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Environmental Sciences Division
Publication No. 3980

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Environmental Sciences Division

Selective Leaching of Uranium from Uranium-Contaminated Soils: Progress Report 1

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Environmental Sciences Division Publication No. 3980

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ABSTRACT

Selective Leaching of Uranium from Uranium Contaminated Soils: Progress Report 1. C. W. Francis, A. J. Mattus, L. L. Farr, M. P. Elless, and S. Y. Lee. ORNL/TM-12177, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Three soils and a sediment contaminated with uranium were used to determine the effectiveness of sodium carbonate and citric acid leaching to decontaminate or remove uranium to acceptable regulatory levels. The objective was to selectively extract uranium using a soil washing/extraction process without seriously degrading the soil's physicochemical characteristics or generating a secondary waste form that would be difficult to manage and/or dispose of. Two of the soils were surface soils from the DOE facility formerly called the Feed Materials Production Center (FMPC) at Fernald, Ohio. This facility is presently called the Fernald Environmental Management Project (FEMP). The two soils collected at the Fernald facility are those being used in an interlaboratory treatability study sponsored by the FEMP Uranium in Soils Integrated Demonstration (UID) program. One of the soils is from near the Plant 1 storage pad and the other soil was taken from near a waste incinerator used to burn low-level contaminated trash. The third soil was a surface soil from an area formally used as a landfarm for the treatment of spent oils at the Oak Ridge Y-12 Plant. The sediment sample was material sampled from a storm sewer sediment trap at the Oak Ridge Y-12 Plant. Uranium concentrations in the Fernald soils ranged from 450 to 550 μg U/g of soil while the samples from the Y-12 Plant ranged from 150 to 200 μg U/g of soil.

Carbonate extractions generally removed from 70 to 90% of the uranium from the Fernald storage pad soil. Uranium was slightly more difficult to extract from the Fernald incinerator and the Y-12 landfarm soils (extraction efficiencies ranged from $\sim$40 to $\sim$75%). Very small amounts of uranium could be extracted ($<$8%) from the storm sewer sediment. Increasing the extraction temperature from 22 to 40°C for extractions of the Fernald waste incinerator soil increased the fraction of uranium leached from $\sim$40 to $\sim$80%. However, the increased extraction temperature did not appear to increase extraction effectiveness for the soil sampled near the Fernald storage pad. Extraction with carbonate at high solution-to-soil ratios were as effective as extractions at low solution-to-soil ratios, indicating attrition by the paddle mixer was not significantly different than that provided in a rotary extractor. Also, pretreatments such as milling or pulverizing the soil sample did not appear to increase extraction efficiency when carbonate extractions were carried out at elevated temperatures (60°C) or long extraction times (23 h). Adding $KMnO_4$ (to oxidize tetravalent uranium forms to hexavalent forms for extraction as the carbonate complex) in the carbonate extraction appeared to increase extraction efficiency from the Fernald incinerator soil but not the Fernald storage pad soil. Also, additions of $KMnO_4$ to the carbonate extractions appeared to be more effective in removing uranium from the silt- and sand-size fractions ($>2\mu$m) of soil than clay-size fractions ($<2\mu$m).

The most effective leaching rates ($>$90% from both Fernald soils) were obtained using a citrate/dithionite extraction procedure designed to remove amorphous (noncrystalline) iron/aluminum sesquioxides from surfaces of clay minerals. Citric acid also proved to be a very good extractant for uranium. At pH values <5, $\sim$90 and $\sim$50% of the uranium could be extracted from the Fernald storage pad and incinerator soils respectively. A citric acid extraction (0.1 M) of the Fernald incinerator soil followed with two carbonate extractions containing

$KMnO_4$ removed >80% of the uranium, indicating that a combination of citric acid and carbonate leaching procedures may be the best approach for soils containing residual forms of uranium. Research to date has shown that significant quantities of uranium can be extracted from the Fernald and Y-12 landfarm soils without seriously degrading the soil's physicochemical characteristics or generating a secondary uranium waste form that is difficult to manage and/or to dispose of.

1. INTRODUCTION

1.1 BACKGROUND

Production of enriched uranium for development of a nuclear industry requires the mining, milling, and fabrication of a large variety of uranium products. One of these involves the production of purified uranium metal. Much of the uranium used in the development of the US weapons complex was processed by a variety of chemical and metallurgical operations at a facility formerly called the Feed Materials Production Center (FMPC) at Fernald, Ohio. Presently, this facility is called the Fernald Environmental Management Project (FEMP) consisting of 1050 acres in a rural area approximately 18 miles northwest of downtown Cincinnati, Ohio. The manufacturing processes were housed in a ~ 136 acres fenced in area and involved many different processes including uranium and thorium metal production, and uranium hexafluoride reduction. Production peaked in 1960 (processing of ~ 10,000 metric tons of uranium) and began a decline in 1964 to a low of about 1230 metric tons in 1975. In the mid-80s, production increased slightly but was terminated in 1989 due to decreased demand.

