Am were the least retained by the soils; uranium isotope retention was intermediate.

A Fuquay soil from South Carolina dissolved plutonium and americium from the insoluble fraction of the waste. The net retention of those two nuclides was negative, i.e., more plutonium was brought into solution than was sorbed by the Fuquay soil.

Two of the factors that could influence the degree of retention by the soil were investigated. Those factors are (1) charge on the radionuclide in solution and (2) degree of calcium carbonate saturation.

All investigated radionuclides and their isotopes were predominately negatively charged within the pH range of about 4 to 12 with the exception of ^{137}Cs; that isotope was positively charged at a pH value as low as 2. Theoretical calculations based on analytical data demonstrated a shift from negative to positive charge in the presence of soil. As a result, some fraction of the observed retention could occur through an ion exchange mechanism.

Calcium carbonate precipitates were shown, by autoradiographic techniques, to occlude alpha emitting radionuclides. The degree of calcium carbonate saturation calculations showed that where sorption of plutonium and americium occurred, the liquid fraction was at or above saturation. In the case of Fuquay soil, the liquid fraction was undersaturated with respect to calcium carbonate. Post precipitation of aluminum also removed

radionuclides from solution. Removal of radionuclides by algal growth was demonstrated; however, biological mechanisms are probably undesirable.

Removal of radionuclides from waste by filtration of the insoluble fraction is an important mechanism in retention. Ion exchange and calcium carbonate precipitation will attenuate radionuclides and inhibit transport. Of the three fractions, the soluble, nonsorbable fraction is of immediate importance because it has the greater potential for mobility.

I. INTRODUCTION

When radioactive wastes are disposed by shallow land burial, an artificial system is created. An understanding of that system requires knowledge from a number of disciplines, e.g., soils, chemistry, physics, hydrology, microbiology, meteorology, and plant sciences.

The buried waste package is the primary container; the waste pit is the secondary container. Because primary containers do fail, dependency for added containment is placed on the secondary container. The ability of the pit to contain will relate to the chemistry and physics of the soil and the waste.

Water will accumulate as an end product of decomposition of organic matter as well as from infiltration. In the presence of water and organic matter a microbiological population will develop provided the pH is compatible. The physical and chemical characteristics of the soil and its interaction with waste will influence the degree and rate of transport of radionuclides from the solution in the pit. The chemical composition of the waste/soil solution will reflect the degree of solubility of the waste components and also will influence sorption, hence transport.

In the artificially created system, interactions often negate a classical theory approach. It follows that each system must be studied as a unit and further that the material transported is determined by a series of complex interactions.

The selection of a site for the burial of radioactive waste and the limits on a license to operate that site require information from which current and future impact on the environment can be predicted. Questions to be answered should include the following:

1. What is the capability of the soil at a proposed or operating site to retain each of the radionuclides to be buried?

2. Is there a partition among radionuclides or species of a single radionuclide as the waste transports through the soil?

3. What chemical and physical characteristics of the soil and/or waste increase or decrease retention?

4. What is the rate of transport of various radionuclides and their species through the soil of interest?

5. What is the effect of organic matter and its decomposition products on retention?

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6. What changes in waste/soil solutions occur with time and how do the changes influence transport?

7. Do radionuclides transport through soil as ions, polymers, colloids, or on inert particles and [illegible] extent is each involved?

8. What treatment of the pit or waste can be accomplished to enhance retention?

9. How can the sum of results of waste/soil interactions be used to the best advantage as a predictive mechanism relative to expected waste transport through the soil?

The above questions formed the basis of a proposal submitted to the Nuclear Regulatory Commission (NRC) in 1976. The objectives of the proposed study are listed chronologically.

1. Collect large volume soil samples, about two tons each, representative of the large soil groups in the United States—the soils to be collected by horizons down to about 1.3 m. Soils should possess a range of physical and chemical properties; they should represent agricultural and non-agricultural soils; soils should include types present at current burial grounds. Sufficient soil should be collected to provide the companion projects at the University of California, Los Angeles (UCLA) and University of California, Berkley (UCB) with volumes necessary for plant uptake experiments. A supply of soil should be available to establish a library.

2. Collect a variety of wastes from known sources including treatment facilities, processing facilities, and waste storage sites.

3. Analyze the soils and wastes for physical and chemical characteristics. Radiochemical analyses are to be conducted at increasing increments of time to determine possible changes as the waste is stored.

4. Assuming the soil to be a container for waste, react each soil with each waste to determine the ability of the soil to retain radionuclides from the waste.

5. Correlate the physical and chemical characteristics of waste and soil with retention of each radionuclide to determine those characteristics that influence retention. Present results as an envelope graph from which retention can be predicted when the characteristics of a waste and a soil are known. That ability to predict is important in site selection and in placing of limits on operation.

6. Determine the influence of organic matter *per se*, decomposing organic matter, and metabolic end products from the growth of the soil microbiological populations on retention of radionuclides by soil. The nature of the metabolic end products will be determined by the soil, the organic matter present, the depth of profile, the population that develops, and the length of time after initiation of catabolism.

7. Determine the physical nature of the entities being transported, i.e., inert particle and size, ion, polymer, colloid, and the net charge on the entity.

8. Determine the fate of the above entities on passage through the soil. For example, is the net negative charge (not sorbable), changed by the soil characteristics to a positive charge (sorbable) and if so at what rate?

9. For those reactions favoring retention of the radionuclide by soil, explore possible methods which will enhance that specific reaction within the containment area.

Project work was initiated late in 1976 and is detailed in previous reports.[1,2,3] A recitation of effort, results, and interpretation through May 1979 follows.

II. SOIL COLLECTION AND SOIL PROPERTIES

The collection of soils was initiated in the fall of 1976; two New Mexico soils were collected before freezing weather and were used in the initial soil interaction experiments. Those soils were a Carjo B horizon and a Puye C horizon. The A and the A and B horizons, respectively, were absent. The soils were surface soils at the collection site.

In the summer and fall of 1977 large volume collections were made at Barnwell, South Carolina, Sheffield, Illinois, West Valley, New York, Maxey Flats, Kentucky and Beatty, Nevada. Other collections have been made in Nebraska and California. Ten soils with a range of chemical and physical characteristics are available in the soils library. A Hanford, Washington soil is to be added to the study; that soil has not been collected.

Data relative to classification of the soils are listed in Table I. Elemental composition of four soils has been determined by emission spectroscopy; results are listed in Tables II and IIA. Classical soil analyses were conducted and are listed in Table III; the analyses were performed by Babcock and Sons, Riverside, California. Mineralogical analyses of the clay fraction were obtained by x-ray diffraction; those analyses were performed by Dr. Robert Schultz (UCB) as part of the cooperative effort between the companion projects. Results are presented in Table IV.

The soils characteristic data (Tables II, IIA, III, and IV) will be correlated with degree of retention of radionuclides by respective soils to determine entities or combinations of entities that influence retention.

III. WASTE COLLECTION AND WASTE PROPERTIES

A raw waste (influent) and a treated waste (effluent) were collected over a period of two weeks and composited. About 150 ℓ of each waste were collected and stored in polyethylene drums. That waste served as the source for the initial waste/soil interaction experiments. Physical and chemical characteristics of the two wastes are listed in Table V.

Arrangements have been made to obtain wastes from Hanford, Washington; more recently waste from Maxey Flats has become available. Those two wastes are to be collected this year (1979).

IV. THE WASTE/SOIL SYSTEM

Radioactive wastes may vary widely in character, depending on the source; the physical and chemical characteristics will influence the degree of retention by soil.

As an example, the early work of Rhodes[4] indicated that plutonium in tracer quantities and above pH 2 would exist as a polymer and that it would be sorbed rapidly by soil. Further, desorption from soil was difficult to accomplish with solutions of organic salts implying immobility in the environment. On the other hand, Hajek and Knoll[5] found essentially zero adsorption of plutonium and americium by soil from a high salt acid waste.

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TABLE I

SOILS COLLECTED[a]

Soil Type	Family	Sub Group	Location
	1977		
Carjo - loam	Clayey, mixed	Mollic Eutroboralf	Los Alamos, New Mexico
Puye - sandy loam	Medial, mixed frigid	Mollic Vitrandept	Los Alamos, New Mexico
Fuquay - loamy sand	Loamy, siliceous, thermic	Arenic Plinthic Paleudults	Barnwell, South Carolina
Fayette - silt loam	Fine - silty, mixed, mesic	Typic Hapludalfs	Sheffield, Illinois
Tilsit - silt loam	Fine - silty, mixed, mesic	Typic Fragiudaults	Hillsboro, Kentucky
Churchville - silt loam	Fine - illitic mesic	Aeric Ochraqualf	West Valley, New York
	1978		
—[b]	Loamy - skeletal, mixed, thermic	Typic Camborthid	Beatty, Nevada
Aiken - sandy loam	Clayey, koalinitic, mesic	Xenic Hoplohumult	Placerville, California
Yolo - loam	Fine - silty, mixed, non-acid, thermic	Typic Xerorthent	Davis, California
Sharpsburg - silty clay	Fine, montmorillonitic, mesic	Typic Agiudoll	Lincoln, Nebraska

---

[a] Classification based on USDA, SCS information. The last three soils were obtained from the UCLA project.

[b] This soil has not been given a soil type classification.

TABLE II

TOTAL CONCENTRATION OF CHEMICAL ELEMENTS IN THE SOILS USED IN BATCH AND COLUMN STUDIES[a]

Element	Concentration (%)			
	Puye C	**Carjo B**	**Fayette Ap**	**Fuquay Ap**
Si	20	20	20	20
Al	10	10	10	3
Fe	2	2	1	0.6
Ca	1	1	1	0.1
Mg	0.4	0.6	0.6	0.1
Na	1	1	0.6	0.02
K	2	2	2	0.06
Ti	0.8	0.8	0.8	0.4
Mn	0.2	0.2	0.2	0.04
Ba	0.1	0.15	0.1	0.01
Sr	0.04	0.06	0.06	0.004
Zr	0.02	0.02	0.05	0.06
Li	0.03	0.015	0.006	<0.004
Zn	0.01	0.006	0.006	<0.006
Be	0.0001-0.001	0.0001-0.001	0.0002	<0.0002
B	0.004	0.004	0.004	0.004
P	<0.06	<0.06	<0.06	<0.06
Sc	0.0006	0.0008	0.001	<0.0006
V	0.008	0.01	0.01	0.004
Cr	0.004	0.008	0.01	0.003
Co	<0.002	<0.002	0.006	<0.002
Ge	<0.004	<0.004	<0.004	<0.004
Rb	<0.03	<0.02	<0.02	<0.02
Nb	<0.006	<0.006	<0.006	<0.006
Mo	<0.002	<0.002	<0.002	<0.002
Ag	<0.0004	<0.0004	<0.0004	<0.0004
Cd	<0.002	<0.002	<0.002	<0.002
In	<0.002	<0.002	<0.002	<0.002
Sn	<0.004	<0.004	004	<0.004
Sb	<0.006	<0.006	006	<0.006
Cs	<0.02	<0.02	<0.02	<0.02
La	0.006	0.006	0.006	<0.01
W	<0.06	<0.06	<0.06	<0.06
Bi	<0.002	<0.002	<0.002	<0.002

---

[a] Samples analyzed by emission spectroscopy with a precision of 50% relative standard deviation.

TABLE IIA

CONCENTRATION OF CHEMICAL ELEMENTS IN AMMONIUM ACETATE SOIL EXTRACTS[*]

Element	Concentration (μg/g soil) Puye C	Carjo B	Fayette Ap	Fuquay Ap
Si	120	240	240	100
Al	6	9	12	8
Fe	4.8	54	3	12
Ca	600	900	480	100
Mg	180	240	240	20
Na	30	42	60	40
K	120	180	60	20
Ti	0.3	0.42	0.6	0.4
Mn	24	54	48	8
Ba	60	90	48	16
Sr	24	36	12	4
Zr	0.18	0.24	0.12	0.06
Li	0.42	0.6	0.3	0.2
Zn	<0.18	<0.24	0.3	0.1
Be	<0.006	<0.009	<0.006	<0.002
B	6	12	12	4
P	1.8	2.4	1.8	0.6
Sc	<0.018	<0.024	<0.018	<0.006
V	0.3	0.42	0.36	0.08
Cr	0.18	0.18	0.12	0.10
Co	0.06	0.36	0.18	0.02
Ge	<0.12	<0.18	<0.12	<0.04
Rb	6	9	1.8	2
Nb	<0.18	<0.24	<0.18	<0.06
Mo	0.06	0.09	0.12	0.10
Ag	0.6	0.018	0.06	0.06
Cd	0.18	0.24	0.6	0.02
In	<0.06	<0.09	<0.06	<0.02
Sn	<0.12	<0.18	<0.12	<0.04
Sb	<0.18	<0.24	<0.18	<0.06
Cs	<0.6	<0.9	<0.6	<0.2
La	0.18	0.36	<0.18	<0.06
W	<1.8	<2.4	<1.8	<0.6
Bi	<0.06	<0.09	<0.06	0.02
Ni	0.6	0.54	1.2	0.6
Cu	0.6	1.2	1.2	0.4
Pb	0.3	0.42	0.18	0.4

---

[*] Samples analyzed by emission spectroscopy with a precision of 50% relative standard deviation.

TABLE III

SOME CHEMICAL AND PHYSICAL CHARACTERISTICS OF THE SOILS USED IN BATCH AND COLUMN STUDIES

	Puye C	**Carjo B**	**Fayette Ap**	**Fuquay Ap**
Loss on ignition, %	2.3	2.5	3.2	2.9
Particle size distribution, %				
Clay	7.5	10	8.5	0
Silt	47.5	37	72.5	14.5
Sand	39.5	48.8	18.8	83.6
Fine gravel & coarser	5.3	4.5	1.5	0.2
pH (Saturated Paste)	7.1	6.4	6.6	5.5
CEC meq/100 g	23	18	15	16
Saturation Extract				
Conduct. EC × 10^3	0.3	0.2	0.8	0.5
B μg/mℓ	0.04	0.2	0.1	0.0
Ca μg/mℓ	33	23	73	52
Mg μg/mℓ	5	5	3	11
Na μg/mℓ	5	3	6	2
1:5 Water Extract				
Cl μg/g	25	35	25	20
NO_3 μg/g	12	10	31	24
SO_4 μg/g	0	10	0	10
Ammonium Acetate Extract				
Ca μg/g	1800	1000	1400	230
Mg μg/g	170	200	330	22
Sodium Bicarbonate Extract				
PO_4 μg/g	7	7	15	8
DTPA Extract				
Fe μg/g	6	7	28	50

TABLE IV

%COMPOSITION OF THE $<2 \mu m$ SOIL FRACTION (MINERALOGICAL)

Soil	Montmorillonite	Vermiculite	Kaolinite	Mica	Quartz	Gibbsite	Feldspar	Fe_2O_3	Amorphous Fe and Al, Organic Matter
Yolo	54	5	26	4	4				7
Egbert (minus organic matter)	4	36	34		2		1		23
Aiken		17	67			4	3	9	
Holtville	57	3	29	2	4				5
Lyman		64	2		4				30
Malbis		57	28	1	4	5			5
Sharpsburg	40	10	20	15	5				10
Fayette Ap	20	14	36	18	7		1		4
Fayette B	35	27	18	8	5				7
Fayette C	40	22	30	7					1
Fuquay Ap		45	35		9	5			6
Fuquay A2		45	35		10	2			8
Fuquay B2t		30	60		1	6			3
Fuquay C		12	77			5			6
Carjo B	23		27	15	6		3		26
Puye C	21		22	22	4		5		26

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TABLE V

CHEMICAL AND PHYSICOCHEMICAL COMPOSITION OF RAW AND TREATED WASTES

	Raw[a]		Treated	
	Total	**Soluble**	**Total**	**Soluble**
EC mmhos	1.33 ± 0.02	1.31 ± 0.01	8.55	8.47 ± 0.04
pH	7.8 ± 0.1	8.14 ± 0.05	12.2	12.2
Eh (mV)	410 ± 15	397 ± 4	171	167
CO_3[b]	0	0	550	510
HCO_3	840	850	0	0
NH_4	---	0.59 ± 0.06	4.4	4.6 ± 0.1
NO_3	1.4	0.8 ± 0.1	750	723 ± 22
NO_2	0.04	0.05	3.26	3.25 ± 0.01
SO_4	14 ± 1	14.1 ± 0.4	240	250 ± 4
PO_4	29	2.23 ± 0.05	0.87	0.64 ± 0.02
Cl	27	26 ± 2	72	73.1 ± 0.3
F	2.1	1.4 ± 0.1	2.6	2.6
Ca	75	51 ± 6	2.9	3.1 ± 0.3
Mg	6.7	3.23 ± 0.03	0.10	0.10 ± 0.01
Na	330	308 ± 4	1350	1283 ± 25
K	5.3	5.0 ± 0.1	8.2	7.5 ± 0.3
COD	168	61 ± 2	59	55 ± 2
Fe	11.7	0.36 ± 0.05	0.4	0.6 ± 0.1
Al	2.0	0.22 ± 0.04	3.8	2.33 ± 0.06

---

[a] Underlined data indicate significant differences between total and soluble composition of waste.

[b] Data for all constituents below and including CO_3 are expressed in ppm.

The above results were not contradictory in the strict sense, rather they indicated at an early date a complexity associated with different wastes and/or different soils.

Because soils also vary widely in characteristics, aqueous solutions derived from different soils will vary. It is the combined waste/soil solution that will determine to a great extent the degree of retention of different radionuclides and their respective isotopes.

At a high ratio of waste to soil solution, retention may be determined by waste characteristics and at a low ratio of waste to soil solution, the soil solution may be determinate. Both the waste and soil systems are dynamic and the complexity of the waste is compounded by the complexity of the soil. The research reported here relates to waste/soil systems with a view toward understanding the influence of those two systems on retention of radionuclides by soils. That information is a prerequisite for siting and for predictive purposes relative to disposal of waste in the environment.

A. Waste/Soil Interactions

1. Methods. The initial waste/soil interactions were conducted in the batch mode. Known weights of soil were reacted with known volume of waste in polyethylene containers for a period of five days. The waste/soil ratio was 4 to 1 on a weight basis; four to six replicates were used for each system. A reagent blank and tracer blank were included. Each of the replicates was traced with ^{242}Pu, ^{232}U, and ^{243}Am.

After the five day reaction period, the polyethylene containers were centrifuged at 7200 × gravity to remove particulate material calculated to be greater than 0.05 μm nominal diameter. That material removed by centrifugation is designated as the *insoluble fraction*, the supernate is designated as the *soluble fraction*. An equal volume of waste without soil was subjected to the same procedure and served as the control.

Chemical and radiochemical analyses were performed on the total waste without soil, the supernate fraction obtained by centrifugation of waste without soil, and the supernate fraction of waste obtained by centrifugation after reaction of the waste with soil.

Analyses for those constituents that change rapidly with time were conducted immediately; those constituents are (1) ammonia, (2) nitrate, (3) nitrite, (4) alkalinity, (5) pH, and (6) Eh. Analyses for other constituents were conducted later.

Radiochemical analyses were in accordance with modifications of methods developed for this and other programs. A flow diagram of the method is given in Fig. 1. Each separate from the ion exchange columns (step 1) was electrodeposited from an ammonium sulfate solution onto an electropolished stainless steel planchet, washed, dried, and counted using solid state detectors. Counting times were those necessary to obtain statistically acceptable data; data were stored on magnetic tape and printout. Concentrations and radionuclides were calculated from the pulse height and energy channels, respectively. Results are given as disintegrations per minute per unit noted with a one sigma counting error.

Differences in radionuclide activities per unit volume of supernate from the centrifuged waste and the centrifuged waste/soil system define the radionuclide activity associated with the soil. That association designated "sorption" may include precipitate formation.

2. Preliminary Batch Studies. A batch technique was employed in the preliminary screening studies to establish the fact of sorption as it might relate to different wastes and different soils. An insoluble fraction was separated from the total waste by centrifugation; the supernate (soluble fraction) may contain particles <0.05 μm nominal diameter.

The percentage of four radionuclides and their respective isotopes associated with the insoluble fractions obtained from raw waste and from treated waste are listed in Table VI. For raw waste, the plutonium isotopes and ^{241}Am are least soluble or more tightly bound to waste particulates; uranium isotopes and ^{137}Cs are more soluble or less tightly bound. In the case of treated waste, only ^{238}Pu was above the detection limits.

In the preliminary sorption studies, raw waste was reacted with a Carjo soil for the five day period. The results presented in Table VII indicate a variation in sorption among soluble radionuclides and possibly among soluble isotopes of the same radionuclide. The data provide a basis for the identification of two fractions in the soluble waste, i.e., *soluble sorbable* and *soluble nonsorbable*. In the case of ^{137}Cs, a nonsorbable fraction may not exist.

3. Changes in Partition of Waste Fractions with Time of Storage. Waste represents a chemically dynamic system; hence, the stability of the soluble fraction was investigated. Tables VIII and IX present data relative to sequential radiochemical analyses on the stored raw waste. Increases in the soluble concentrations of all radionuclides were observed over the

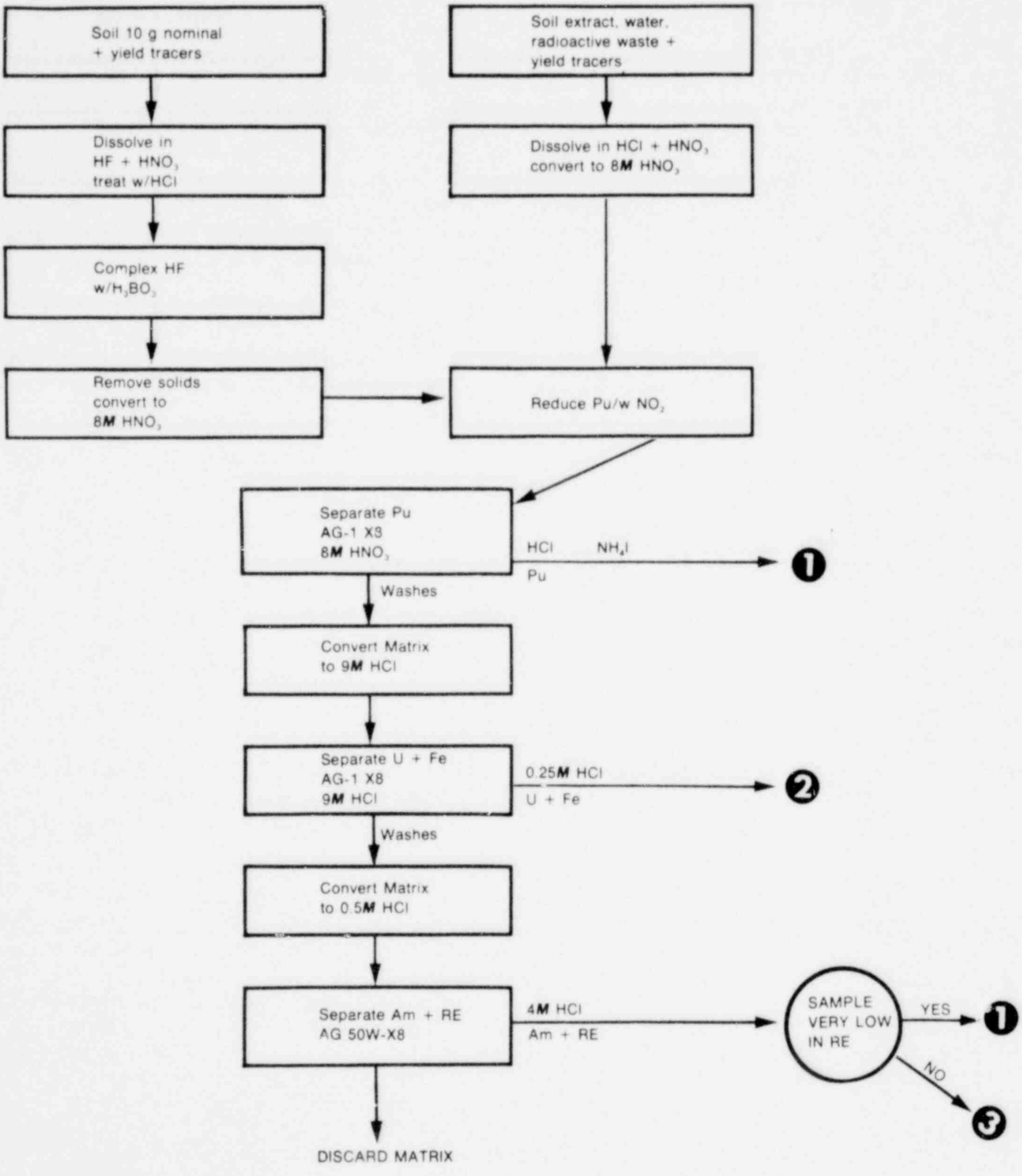

Fig. 1.
Radiochemical separation flow chart.

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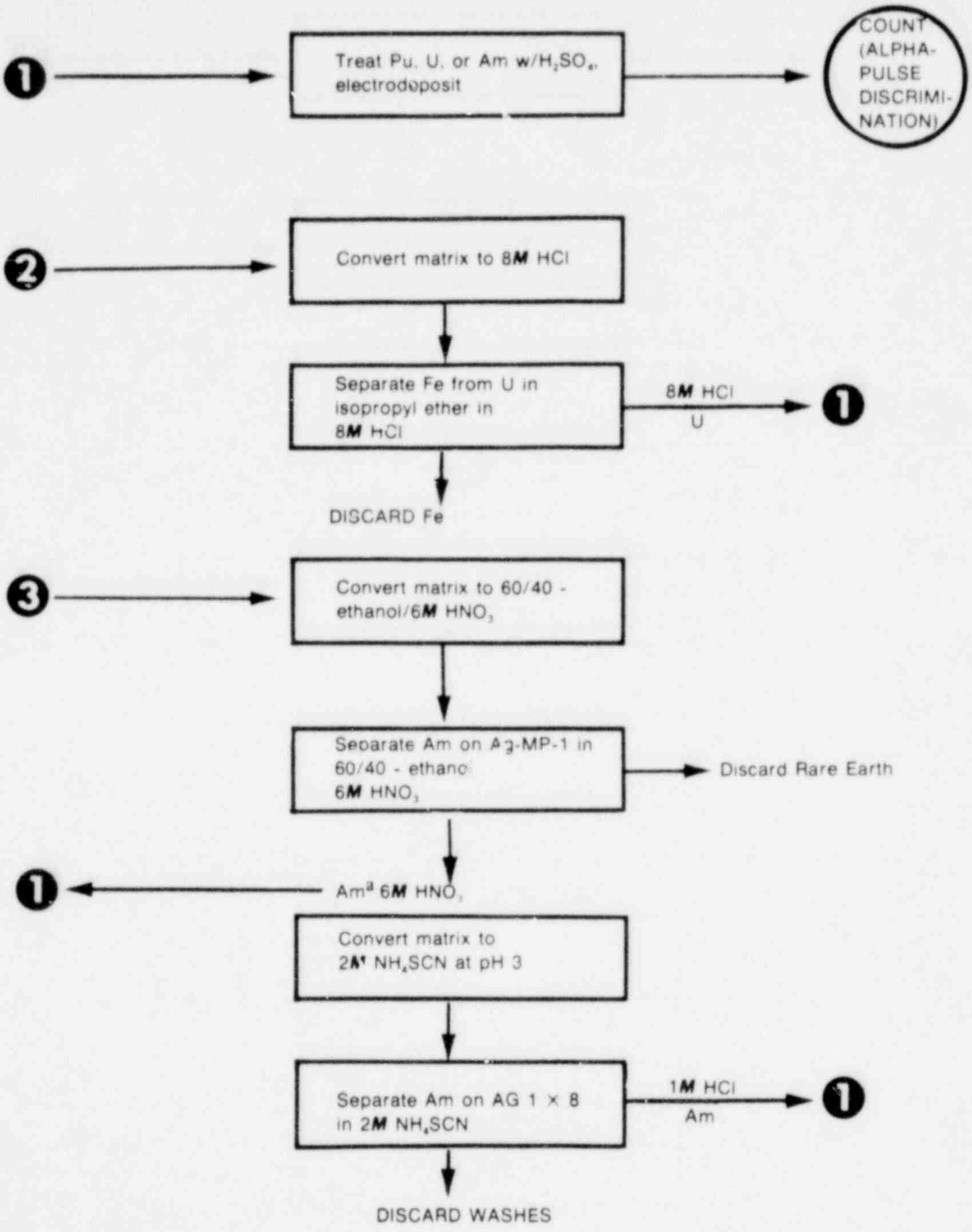

[a] Certain samples may be submitted for electrodepositing and alpha counting at this point if rare-earth content is sufficiently low.