As a consequence of these production efforts, soils have become contaminated with uranium from a variety of sources. These sources include deposition of uranium airborne particulates coming from stacks of the facilities as well as leaks and spills of uranium-rich solvents and process effluents generated in the wide assortment of aqueous and nonaqueous extraction/treatment processes. The exact quantity of soil contaminated with uranium is unknown. Some estimates are as high as 2,000,000 m^3 of soil containing unacceptable levels of uranium. To avoid the disposal of these soils in conventional low-level radwaste burial sites, a specific technology is needed to extract/leach and concentrate uranium in soil into small volumes of an acceptable waste form and returning the soil to its original place.

Another DOE facility that has considerable quantities of uranium-contaminated soil is the Oak Ridge Y-12 Plant. In this instance, most of the contaminated soil resulted from landfarming operations or collection of sediment from storm sewers within the Y-12 Plant production area. In both cases, these soils have been classified as mixed wastes and efforts are under way to extract the uranium component so that the soils can be disposed of as RCRA hazardous wastes. Thus, for the Y-12 uranium-contaminated soils, the goal is to remove uranium to below regulatory levels so that these soils can be reclassified from mixed to a RCRA hazardous waste.

1.2 OBJECTIVE

The objective of this research is to selectively extract uranium from the soil using a washing/extraction process without seriously degrading the soil's physicochemical characteristics or generating a secondary uranium waste form that is difficult to manage and/or dispose. Soil washing in a conventional sense is based on a physical separation process. Methods of physical separation such as screening, classification (separation of soil particulate according to their settling velocities), and flotation are effective for soils in which a large fraction of the contamination is concentrated in the fine grain fraction, which in turn occupy only a small percentage of the soil volume. These systems characteristically are not effective in the removal of contaminants from heavy textured soils [those soils containing high concentrations of clays

(2μ) and silts (50 μ to 2 μ)] which often contain an appreciable fraction of the contaminant within these fractions. This is generally the case for the Fernald uranium-contaminated soils. For example, initial soil characterization studies of samples collected at Fernald by Lee and Marsh (1992) indicated that the particle size distribution in three of the six samples contained >66% clay and silt-size fractions and these fractions contained approximately 50% of the uranium (see Table 1). Most importantly, all of the size fractions contained uranium concentrations >50 μg/g, the proposed screening level for applicable cleanup technologies. In three of the six samples the most highly contaminated fraction was the sand fraction (2000 μ to 53 μ particle size range) indicating that a simple physical separation processes would not be an effective cleanup technology. Thus, a likely approach will depend on a chemical extraction process.

1.3 APPROACH

Uranium is characteristically leached from uranium ores using acid and carbonate based extractants. Alkaline leaching of uranium from various ores has an established history in the uranium industry which extends back to the mid-50s when uranium milling operations were at peak production. Compared with acid leaching systems, however, only a few mills employed carbonate leaching due primarily to slower kinetics associated with the alkaline route. The use of sodium carbonate-sodium bicarbonate as the lixiviant was used in the Grand Junction Pilot Plant, operated by National Lead Co., Inc. (Beverly et al. 1957). Such use of carbonate became attractive when the uranium grade was high or in cases where the carbonate or lime content of the ore was high, then such alkalinity of the ore resulted in excessive acid consumption if an acid leach were used. The alkaline leaching also produced a clean separation of uranium from its ores without solubilizing other metals, as many metals are not soluble in such solutions. This advantage is also realized when leaching soils which may contain hazardous metals.

In acid leaching of uranium ores, sulfuric acid, being less expensive than nitric acid, was the most often used acid extractant, and combined with milling the ore to pass a 200 mesh sieve can remove 90 to 98% of the uranium. Because of strong acid's destructive nature on layer silicates, acid leaching of this type is not appropriate for leaching uranium from the Fernald soils; however, acid leaching may be useful for removal of uranium from Y-12 soils as the final product is another waste form.