Fig. 1 (continued).

TABLE VI

INSOLUBLE FRACTION AS PER CENT OF TOTAL RADIONUCLIDES IN WASTES

Radionuclide	Per Cent of Total ± S.E.	
	Raw[a]	Treated[b]
^{238}Pu	99.84 ± 0.01	64 ± 5
^{239,240}Pu	99.80 ± 0.06	c
^{241}Am	99.89 ± 0.02	c
^{238}U	54 ± 6	c
^{235,236}U	65 ± 10	c
^{233,234}U	55 ± 3	c
^{137}Cs	56 ± 5	c

---

[a] Waste sampled 2/23/77.
[b] Waste sampled 3/4/77.
[c] Not detectable.

TABLE VII

SORPTION OF SOLUBLE WASTE RADIONUCLIDES IN WASTE/CARJO SOIL SYSTEM

Radionuclide	Per Cent Sorption ± S.E.	
	Raw Waste[a]	Treated Waste[b]
^{238}Pu	7 ± 4	78 ± 12
^{239,240}Pu	35 ± 25	---
^{238}U	37 ± 4	---
^{235,236}U	46 ± 9	---
^{233,234}U	83 ± 3	---
^{137}Cs[c]	97 ± 4	---

---

[a] Analyses performed on 2/23/77.
[b] Analyses performed on 9/8/77.
[c] Analyses performed on 9/29/77.

TABLE VIII

TOTAL AND SOLUBLE PLUTONIUM, AMERICIUM, AND CESIUM IN RAW WASTE

Raw Waste	Sampling Date	Mean Concentration ± S.E. × 10^2 (dpm/mℓ) ^{238}Pu	 ^{239,240}Pu	 ^{241}Am	 ^{137}Cs
Total[a]	3/17/77	11 300 ± 400	980 ± 30	1130 ± 50	410 ± 10
Soluble[b]	2/23/77	18.0 ± 0.6	2.0 ± 0.6	1.2 ± 0.2	---
	3/17/77	23 ± 1	1.7 ± 0.1	1.3 ± 0.2	---
	4/28/77	125 ± 3	11.0 ± 0.2	3.6 ± 0.1	---
	9/29/77	200 ± 10	17.9 ± 0.8	7.8 ± 0.6	230 ± 20
	1/18/78	176 ± 2	15.3 ± 0.3	9.2 ± 0.8	280 ± 10
	1/25/78	166 ± 4	14.5 ± 0.6	5.6 ± 0.6	280 ± 10

---

[a] Composited sample collected 12/3/76 to 12/17/76.

[b] Soluble may include particles up to 0.05 μm in diameter.

TABLE IX

TOTAL AND SOLUBLE URANIUM IN RAW WASTE

Raw Waste	Sampling Date	Mean Concentration ± S.E. × 10^2 (dpm/mℓ) ^{238}U	 ^{235,236}U	 ^{233,234}U
Total[a]	3/17/77	9 ± 1	4 ± 1	20 ± 1
Soluble[b]	2/23/77	4.1 ± 0.2	1.4 ± 0.2	8.9 ± 0.5
	3/17/77	4.3 ± 0.1	1.7 ± 0.1	9.6 ± 0.1
	4/28/77	6.20 ± 0.05	2.27 ± 0.03	14.1 ± 0.2
	9/29/77	8.3 ± 0.3	3.0 ± 0.2	17.9 ± 0.7
	1/18/78	7.5 ± 0.3	2.9 ± 0.1	16.9 ± 0.2
	1/25/78	10.5 ± 0.5	4.3 ± 0.2	23.1 ± 0.2

---

[a] Composited sample collected at 12/3/76 to 12/17/76.

[b] Soluble may include particles up to 0.05 μm in diameter.

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period of storage; for the soluble fractions of ^{238}Pu and ^{239,240}Pu, and ^{241}Am, the order of increase was ^{238}Pu>^{239,240}Pu>^{241}Am (Table VIII). Although data are insufficient to draw firm conclusions, there is a suggestion of species difference between ^{238}Pu and ^{239,240}Pu. The soluble fraction of ^{137}Cs remained constant for the three months for which data are available. Table IX presents similar data for changes in concentration of soluble uranium species; an increased solubility of all isotopes was noted. Essentially all of the uranium was in the soluble form after a period of 11 months.

For the treated waste, changes in the soluble fraction with time are presented in Table X. Changes over the period were considered insignificant indicating a more nearly stable waste at the higher pH of 12.2; however, an unambiguous explanation is not available from present data.

In a waste disposal pit it is assumed that the insoluble fraction is removed by a filtration mechanism at the liquid waste/soil interface; the soluble fraction is free to move into the soil. However, physical ion exchange processes and chemical reactions between soil solution solutes and transporting radionuclides may attenuate the radionuclides and influence the rate of their transport. The characteristics of the waste and soil will determine the degree of attenuation. At the ideal burial ground, those characteristics should be such that the radionuclides are attenuated in the immediate vicinity for periods of time that will render them nonhazardous because of decay.

4. Differences in Sorption Among Different Soils—Raw Waste. Increases in the soluble radionuclides in raw waste, especially ^{238}Pu and uranium species, pose questions regarding possible increases in sorbability. Table XI presents data for raw and treated waste reacted with the Carjo soil. Separate determinations were made at intervals over a period of 8 and 15 months, respectively. In the raw waste system there was a trend toward an increase in soluble ^{238}Pu over the 8 month period with an increase of 4 to 5 in the fraction sorbed. However, in the case of the treated waste system, the soluble fraction showed no consistent trend, but the fraction sorbed increased over the 15 month period. The data suggest that ^{238}Pu waste retained in a pit at a high pH (about 12.0) becomes more amenable to sorption as the waste ages and thus

TABLE X

TOTAL AND SOLUBLE ^{238}Pu IN TREATED WASTE

Treated Waste	Sampling Date	Mean Concentration ± S.E. × 10^2(dpm/mℓ)
Total[a]	3/17/77	4.5 ± 0.6
Soluble[b]	3/4/77	1.6 ± 0.1
	3/17/77	2.7 ± 0.5
	3/31/77	2.6 ± 0.5
	9/8/77	1.8 ± 0.3
	10/6/77	2.9 ± 0.9
	6/22/78	2.35 ± 0.05

---

[a] Composited sample collected 1/77/77 to 1/21/77.

[b] Soluble may include particles up to 0.05 μm in diameter.

TABLE XI

EFFECT OF WASTE STORAGE ON THE DISTRIBUTION OF SORBABLE ^{238}Pu IN THE SOLUBLE FRACTION OF WASTE

Waste/Soil System[a]	Sampling Date	Soluble ^{238}Pu (% of Totals ± S.E.)	Sorbable ^{238}Pu (% of Soluble ± S.E.)
Raw/Carjo	2/23/77	0.16 ± 0.01	7 ± 4
	4/28/77	1.11 ± 0.05	1 ± 4
	9/29/77	1.77 ± 0.11	32 ± 5
Treated/Carjo	3/4/77	36 ± 5	6 ± 20
	3/31/77	58 ± 14	>85
	9/8/77	40 ± 9	78 ± 12
	10/6/77	64 ± 22	86 ± 5
	6/22/78	52 ± 7	89 ± 4

---

[a] Raw waste collected 12/76.
Treated waste collected 1/77.

confines the ^{238}Pu to the more immediate area surrounding the pit. That conclusion applies to a short time span; changes occurring over extended periods of time may favor other reactions such as desorption and transport.

The percent of the radioisotope in the soluble fraction that is sorbed by the soil does change; for the plutonium species, the trend is toward an increase in sorption.

Although there is a suggestion of differences in the degree of sorption among isotopes of the same radionuclide, data are insufficient to support such a conclusion; however, the possibility can not be ruled out at this time.

The data for extended experiments conducted on raw waste/Carjo, Puye, Fayette, and Fuquay soil systems are presented in Tables XII through XV. Degrees of sorption are expressed as percent. A summary is presented in Table XVI. Degrees of sorption relative to the raw waste/Carjo soil system for the plutonium isotopes were considerably higher than degrees of sorption noted for the raw waste/Puye soil system.

Although Carjo and Puye soils are similar in absolute characteristics, data in Table II-A show differences relative to ammonium acetate extractable ions. In general, the higher concentrations extracted are from Carjo soil, are cations, and possess a charge of 2 or greater. Differential extraction of ions from soils, as could occur with water of infiltration or with waste, will result in different ionic strengths of the solutions derived and will influence complexation or precipitation. A difference in pH and Eh may also result; those factors may influence sorption of the radionuclide by the soil. Fayette and Carjo have similar sorptive properties.

Under the conditions of the experiments, the uranium isotopes were sorbed to soils to a greater degree than were the plutonium isotopes. In part, the differences in sorption may be related to the differences in solubility, as was shown in Table VI, the higher degree of solubility yielding a higher percentage of ions available for exchange. The uranium ion would necessarily be positively charged for ion exchange on soil to proceed, but data obtained using synthetic ion exchange resins do not support that suggestion, however, soil influence on charge is not a part of that experiment. Data obtained to date do not explain the consistent differences observed between uranium and plutonium in radionuclide/soil reactions.

TABLE XII

SOLUBLE PLUTONIUM, AMERICIUM, AND CESIUM IN RAW WASTE AND IN RAW WASTE/CARJO AND FUQUAY SOIL SYSTEMS

System	Sampling Date	Mean Concentration ± S.E. × 10^2 (dpm/mℓ)			
		^{238}Pu	^{239,240}Pu	^{241}Am	^{137}Cs
Raw Waste	2/23/77	18.0 ± 0.6	2.0 ± 0.6	1.2 ± 0.2	---
Raw Waste/Carjo		16.7 ± 0.3	1.3 ± 0.3	1.6 ± [illegible]	---
% Sorbed		7 ± 3	35 ± 24	−33 ± 24	---
Raw Waste	4/28/77	125 ± 3	11.0 ± 0.2	3.6 ± 0.1	---
Raw Waste/Carjo		124 ± 4	11.0 ± 0.4	2.3 ± 0.2	---
% Sorbed		1 ± 4	0 ± 4	36 ± 6	---
Raw Waste	9/29/77	200 ± 10	17.9 ± 0.8	7.8 ± 0.6	230 ± 20
Raw Waste/Carjo		136 ± 6	12.2 ± 0.8	4.0 ± 0.4	6 ± 10
% Sorbed		32 ± 5	32 ± 5	49 ± 6	97 ± 4
Raw Waste	1/25/78	166 ± 4	14.5 ± 0.6	5.6 ± 0.6	280 ± 10
Raw Waste/Carjo		127 ± 3	11.2 ± 0.2	3.2 ± 0.1	6 ± 4
% Sorbed		23 ± 3	23 ± 3	48 ± 6	98 ± 1
Raw Waste	3/28/79	41 ± 3	4.0 ± 0.5	4.2 ± 0.5	25.0 ± 0.1
Raw Waste/Carjo		6.1 ± 0.4	0.9 ± 0.1	0.41 ± 0.06	0.02 ± 0.04
% Sorbed		85 ± 2	78 ± 4	90 ± 2	99.9 ± 0.2
Raw Waste	3/28/79	41 ± 3	4.0 ± 0.5	4.2 ± 0.5	25.0 ± 0.1
Raw Waste/Fuquay		150 ± 1	12.1 ± 0.2	8.5 ± 0.5	0.14 ± 0.05
% Sorbed		−266 ± 27	−203 ± 41	−102 ± 27	99 ± 0

TABLE XIII

SOLUBLE URANIUM IN RAW WASTE AND RAW WASTE/CARJO AND FUQUAY SOIL SYSTEMS

System	Sampling Date	Mean Concentration ± S.E. × 10^{2} (dpm/mℓ) ^{238}U	^{235,236}U	^{233,234}U
Raw Waste	2/23/77	4.1 ± 0.2	1.4 ± 0.2	8.9 ± 0.5
Raw Waste/Carjo		2.6 ± 0.1	0.75 ± 0.06	4.2 ± 0.1
% Sorbed		37 ± 4	46 ± 25	53 ± 3
Raw Waste	4/28/77	6.20 ± 0.05	2.27 ± 0.03	14.1 ± 0.2
Raw Waste/Carjo		3.13 ± 0.05	0.85 ± 0.02	5.8 ± 0.1
% Sorbed		49 ± 1	63 ± 1	59 ± 2
Raw Waste	9/29/77	8.3 ± 0.3	3.0 ± 0.2	17.9 ± 0.7
Raw Waste/Carjo		4.6 ± 0.1	1.20 ± 0.04	8.5 ± 0.3
% Sorbed		45 ± 2	60 ± 3	52 ± 2
Raw Waste	1/25/78	10.5 ± 0.5	4.3 ± 0.2	23.1 ± 0.2
Raw Waste/Carjo		7.6 ± 0.2	2.1 ± 0.2	14.5 ± 0.2
% Sorbed		28 ± 4	51 ± 5	37 ± 1
Raw Waste	3/28/79	7.2 ± 0.2	3.0 ± 0.2	17 ± 2
Raw Waste/Carjo		4.1 ± 0.3	0.8 ± 0.1	6.5 ± 0.4
% Sorbed		43 ± 14	73 ± 7	62 ± 5
Raw Waste	3/28/79	7.2 ± 0.2	3.0 ± 0.2	17 ± 2
Raw Waste/Fuquay		0.23 ± 0.03	0.26 ± 0.07	2 ± 2
% Sorbed		96.8 ± 0.5	93 ± 3	87 ± 10

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TABLE XIV

SOLUBLE PLUTONIUM, AMERICIUM, AND CESIUM IN RAW WASTE AND IN RAW WASTE/PUYE AND FAYETTE SOIL SYSTEMS

System	Sampling Date	Mean Concentration ± S.E. $\times 10^2$ (dpm/mℓ)			
		^{238}Pu	^{239,240}Pu	^{241}Am	^{137}Cs
Raw Waste	3/17/77	23 ± 1	1.7 ± 0.1	1.3 ± 0.2	---
Raw Waste/Puye		23 ± 3	2.0 ± 0.2	1.0 ± 0.1	---
% Sorbed		0 ± 15	−0.3 ± 14	23 ± 14	---
Raw Waste	9/29/77	200 ± 10	17.9 ± 0.8	7.8 ± 0.6	230 ± 20
Raw Waste/Puye		180 ± 10	17 ± 1	4.7 ± 0.3	9 ± 14
% Sorbed		10 ± 1	7 ± 7	40 ± 6	96 ± 6
Raw Waste	1/18/78	176 ± 2	15.3 ± 0.3	9.2 ± 0.8	280 ± 10
Raw Waste/Fayette		140 ± 4	12.6 ± 0.8	6 ± 1	0 ± 4
% Sorbed		20 ± 2	18 ± 5	34 ± 15	100 ± 0

TABLE XV

SOLUBLE URANIUM IN RAW WASTE AND RAW WASTE/PUYE AND FAYETTE SOIL SYSTEMS

System	Sampling Date	Mean Concentration ± S.E. $\times 10^2$ (dpm/mℓ)		
		^{238}U	^{235,236}U	^{233,234}U
Raw Waste	3/17/77	4.3 ± 0.1	1.7 ± 0.1	9.6 ± 0.1
Raw Waste/Puye		3.8 ± 0.1	1.1 ± 0.1	7.5 ± 0.2
% Sorbed		12 ± 3	35 ± 7	22 ± 2
Raw Waste	9/29/77	8.3 ± 0.3	3.0 ± 0.2	17.9 ± 0.7
Raw Waste/Puye		6.6 ± 0.2	2.0 ± 0.1	13.7 ± 0.7
% Sorbed		21 ± 4	34 ± 6	24 ± 5
Raw Waste	1/18/78	7.5 ± 0.3	2.9 ± 0.1	16.9 ± 0.2
Raw Waste/Fayette		3.8 ± 0.1	1.2 ± 0.1	7.4 ± 0.1
% Sorbed		49 ± 2	59 ± 4	56.2 ± 0.8

TABLE XVI

SUMMARY OF DEGREES OF SORPTION OF WASTE RADIONUCLIDES BY FOUR SOILS/RAW WASTE

Radionuclide and Isotope	Date	Soil Carjo	 Puye	 Fayette	 Fuquay
^{238}Pu	2/77	7 ± 3	---	---	---
	3/77	---	0 ± 15	---	---
	4/77	1 ± 4	---	---	---
	9/77	32 ± 5	10 ± 1	---	---
	1/78	23 ± 3	---	20 ± 2	---
	3/79	85 ± 2	---	---	−266 ± 27
^{239,240}Pu	2/77	35 ± 24	---	---	---
	3/77	---	0.3 ± 14	---	---
	4/77	0 ± 4	---	---	---
	9/77	32 ± 5	7 ± 7	---	---
	1/78	23 ± 3	---	18 ± 5	---
	3/79	78 ± 3	---	---	−203 ± 41
^{241}Am	2/77	−33 ± 24	---	---	---
	3/77	---	23 ± 14	---	---
	4/77	36 ± 6	---	---	---
	9/77	49 ± 6	40 ± 6	---	---
	1/78	43 ± 6	---	34 ± 15	---
	3/79	90 ± 2	---	---	−102 ± 27
^{137}Cs	2/77	---	---	---	---
	3/77	---	---	---	---
	4/77	---	---	---	---
	9/77	97 ± 4	96 ± 6	---	---
	1/78	98 ± 1	---	100 ± 0	---
	3/79	99.9 ± 0.2	---	---	99 ± 0
^{238}U	2/77	37 ± 4	---	---	---
	3/77	---	12 ± 3	---	---
	4/77	49 ± 1	---	---	---
	9/77	45 ± 2	21 ± 4	---	---
	1/78	28 ± 4	---	49 ± 2	---
	3/79	43 ± 14	---	---	96.8 ± 0.5
^{235,236}U	2/77	46 ± 25	---	---	---
	3/77	---	35 ± 0	---	---
	4/77	63 ± 1	---	---	---
	9/77	60 ± 3	34 ± 6	---	---
	1/78	51 ± 5	---	59 ± 4	---
	3/79	73 ± 7	---	---	93 ± 3
^{233,234}U	2/77	53 ± 3	---	---	---
	3/77	---	22 ± 2	---	---
	4/77	59 ± 2	---	---	---
	9/77	52 ± 2	24 ± 5	---	---
	1/78	37 ± 1	---	56.2 ± 0.8	---
	3/79	62 ± 5	---		87 ± 10

Interactions in the raw waste/Fuquay soil system are markedly different from those observed in the previously-discussed three systems. Net sorption of plutonium isotopes was not observed; in fact, the supernate obtained from the waste/soil reaction was higher in plutonium concentration than the raw waste supernate by a factor of about 2.5. The results presented in Table XII show percent sorptions of −266 ± 27 and −203 ± 41 for ^{238}Pu and ^{239,240}Pu, respectively.

The increase in the soluble nonsorbed fraction results from the interaction of a soil entity or entities with the insoluble fraction of the waste. One possibility is the effect of pH; the pH of the supernate from the Fuquay raw waste/soil system was 7.5; comparable pH values for the other three soil systems were Carjo 8.0, Puye 7.7, and Fayette 7.9. Further, Nishita[6] has shown a positive influence of manganese on the retention of certain radionuclides by soils. The manganese content of Fuquay is the lowest of the soils studied.

The lower pH of the Fuquay system may cause calcium carbonate to dissolve and release associated plutonium; hence, degree of carbonate saturation calculations were made. The theoretical K_{sp} of $CaCO_3$ for the waste system would be $10^{-8.32}$ (25°C). For the raw waste supernate and for the raw waste/Carjo supernate, K_{sp} values are $10^{-8.08\pm0.06}$ and $10^{-8.00\pm0.01}$. Those two systems were at, or very near saturation. However, the K_{sp} value for the waste/Fuquay supernate was $10^{-9.97\pm0.05}$; that supernate is undersaturated with respect to calcium carbonate. Fuquay soil has the lowest calcium concentration of the four soils (Tables II and II-A).

One possible explanation for the negative sorption in the waste/Fuquay system relates to the solubilization of a calcium carbonate precipitate from the insoluble fraction by the waste/soil solution and the release of its associated plutonium. The undersaturation of the waste/Fuquay soil supernate, coupled with the low calcium concentration in the soil, supports that suggestion. Reasons for the lack of sorption of the released plutonium are not immediately clear; however, maintenance of a negative charge on plutonium in the presence of soluble constituents from the soil could produce the observed result.

A second explanation relates to the presence of natural organic complexers. In the waste/Fuquay supernate discussed, the COD was 90 ppm, whereas in the companion experiment with the control soil (Carjo), COD was 30 ppm. The higher concentration of organic matter in the former is not *a priori* evidence for higher concentration of complexers but is suggestive.

A similar, though much smaller, increase in soluble americium was observed in the waste/Fuquay soil supernate indicating solubilization of that radionuclide also from the insoluble fraction and again emphasizing the similarity of reactions between plutonium and americium.

It is important to note that the results reported are for net solubilization/sorption. Both reactions are probably occurring and the results reported are the algebraic sums of those reactions. Under the conditions of the experiment, the two reactions can not be separated.

Iron and aluminum were also solubilized in the Fuquay/waste system; aluminum increased by a factor of 3 in the waste/soil supernate and iron by a factor of 5 over and above the respective concentration in the waste/Carjo system. The increase, especially for iron, supports a suggested action by organic complexers.

Differences in the sorption of uranium by Fuquay soil were also observed (Table XIII). In contradistinction to plutonium and americium, uranium sorption was positive. Evidence for solubilization of uranium can not be deduced in the case of positive sorption; however, as stated elsewhere, essentially all of the uranium was in solution in the waste used (Table IX).

In summary, with respect to raw waste, definite increases in the concentration of plutonium isotopes occur in the soluble fraction; increases are observed also in the concentration of uranium isotopes in that fraction. Some increases in the sorbable fraction are noted as the soluble fraction increases with time of storage; however, the sorbable fraction increases are not consistent and are not directly related to soluble fraction increases.

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Reactions between waste and Fuquay soil are different from those observed for Puye, Carjo, and Fayette. Fuquay would be desirable for the retention of uranium isotopes; however, it would be most undesirable for the retention of plutonium isotopes. The sorption of cesium is high on Fuquay and comparable to the other soils investigated. The results point out the need for waste/soil interaction data in the siting of waste burial pits.

Results from the batch studies conducted on the Carjo, Puye, Fayette, and Fuquay soils indicate differences among them with respect to sorptive capacity for the radionuclides in the waste. Cesium-137 is sorbed about equally on the four soils, the degree of sorption ranging from 95 to 100%.

Although the fate of all three fractions—filterable, soluble sorbable, and soluble nonsorbable—is important, it is the nonsorbable fraction that is of immediate importance. That fraction is free to migrate and in the absence of change will be the fraction that transports.

Data to date indicate that, of the four soils with raw waste, those with the characteristics of Fuquay are most desirable for immediate retention of the soluble uranium radionuclides; Carjo is more effective for the retention of soluble plutonium.

5. Differences in Sorption Among Different Soils—Treated Waste. Data for treated waste are presented in Table XVII; plutonium-238 was the only radionuclide present at detectable levels. A summary of data is presented in Table XVIII. The data indicate a change in sorbable fraction with time as it relates to interaction with Carjo soil. In the initial reaction with that soil on March 4, 1977 no sorption was observed; however, after 13 days of storage (and subsequently) sorption was observed. Sorption occurred in the three waste/Puye soil experiments and in the one waste/Fayette and one waste/Fuquay experiment. There is no positive indication of differences among soils as related to degree of sorption with the possible exception of Fuquay where a lower degree of sorption of ^{238}Pu was noted. The fact that some sorption occurred in the treated waste/Fuquay soil system, whereas solution occurred in the raw waste/Fuquay system, again suggests the importance of the influence of pH on sorption. The pH values for the two systems are raw waste/Fuquay supernate 7.50 and treated waste/Fuquay supernate 9.55.

All soils are more effective in the sorption of ^{238}Pu from treated waste than for comparable sorptions from raw waste. In the raw waste/soil systems, ^{239,240}Pu performed similar to ^{238}Pu with respect to sorption; the same holds true for treated waste. Based on the assumption that increased pH is a partial cause for the increased removal, then for plutonium isotopes an increase in the pH of the liquid in the shallow earth burial pit should provide benefaction of retention resulting in a decreased rate of transport for plutonium.

Experiments are underway with spiked treated waste to determine whether similar results will be obtained with the isotopes of uranium, cesium, and americium. Further, it is probable that other characteristics of the treated waste (Table V), especially its high sodium content, override soil influences. Serial dilution of waste and subsequent reaction with soil will simulate to some extent the dilution of waste as it passes through soil and mixes with ambient soil solution.

6. Column Studies. Passage of waste through columns of soil more nearly represents the real world condition of dynamic flow and allows for an evaluation of changing sorption with changing waste characteristics. Those characteristics will change as solubilization and sorption of waste and soil entities occurs.

Sorption studies were conducted in the column mode using the same soils as used in the batch studies. Wastes were collected and composited as described, but over a different time period. Methods are described by Essington, *et al.*[7]

TABLE XVII

SORPTION FOR ^{228}Pu BY FOUR SOILS/ TREATED WASTE

System	Date	^{238}Pu	System	Date	^{238}Pu
Treated Waste	3/4/77	1.6 ± 0.1	Treated Waste	10/6/77	2.9 ± 0.9
Treated Waste/Carjo		1.5 ± 0.3	Treated Waste/Carjo		0.4 ± 0.1
% Sorbed		6 ± 22	% Sorbed		86 ± 6
Treated Waste	3/17/77	2.7 ± 0.5	Treated Waste	6/22/78	2.4 ± 0.1
Treated Waste/Puye		0.1 ± 0.1	Treated Waste/Fayette		0.26 ± 0.02
% Sorbed		96 ± 4	% Sorbed		89 ± 1
Treated Waste	3/31/77	2.6 ± 0.5	Treated Waste	6/22/78	2.4 ± 0.1
Treated Waste/Carjo		0.4 ± 0.1	Treated Waste/Carjo		0.27 ± 0.09
% Sorbed		85 ± 5	% Sorbed		89 ± 4
Treated Waste	9/8/77	1.8 ± 0.3	Treated Waste	3/20/79	2.0 ± 0.1
Treated Waste/Puye		0.03 ± 0.1	Treated Waste/Fuquay		0.77 ± 0.08
% Sorbed		98 ± 6	% Sorbed		67 ± 4
Treated Waste	9/8/77	1.8 ± 0.3	Treated Waste	3/20/79	2.0 ± 0.1
Treated Waste/Carjo		0.4 ± 0.2	Treated Waste/Carjo		0.17 ± 0.03
% Sorbed		78 ± 12	% Sorbed		92 ± 2
Treated Waste	10/6/77	2.9 ± 0.9			
Treated Waste/Puye		0.4 ± 0.1			
% Sorbed		86 ± 6			

The initial soil column experiments were designed to provide information that could not be obtained from batch studies, e.g., the differential sorption of radionuclides with depth as waste passes through a soil profile. Further, the influence of change in ionic strength of the waste/soil solution as well as filtration mechanisms could be observed in soil columns.

If the fractional amount of the total column concentrations (A/A°) at discrete depths is plotted against the respective depths, a plot similar to that of Fig. 2 is obtained. The data presented are for sorption of ^{241}Am by soil; about 40 column volumes of waste were passed through the soil over a period of 3 months.

Although the activity in the column effluent was constant at about 50% of that in the influent after the third addition of waste (Fig. 3), equilibrium is not assumed. It is probable that the chemical dynamics of the waste/soil solution are such that a true equilibrium, if ever attained, would require unrealistic periods of time, hence, no attempt has been made to apply K_d values to the results.

TABLE XVIII

SUMMARY OF DEGREES OF SORPTION OF WASTE RADIONUCLIDES BY FOUR SOILS/TREATED WASTE

Radionuclide and Isotope	Date	Soil			
		Carjo	Puye	Fayette	Fuquay
^{238}Pu	3/77	6 ± 22	---	---	---
	3/77	---	96 ± 4	---	---
	3/77	85 ± 5	---	---	---
	9/77	---	98 ± 6	---	---
	9/77	78 ± 12	---	---	---
	10/77	---	86 ± 6	---	---
	10/77	86 ± 6	---	---	---
	6/78	---	---	89 ± 1	---
	6/78	89 ± 4	---	---	---
	3/79	---	---	---	67 ± 4
	3/79	92± 2	---	---	---

The high percentage removal of ^{241}Am by the silica sand layer (20-50 mesh) placed on the top of the soil column is of importance. About 90% of the total activity in the column was associated with the sand layer and because the ion exchange capacity of the acid washed sand is essentially zero, that removal is by filtration.

Table XIX lists the degrees of solubility as percentages of six radionuclides; ^{241}Am is highly insoluble in the waste used. Of the radionuclides listed in the table, ^{241}Am, ^{172}Hf, and ^{88}Y are the least soluble. The removal of those three radionuclides by Puye soil is shown in Fig. 4; the percentage removals by the sand layer are comparable at about 90%. Significant amounts of those three radionuclides could be removed from pit seepage at a waste/soil interface. In the Puye soil, more than 99% would be removed within the first 7.5 cm of the column. Comparable data have been obtained for Carjo and Fuquay soils.

A second group of radionuclides, ^{137}Cs, ^{83}Rb, and ^{85}Sr, are more than 50% soluble in the waste under study. Removals by the sand layer were about 20% for ^{137}Cs and ^{85}Sr and about 15% for ^{83}Rb, reflecting their solubility. However, about 55% was removed by the first 2.5 cm layer of soil in the column (Fig. 5) suggesting the importance of charge associated with soluble entities or of finer particulate matter that was filtered by the soil but not by the sand.

The presence of ^{137}Cs at depth of 20 cm was not expected in view of its persistent positive charge as determined by ion exchange techniques. The results emphasize the importance of the waste/soil solution as a factor in determining the characteristics of the entity being transported or sorbed.

Radionuclides are sorbed to particulate matter which is filterable, as was discussed earlier. Because particulate matter in the waste and in the soil may vary from macro down to submicron size, removal by filtration may also vary with the soil structure. The transport of submicron particles and their associated radionuclides would be expected to reach greater depths than would the more nearly macro particles. A range of small particles may be reached where it is difficult to determine whether they are in solution or are discrete particles; those

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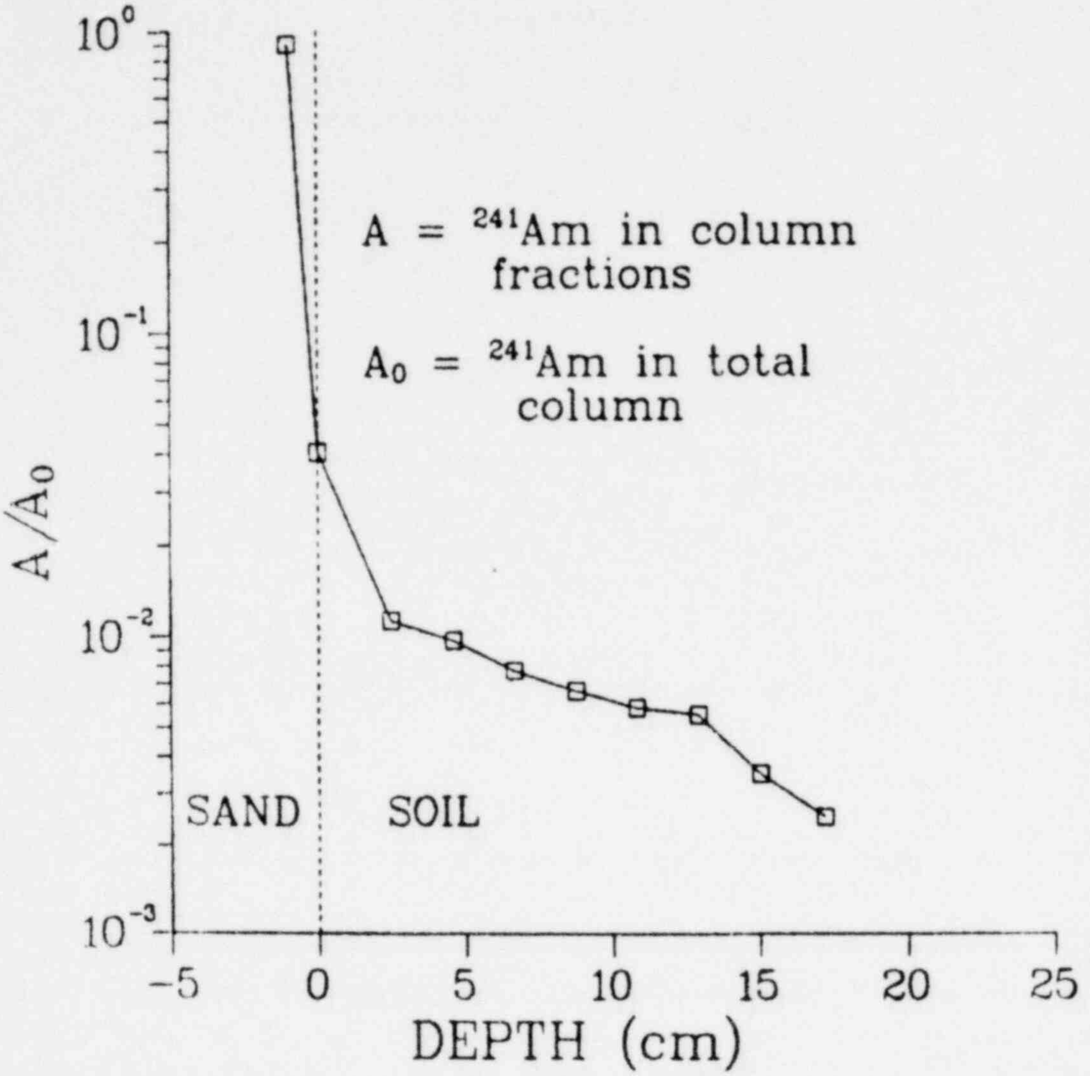

Fig. 2.
Retention of ^{241}Am in sand and soil.

micro particles may transport in a manner similar to negatively charged ions. Attenuation of the associated radionuclides may be enhanced if the particulates are made to agglomerate in order to improve filtration. A study of particle size and associated radionuclides is underway using gel chromatography as a sizing medium.

B. Particulate Studies

1. Autoradiography. The association of a high percentage of radioactivity with the insoluble fraction is one important mechanism of attenuation. Elucidation of the mechanism and its application could lead to increased removals of radionuclides from the waste solution and filtration at the liquid waste/soil interface of a burial pit. Autoradiographic and visual techniques were employed to demonstrate insoluble particulate matter and the associated radionuclide. Results are presented pictorially in Figs. 6 through 9.

The insoluble fraction from centrifuged raw waste and the soluble, nonsorbable fraction obtained from the raw waste/soil interaction after centrifugation were allowed to expose sensitive film. Development of the exposed film displayed the tracks caused by alpha emissions; embedding techniques permitted observation of the associated particles.[8]

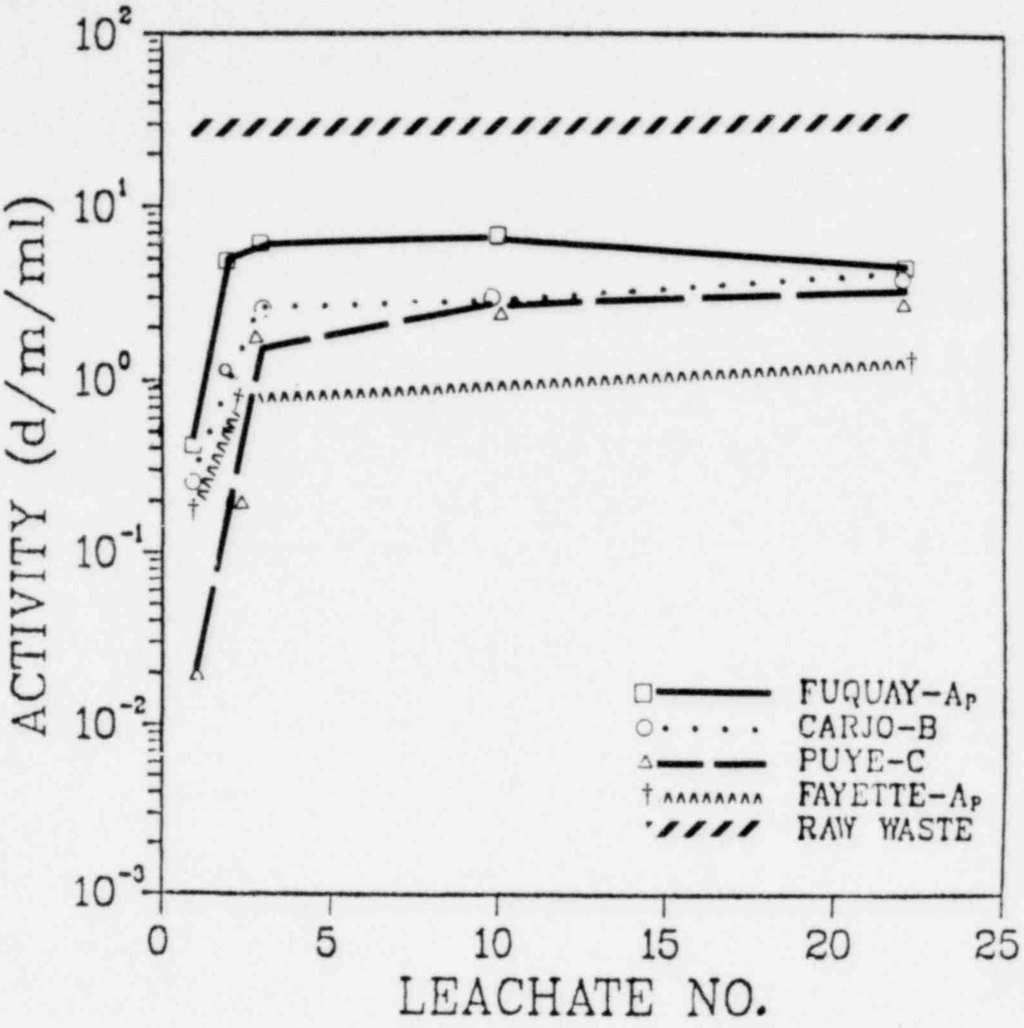

Fig. 3.
Plutonium-238 in soil column leachates.

The star pattern seen in Fig. 6 is typical of a discrete particle of alpha radioactive material. Although the raw waste contained some discrete particles, they were few in number; colloids are possible; polymers and/or ions predominate.

The discrete particles will be removed by soil filtration of the insoluble fraction. Price and Ames[9] observed a predominance of particulates in the first 30 cm beneath the floor of a disposal trench, also indicating a filtration mechanism.

In Fig. 7 the tracks produced by alpha emissions are randomly associated with an agglomerate. The agglomerate is crystalline in part and the association is probably by specific ion exchange; the agglomerate is about 18 μm nominal diameter and would be removed by filtration at the pit soil surface. In contradistinction to a PuO_2 discrete particle, which is very slowly soluble, the crystalline particle will respond to the environmental solution; it could dissolve, thus releasing the radionuclide, or could grow, thus entrapping more activity. Those particles were also analyzed by x-ray diffraction; about 60% was identified as calcium carbonate and about 30% was identified as an iron silicate.

Other agglomerates are present. The agglomerate seen in Fig. 8 is amorphous and may be organic or inorganic aluminum or iron. If organic, its fate will be determined in part by the microbiological population. If inorganic, reactions as above will be determinate.

TABLE XIX

PER CENT OF INSOLUBLE RADIONUCLIDES IN RAW WASTE COLUMN STUDIES

Nuclide	Insoluble
^{241}Am	98.8
^{88}Y	98.2
^{175}Hf	99.9
^{137}Cs	40
^{83}Rb	33
^{85}Sr	46

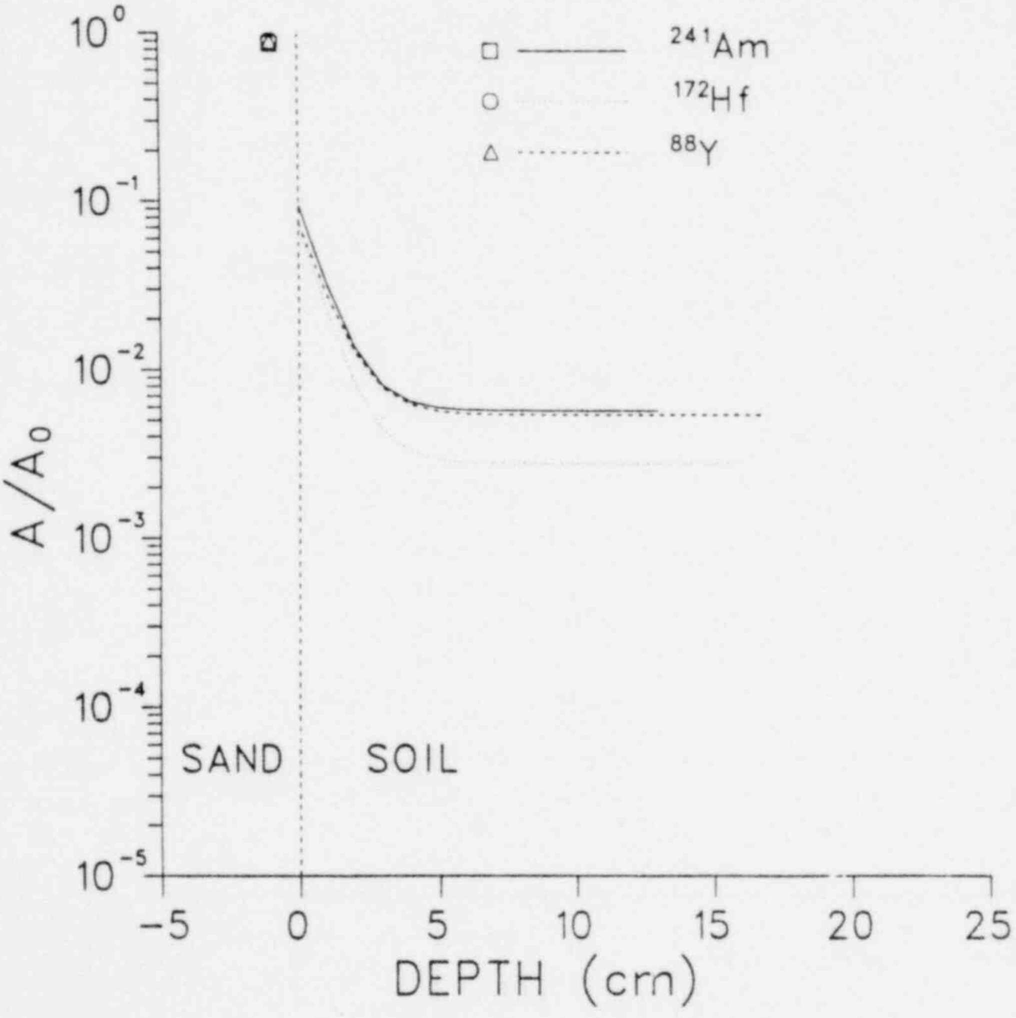

Fig. 4.
Distribution of highly insoluble radionuclides in sand and soil.

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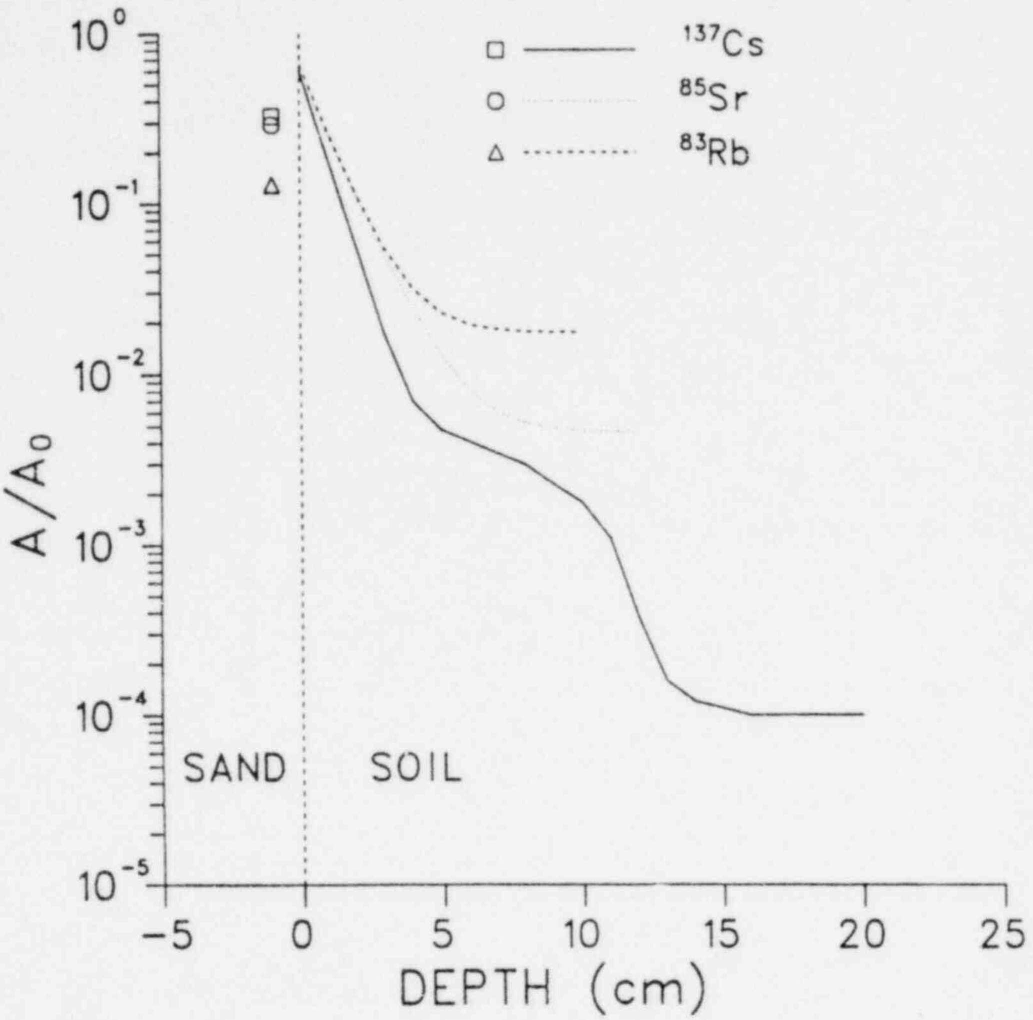

Fig. 5.
Distribution of soluble radionuclides in sand and soil.

The radioactivity associated with the soluble-nonsorbable fraction is demonstrated in Fig. 9. The single tracks appear to be nonassociated and may arise from polymers, small colloids, or possibly ions. However, an association may exist with inert particles that are not visible at the magnifications used (250X). That material will not be filtered and would be free to migrate depending on its charge.

2. Charge Characteristics. Mechanisms other than precipitation are involved in the attenuation of radionuclides as their solutions react with soils. One such mechanism is that of ion exchange. An ion or polymer in solution and possessing a net positive charge will be exchanged for a positively charged entity, which is sorbed on a solid whose net charge is negative. In like manner, a net negatively charged entity will be sorbed to a net positively charged particle. The soil micelle possesses a net negative charge and cations are sorbed; the sorption of anions by soil is a rare exception. Whether the indicated exchange will occur is determined by chemical and physical characteristics of the soil and solution, such as pH, Eh, ionic strength, ionic radii, competing ions, net charge of both entities, and binding energy.

The nature of net charge of the radionuclides in the soluble fraction was investigated. Cation exchange resin (CER) and anion exchange resin (AER), as well as a mixed bed of those two, were employed in the column mode to determine probable charge. Two CER columns were

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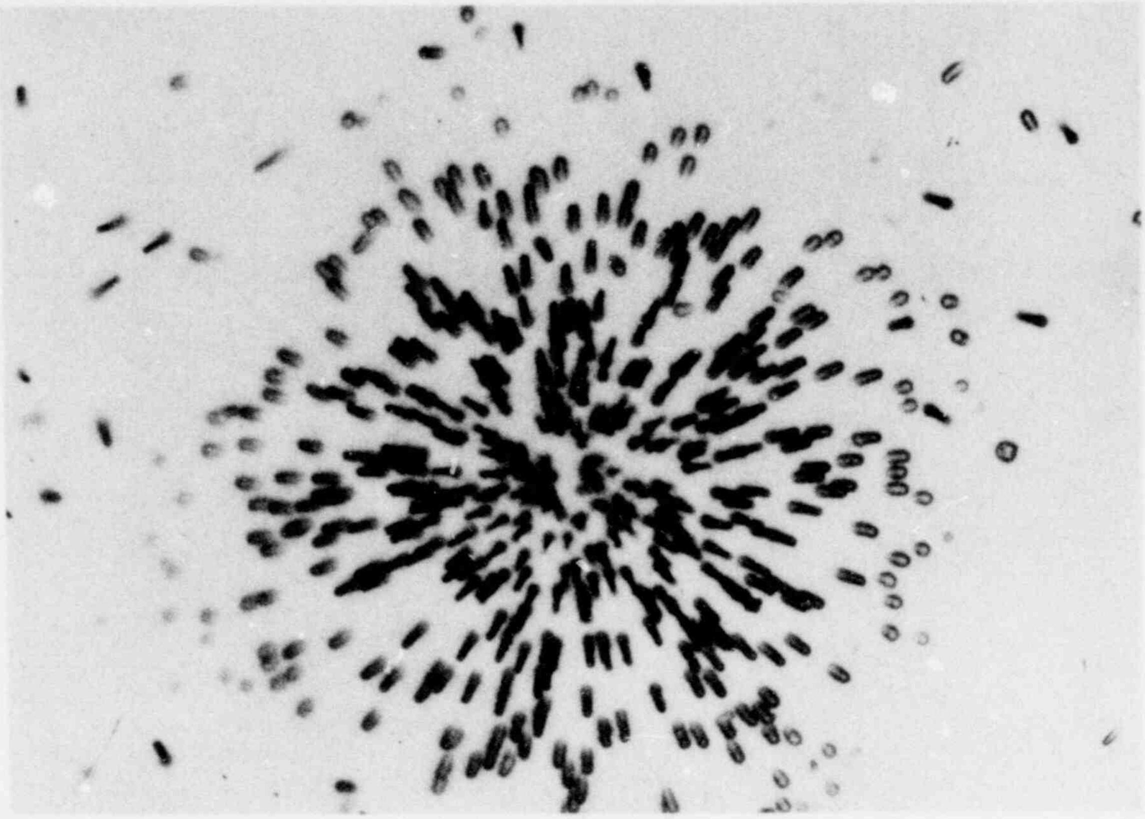

Fig. 6.
Autoradiograph of discrete radioactive particles from raw waste solids.

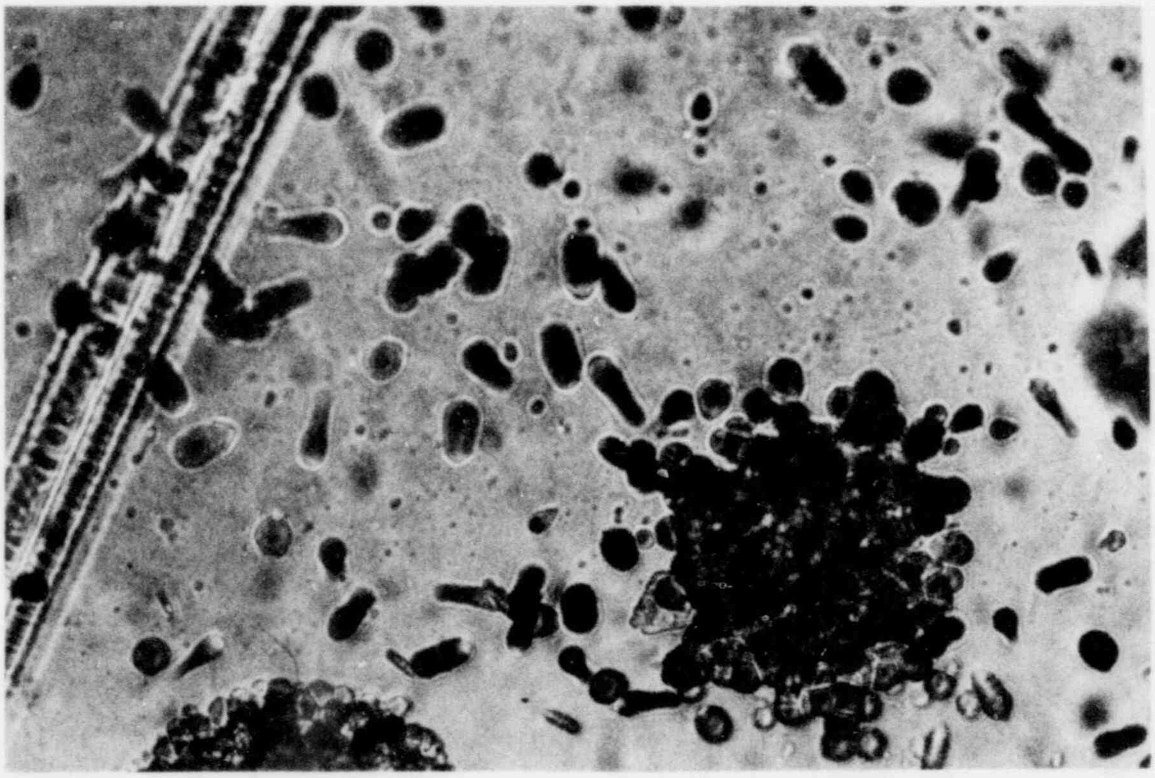

Fig. 7.
Autoradiograph of crystalline particle from raw waste solids.

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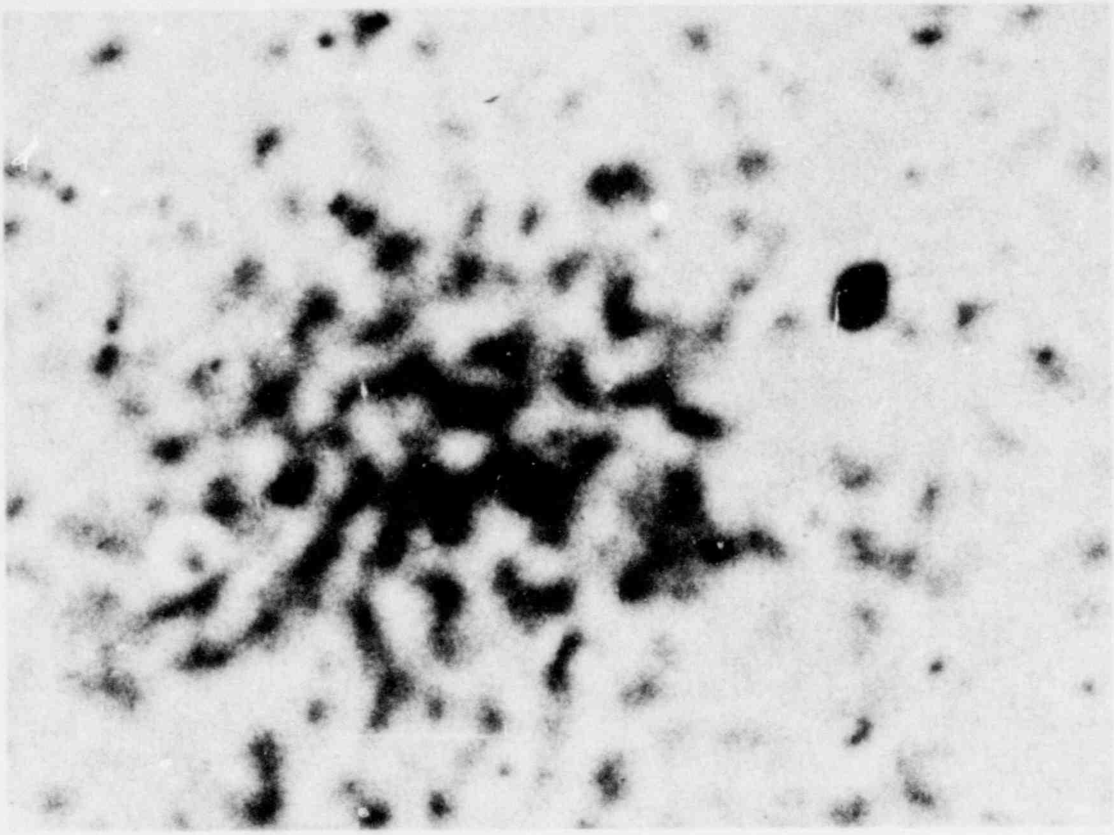

Fig. 8.
Autoradiograph of amorphous agglomerate from raw waste solids.

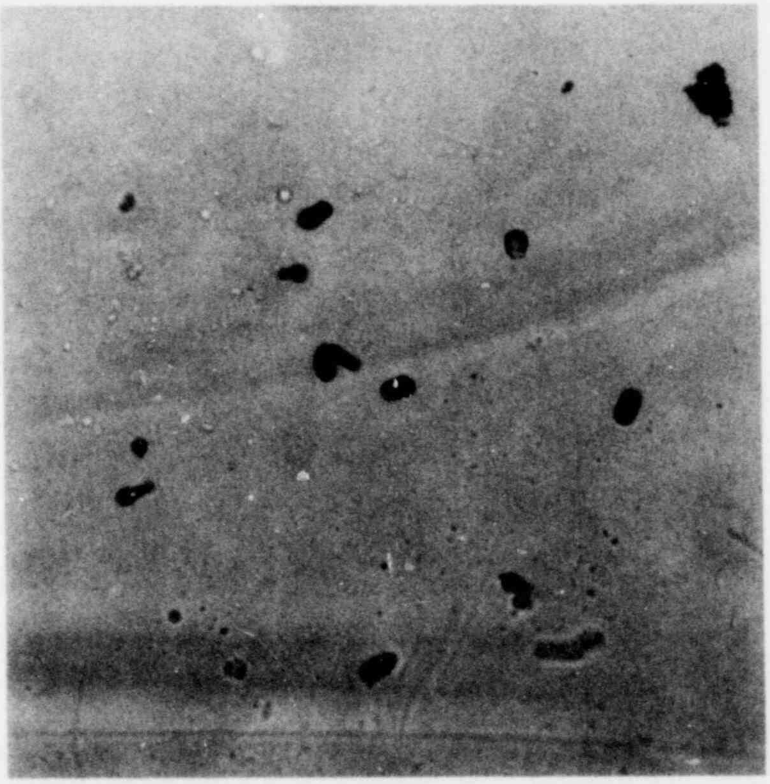

Fig. 9.
Autoradiograph of nonsorbable-soluble fraction from raw waste.

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regenerated—one to provide an H^+ form and one to provide an Na^+ form. In like manner, two AER columns were regenerated to provide a Cl^- form and an OH^- form. The pH of the column solution and effluent would be determined by the exchanged ions. Results for three experiments using the supernate from centrifuged raw waste are presented in Table XX. In Experiment I, the supernate as obtained (pH = 8.6) was passed through the respective columns. In Experiment II, the pH of the supernate was adjusted to 10.0 and passed through similar columns. Experiment III was performed using treated waste supernate; in this experiment only ^{238}Pu and ^{239,240}Pu were present at a detectable level.

The concentrations of radionuclides in the effluent from a mixed bed column represent those radionuclides that have a zero charge. In those cases where effluents from CER, AER, and mixed bed do not have essentially the same pH values regardless of regenerant, estimates of charge partition have been made by inspection and interpolation. Thus, a certain degree of uncertainty has been introduced and has been noted by "~." The data for plutonium and cesium obtained from Experiment II are comparable to those from Experiments I and III. The data for ^{241}Am (Experiment II) in which the pH of the waste was adjusted to 10 are not comparable to those from Experiment I and do not provide a clue regarding species charge. The formation of a stable polymer or colloid may be involved. The observation is important to the transport of ^{241}Am and will be investigated further.

The influence of pH on the ratios of negative, zero, and positive charge is of interest. In all cases except for cesium and the anomaly noted for ^{241}Am, the percentage of negative charge increases from a pH of 2.7 to a pH of 8.8. Entities in the soluble fraction leaving a burial pit at solution pH values of about 4 to 9 would contain the highest percentage of nonsorbable radionuclide. Again, the stability of the negative charge with time is not known but at the point of contact with the soil the entities are most potentially mobile.

Cesium-137 differs from the other radionuclides reported in that it is predominantly positively charged regardless of pH. Cesium should, and does, readily sorb to most soils.

Although a pH below 4.3 in these experiments results in a degree of positive charge, that pH also results in a degree of negative and zero charge; the latter would migrate. Ion exchange sorption benefaction by pH adjustment is confounded by the lack of a pH value that will produce a maximum of positive charge and at the same time reduce zero and negative charge to a minimum.

Alberts, et al.[10] reported a negative charge on plutonium species found in Lake Michigan waters. The pH of the water was approximately 8. The water was supersaturated with respect to calcium carbonate.

It is important to note that the above results were obtained using synthetic ion exchange resins having a high exchange capacity relative to that of soil; further, any influence of soil solution ionic strength is lacking. However, the high percentage of negative charge at a pH of 8.8, comparable to the 8.6 of the raw waste supernate, strongly suggests that the nonsorbable fraction noted in waste/soil interactions is due in part to radionuclides that retain a negative charge. It is concluded that some radionuclides will always "weep" from a soil containment system.

V. THEORETICAL STUDIES

A. Influence of Soils on the Particulate Charge Distribution

The partition of the soluble fraction into sorbable and nonsorbable may result from species change of charge. In the raw waste system considering pH, Eh, CO_3^{2-} and Fig. 10, the expected predominant species could be $PuO_2OHCO_3^-$. Experimental data reported in Section IV.B.2 also show a predominance of negatively charged species; theoretically for the negatively charged

TABLE XX

PERCENTAGE DISTRIBUTION OF CHARGE AMONG SOLUBLE RADIONUCLIDES

Column Effluent	^{238}Pu			^{239,240}Pu			^{241}Am			^{238}U			^{235,238}U			^{233,234}U			^{137}Cs		
pH	+	−	0	+	−	0	+	−	0	+	−	0	+	−	0	+	−	0	+	−	0
Experiment I—Raw Waste Supernate—pH 8.6																					
2.5 and 2.8	26	74	0	30	70	0	100	0	0	97	3	0	95	5	0	99	1	0	100	0	0
4.3 and 4.4	0	98	2	0	90	10	0	100	0	0	100	0	0	100	0	0	100	0	100	0	0
8.8	0	~100	~0	0	~100	~0	20	~80	~0	0	~100	~0	8	~92	~0	9	~91	~0	100	0	0
11.8	0	100	0	0	100	0	0	100	0	0	99	1	0	100	0	0	100	0	100	0	0
Experiment II—Raw Waste Supernate—pH Adjusted to 10																					
2.5 and 2.7	55	44	1	50	50	0	15	44	41	100	0	0	100	0	0	99	1	0	100	0	0
5.5 and 6.0	0	100	0	0	100	0	28	48	24	0	100	0	0	100	0	0	100	0	100	0	0
9.9	10	~90	~0	12	~88	~0	26	~45	~29	14	~86	~0	3	~97	~0	9	~91	~0	100	0	0
11.8	0	100	0	0	100	0	~26	42	~22	0	100	0	0	100	0	0	100	0	100	0	0
Experiment III—Treated Waste Supernate—pH 12.2																					
2.0 and 2.2	100	0	0	100	0	0	---	---	---	---	---	---	---	---	---	---	---	---	100	0	0
6.3	0	~100	~0	0	~100	~0	---	---	---	---	---	---	---	---	---	---	---	---	100	0	0
11.6 and 11.7	0	100	0	0	100	0	---	---	---	---	---	---	---	---	---	---	---	---	100	0	0

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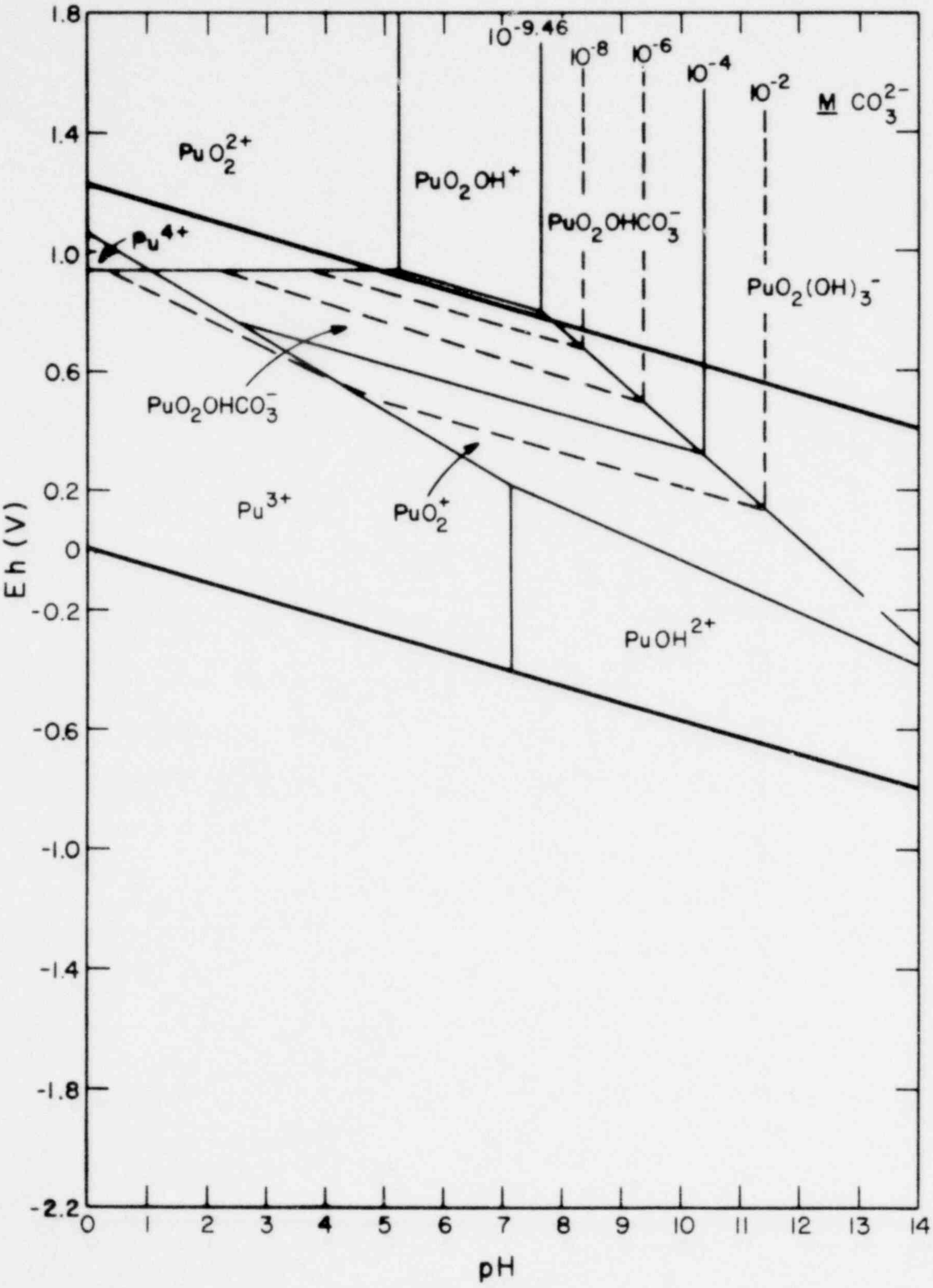

Fig. 10.
Predicted speciation of soluble plutonium as a function of pH, Eh, and CO_3^{2-} concentration.

species, an appreciable fraction of those radionuclides would not sorb to soil. That some sorption does occur leads to questions regarding the influence of the soil solution on the stability of the negative charge associated with waste radionuclides. If changes in the ratio of negative to positive species are observed when those values for the soluble waste/soil system are compared to those for the soluble waste system, an influence of soil solution on species charge is indicated.

Values for the ratio $PuO_2OHCO_3^-/PuO_2^+$ were calculated from experimental data using the respective values for Eh, CO_3^{2-}, and OH^-; the results are reported in Table XXI. Absolute values will vary depending on the stability constants used; there are a number of such values in the literature. The values used here are those used by Polzer and Miner.[11] It is the relationship among the values as calculated rather than the absolute value that is important to this interpretation.

For the two soils Fayette and Carjo, the ratios obtained are considerably lower than those ratios obtained for the soluble waste systems. That is, there is a reduction in the concentration of the negatively charged species when waste interacts with those two soils.

The reduction of negatively charged species would result in a benefaction of attenuation and for the soils investigated the secondary container (burial pit soil) would act to reduce the rate of, and possibly the extent of, transport through increased sorption of the resulting positively charged species.

The differences in the ratio vary among soils. In theory, the most desirable soils for attenuation would be those that result in the lowest ratio. It should be emphasized that the data are derived from theoretical calculations based on two species only; other factors based on the interactions of the waste and soil solutions are important. However, the importance of the soil in changing the charge of a species is indicated.

TABLE XXI

INFLUENCE OF TWO SOILS ON CHARGE DISTRIBUTION IN SOLUBLE RAW WASTE

System	Charge Distribution[a]
Soluble Raw Waste	0.3
Soluble Raw Waste/Fayette	0.003
Soluble Raw Waste/Carjo	0.006

---

[a] $$\frac{[PuO_2OHCO_3^-]}{[PuO_2^+]} = 10^{18.2}[OH^-]\,[CO_3^{2-}]\,10^{\left[\frac{-0.94+Eh}{0.0592}\right]}$$

B. Precipitates

Both the raw and treated waste contained particulate matter having a wide range of particle size. The chemical composition of the two wastes suggests several possibilities relative to precipitation, e.g., carbonate, phosphate, calcium, magnesium, iron, and aluminum; the formation of a precipitate will relate to pH, solubility product, concentration, and competing ions. The removal of radionuclides from waste by controlled precipitation is a treatment method of long standing.

That radionuclides in the waste are associated with the inherent particulate matter and are removable by centrifugation was shown in Table VI. For raw waste, plutonium and americium species are the least soluble and are assumed to be strongly associated with particulate matter; that assumption is supported by column data (Section IV.A.6).

Calcium as lime is used at an elevated pH in the treatment of some radioactive wastes. The floc that forms occludes certain radionuclides, resulting in decontamination of the waste; post precipitation is often observed in the treated effluent and may be due in part to solution of carbon dioxide and formation of carbonates. On the other hand, carbonate ion may also form a soluble complex with plutonium.

In the batch studies, radionuclides were removed on reaction of the waste with soil; at least part of the removal is associated with particulate removal on centrifugation. Removal of some other part of the concentration in the soluble fraction may be accomplished by several mechanisms. One mechanism would involve the precipitation reactions discussed above; another mechanism would involve ion exchange. The two mechanisms can not be separated in batch studies. However, in a solution supersaturated with calcium carbonate, precipitation should occur and if some radionuclides are occluded, reductions in their concentrations should be observed. Results from an experiment to determine the influence of degree of $CaCO_3$ saturation are presented in Table XXII.

A theoretical calculation for the degree of calcium carbonate saturation in the soluble raw waste fraction and in the soluble raw waste fraction that had been equilibrated for an additional five days does indicate a change.

The degree of calcium carbonate saturation in the soluble fraction of raw waste immediately after centrifugation is calculated to be 2.4 times higher than that after a 5 day equilibration period for an aliquot of the same sample. Concurrently, there was a reduction in calcium concentration by a factor of about three. Plutonium-238, ^{239,240}Pu, and ^{241}Am concentrations were also reduced; concentrations of uranium species did not change. The results suggest that some fraction of the radionuclides, though possibly small, is removed by a precipitation reaction involving calcium and carbonate ion.

Results from further investigations of the theoretical importance of precipitation in the removal of radionuclides from waste are reported in Table XXIII. The supernate from a centrifuged raw waste, pH 8.6, was adjusted to pH 12 and aged for a period of 2.5 months. A fine grained, white precipitate formed during the period of aging. The solution was then recentrifuged and the supernate analyzed for the radionuclides listed. Again, the highest percentages of removal with the precipitate were those for the plutonium species and ^{241}Am.

The precipitate was not carbonate as shown by a qualitative test. Examination under the light microscope revealed a crystalline material similar to bayerite, a polymorph of aluminum hydroxide. Such post precipitation is common in many clarified waste systems.

Table XXIV reports the results of radiochemical analyses for the precipitate, the supernate from centrifugation of the precipitates, and the alcohol wash for the precipitates. The alcohol wash was employed to remove radionuclides that may have been associated with the liquid in the precipitate fraction and not specifically associated with the precipitate *per se*. The precipitate removed essentially all of the plutonium species and ^{241}Am. None of the ^{137}Cs was removed by the precipitate.

TABLE XXII

CHEMICAL AND RADIOCHEMICAL PROPERTIES OF SOLUBLE RAW WASTE AND EQUILIBRATED SOLUBLE RAW WASTE

	Soluble Raw Waste	Equilibrated Soluble Raw Waste[a]
Chemical		
pH	8.37 ± 0.04	8.47 ± 0.01
Ca (moles/liter)	$(9 \pm 1) \times 10^{-4}$	$(3.1 \pm 0.5) \times 10^{-4}$
CO_3 (moles/liter)	$(2.2 \pm 0.2) \times 10^{-4}$	$(2.70 \pm 0.07) \times 10^{-4}$
Degree of $CaCO_2$ Saturation		
$\left(\frac{IAP}{K_{sp}}\right)$[b]	17 ± 3	7 ± 1
Radiochemical (dpm/mℓ)		
^{238}Pu	1.76 ± 0.01	1.33 ± 0.01
$^{239,240}Pu$	$(1.54 \pm 0.03) \times 10^{-1}$	$(1.10 \pm 0.04) \times 10^{-1}$
^{241}Am	$(7.2 \pm 0.5) \times 10^{-2}$	$(4.9 \pm 0.1) \times 10^{-2}$
^{238}U	$(9.7 \pm 0.1) \times 10^{-2}$	$(8.2 \pm 0.0) \times 10^{-2}$
$^{235,236}U$	$(3.3 \pm 0.1) \times 10^{-2}$	$(3.2 \pm 0.2) \times 10^{-2}$
$^{233,234}U$	$(2.10 \pm 0.03) \times 10^{-1}$	$(2.12 \pm 0.01) \times 10^{-1}$

---

[a] Equilibrated soluble raw waste is waste that was equilibrated for 5 days after the insoluble fraction had been removed.

[b] IAP—ion activity product.

[c] K_{sp}—solubility product.

Although the transuranics could be precipitated at a high pH (12) and removed by filtration at the liquid/soil interface of the disposal pit, no ^{137}Cs would be thus removed and it would be free to migrate; extent of migration would be determined by its charge.

VI. ALGAE STUDIES—SORPTION

Algae are photosynthetic and actively metabolize only at or near the surface of soils or in surface water. However, algae have been shown to be scavengers for some radionuclides and hence might be important in attenuating them should the radionuclides reach a surface soil or surface water.

Algae were allowed to develop for a period of 2.5 months in raw waste in which the pH had been adjusted to 6.0. The algae were then removed by centrifugation and the supernate analyzed for radionuclide content. Results are presented in Tables XXV and XXVI. The algae effectively removed plutonium and uranium species, only 31% of the original ^{137}Cs was associated with the algal mass.

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TABLE XXIII

REMOVAL OF RADIONUCLIDES FROM A SOLUBLE RAW WASTE SOLUTION BY PRECIPITATION[a]

Radionuclide	Per Cent Removed
^{238}Pu	66
^{239,240}Pu	63
^{241}Am	94
^{238}U	11
^{235,236}U	10
^{233,234}U	11
^{137}Cs	0

---

[a] The pH of the soluble raw waste was adjusted to 12.0 and the solution then aged for 2.5 months.

TABLE XXIV

CONCENTRATIONS OF RADIONUCLIDES ASSOCIATED WITH THE POST PRECIPITATE AND WITH ITS SOLUTION

Radionuclide	Washed[a] Precipitate (dpm/sample)	Supernate (dpm/mℓ × 10^2)	Alcohol Wash (dpm/sample)
^{238}Pu	269 ± 6	7.4 ± 0.2	1.9 ± 0.1
^{239,240}Pu	21.7 ± 0.5	0.66 ± 0.04	0.08 ± 0.02
^{241}Am	76.4± 0.6	0.30 ± 0.02	0.38 ± 0.05
^{238}U	6.7 ± 0.2	4.5 ± 0.1	0.02 ± 0.01
^{235,236}U	2.17 ± 0.08	1.55 ± 0.05	0.03 ± 0.02
^{233,234}U	14.8 ± 0.3	9.9 ± 0.2	−0.1 ± 0.04
^{137}Cs	−10 ± 7	260 ± 10	6 ± 4

---

[a] Volume of soluble raw waste from which the precipitate was obtained was estimated to be about 770 mℓ.

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TABLE XXV

REMOVAL OF RADIONUCLIDES FROM A SOLUBLE RAW WASTE SOLUTION BY ALGAL GROWTH[a]

Radionuclide	Per Cent Removed
^{238}Pu	94
^{239,240}Pu	94
^{241}Am	86
^{238}U	92
^{235,236}U	92
^{233,234}U	92
^{137}Cs	31

---

[a] The pH of the soluble raw waste was adjusted to 6.0 and solution then aged for 2.5 months.

TABLE XXVI

CONCENTRATIONS OF RADIONUCLIDES ASSOCIATED WITH ALGAE AND WITH ITS SOLUTION

Radionuclide	Washed Algae[a] (dpm/sample)	Supernate (dpm/mℓ × 10^2)	Alcohol Wash (dpm/sample)
^{238}Pu	202 ± 5	2.48 ± 0.09	1.5 ± 0.1
^{239,240}Pu	17.0 ± 0.5	0.26 ± 0.03	0.18 ± 0.05
^{241}Am	44.3 ± 0.5	1.41 ± 0.05	0.14 ± 0.04
^{238}U	23.1 ± 0.5	0.39 ± 0.03	0.13 ± 0.03
^{235,236}U	7.9 ± 0.2	0.13 ± 0.02	0.01 ± 0.03
^{233,234}U	51 ± 1	0.88 ± 0.05	0.17 ± 0.05
^{137}Cs	440 ± 30	190 ± 10	26 ± 5

---

[a] Volume of soluble raw waste from which the algae were obtained was approximately 520 mℓ.

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During the 2.5 month growth period the pH of the solution increased from 6.0 to 10.5, reflecting the metabolic activity of the organisms and the possible production of amides and amines. The possibility of precipitate formation can not be ruled out; any precipitate that might have formed could not be separated from the algae under the conditions of the experiment. Hence, the percent removal reported in Table XXV may include some removal by precipitates. However, the generally high solubility of cesium salts would preclude extensive removal by precipitation and the 31% removal is considered due to algae alone.

Radionuclides attenuated by algae merely shunt the radionuclide into a biologically dynamic section of the food web. The temporary attenuation is of little value to long-term transport control, especially in soils. In a series of treatment ponds, some mechanism for algal removal may be of value; however, the algal mass must then be disposed. Algae as a source of food for certain animals may make their sorption characteristics less than desirable.

VII. SUMMARY

Two wastes and four soils have been intensively investigated with respect to their interactions to determine the influence of their physical and chemical characteristics on the degree of sorption of waste radionuclides.

The interactions of soils with the wastes were studied in the batch and column modes. The degrees of retention were investigated for ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{238}U, ^{235,236}U, ^{233,234}U, and ^{137}Cs.

Three fractions, insoluble, soluble sorbable, and soluble nonsorbable, were demonstrated in both wastes. The nonsorbable fraction is considered of immediate importance because it will be mobile, provided its characteristics are not changed during transport through the soil.

The insoluble fraction contained the highest concentration of radionuclides and is the fraction that would be removed by filtration. Filtration then, is an important mechanism in decontamination of the burial pit liquid that seeps from the pit. The ultimate fate of the insoluble fraction is not known; a degradation with time may release the associated radionuclides and permit eventual transport.

The partition of radionuclides between the soluble sorbable and the soluble nonsorbable fraction changes with storage time. In general, the soluble fraction of raw waste increases with time; the increase is not related to sorbability. In the case of treated waste, the soluble fraction does not increase with time, but the sorbable fraction does. Plutonium-238 in waste in an earthen pit at a pH of about 12 will be more amenable to sorption resulting in retardation of transport.

The sorption characteristics of the different soils for the different radionuclides have been defined. Some data, e.g., sorption of radionuclides by soils, are considered quantitative; other data are theoretical or require additional information for quantification. Data relative to the following parameters are presented: (1) the effects of filtration at a waste/soil interface, (2) precipitation (including post precipitation), (3) ion exchange reactions, (4) net charge on the radionuclide entity, (5) radionuclide/particle association, and (6) sorption by algae.

Under the conditions of the experiment and with the soils studied, there were statistical differences in degrees of sorption of waste radionuclides; the differences were demonstrated among soils and among radionuclides. There is some indication of differences in sorption among isotopes of the same radionuclide. The results indicate that a soil with the physical and chemical characteristics of the Carjo B horizon soil is most desirable from the standpoint of retention of plutonium by sorption; the Fuquay soil is most sorptive for uranium isotopes.

In the wastes investigated, a predominance of negatively charged species of radionuclides exists above a pH of about 4. The negatively charged species would not sorb to the negatively charged soil micelle and hence would be mobile as long as the negative charge persists. However, based on calculations from experimental data, the interaction of the waste with soil reduced the negative charge; from present data, that reduction is interpreted as an increase in the potential for sorption. The extent to which that charge may perturbate a prediction for a system requires further study. It is probable that some seepage of radionuclides from an earth pit will always occur.

Precipitates, including post-precipitates, were shown to occlude waste radionuclides. Autoradiographic techniques demonstrated association of alpha radionuclides with crystalline and amorphous particles. The crystalline particles were shown to be about 60% $CaCO_3$ by x-ray diffraction, indicating the importance of calcium carbonate in the removal of some radionuclides, possibly by specific ion exchange. The amorphous material was not identified but may be organic or inorganic iron or aluminum. Some radionuclides were removed by post precipitation; the precipitate was tentatively identified, by microscopic examination, as an aluminum compound.

The extent to which precipitates remove radionuclides and the ultimate fate of the precipitate in the soil solution at distances from a shallow earth burial pit require further investigation. Data regarding their extent and stability are necessary for predictive purposes.

An algal culture developing in waste where the pH had been adjusted to 6 was assayed for radionuclide content. Algae effectively scavenged all radionuclides. However, decontamination of shallow earth burial pit effluents by algae (in holding ponds) only serves to transfer the radionuclides to a more biologically dynamic system, which forces their entrance into the food web, thus creating further problems.

One general conclusion, based on results obtained to date, is that the soil as a container for buried waste has a number of undesirable features. A contained system, which provides for chemical and physical treatment of burial pit effluents, could solve problems that have been indicated by the research reported here.

It should be emphasized again that the above conclusions are based on four soils and two wastes only. Results from other soils now being investigated are expected to provide additional information regarding attenuation of radionuclides from waste.

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Retention of waste radionuclides by four soils of different types was determined using the batch and column methods. Raw and treated liquid wastes from a large laboratory complex were used. Three fractions identified in each waste were (1) insoluble, (2) soluble and sorbable by soil, and (3) soluble but nonsorbable by soil. The soluble fraction (<0.05μm) in raw and treated wastes increased with storage time but the increase did not directly relate to the amount retained by the soil. The degree of retention of each radionuclide is influenced by both soil type and waste composition. Ninety-five to one hundred percent of raw waste ^{137}Cs was retained by all soils. Plutonium isotopes and ^{241}Am were least retained by the soils; uranium isotope retention was intermediate. Reaction of a Fuquay soil with the insoluble fraction of the waste resulted in a net dissolution of Pu and Am. Two of the factors investigated that could influence the degree of retention by the soil were (1) charge on the radionuclide in solution, and (2) degree of calcium carbonate saturation. Retention of radionuclides by the soils occurs through ion exchange, occlusion in calcium carbonate precipitates, precipitation of aluminum, and filtration of particulates from the liquid wastes.

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