Leaching of ores containing uranium in the hexavalent state with sulfuric acid forms stable highly soluble complexes of uranyl sulfates. Leaching ores containing uranium in the tetravalent state is more difficult, and oxidizing agents (such as sodium perchlorate, pyrolusite, etc.) are often added to convert the uranium to the hexavalent state. Carbonate-bicarbonate solutions may be more applicable for leaching uranium from Fernald soils because these solutions do not destroy aluminosilicate clay minerals to the extent as do strong acid extractants. The efficiency of the extractions is based on the formation of sodium or ammonium uranyl tricarbonates (highly stable water-soluble complexes). Ammonium carbonate extractions generally extract less silica than sodium carbonate extractions and thus may be preferred for extraction of uranium from the Fernald soils. Oxidants, such as potassium permanganate, and catalysts, such as ferrocyanide or copper salts, are often used to increase the carbonate-bicarbonate extraction efficiency of uranium contained in primary minerals in the tetravalent form. Uranium dioxide, uraninite, is not soluble in dilute sulfuric acid; however, it is readily soluble in alkaline solutions of hydrogen peroxide. Also, tetravalent uranium is

Table 1. Soil particle size distribution and uranium distribution among size fractions of the soil[a].

Soil sample	Particle size fraction (mm)	Particle size distribution (%)	Uranium conc. (μg/g)	Particle size load (μg U/g soil)	Uranium contribution by size fraction (%)
SP2-2-ABC	Whole soil	-	931	-	-
	>4	48	134	64	8
	4-2	11	297	33	4
	2-0.053	14	1070	150	19
	0.053-0.002	19	1990	378	49
	<0.002	8	1980	158	20
SP2-3-ABC	Whole soil	-	1299	-	-
	>4	46	197	91	3
	4-2	10	207	21	<1
	2-0.053	12	13900	1668	46
	0.053-0.002	18	5290	952	27
	<0.002	14	6130	858	24
SP4-1A/2A	Whole soil	-	4355	-	-
	>2	8	50	4	<1
	2-0.053	20	15900	3180	48
	0.053-0.002	54	4560	2462	37
	<0.002	18	5560	1000	15
SP5-1-AB	Whole soil	-	428	-	-
	>4	39	159	62	14
	4-2	15	924	138	30
	2-0.053	25	653	163	36
	0.053-0.002	16	386	62	13
	<0.002	5	600	30	7
SP8-1A/2A/3A	Whole soil	-	209	-	-
	2-0.053	34	283	96	47
	0.053-0.002	47	125	59	28
	<0.002	19	267	51	25
SP9-1A/3A	Whole soil	-	5469	-	-
	>2	13	791	103	3
	2-0.053	21	8770	1842	48
	0.053-0.002	53	2220	1177	31
	<0.002	13	5220	679	18

[a]Taken from Lee and Marsh (1992), concentrations of uranium (μg/g) for the whole soil determined from activities of ^{238}U in pCi/g times 3.03 (Tables 4, 6, 7, 10, 11, and 13).

oxidized to the hexavalent form in carbonate solutions considerably faster than in sulfate solutions. Thus, to develop an effective uranium leaching process, the roles of oxidants, chelators, and catalysts need to be characterized and understood.

Just as in the uranium industry, when leaching uranium from its numerous mineral forms, a few necessary prerequisites are important to achieve adequate extractions of uranium from either nature's minerals or from contaminated soils. The various prerequisites can be summarized briefly as follows in the necessary order:

(1.) The uranium must be exposed to the solution in order to be solubilized. The use of chemical chelating agents such as citrates can be used to remove oxide coatings, or, simply, physical attrition may be adequate to expose uranium by removing weathering products on soil surfaces.

(2.) The uranium must be oxidized to the hexavalent state, if not already oxidized.

(3.) The solution chemistry must be controlled to ensure that an adequate supply of complexing anions such as carbonate are available to complex and stabilize uranium in solution. Additionally, chemistries which promote premature, unwanted precipitation of uranium must be avoided.

Work performed at Los Alamos (Morris et al. 1992) has shown that most of the uranium is present as hexavalent uranium, meaning that once dissolution from the solid phase occurs, it is readily complexed by the carbonate anion. However, in cases where the uranium is present in the soil as the insoluble tetravalent state (IV), it must first be oxidized to the hexavalent uranium form (VI) to be effectively complexed by the carbonate ion. For that uranium which is in the tetravalent state, an oxidant such as potassium permanganate will be necessary to oxidize it. Only when the uranium is in the hexavalent state can it be complexed by an anion such as carbonate to stabilize it in solution.

Many sufficiently strong oxidants can be used to oxidize the tetravalent uranium in the soil. Permanganate salts are good oxidants in alkaline or acid solutions and from Eqs. (1) and (2) below, it can be seen that the reduction of permanganate is much more positive than the minimum formal potential necessary to reduce uranium in carbonate solutions, and, therefore, a suitable oxidant. The formal reduction potentials of the two indicate that a 0.9 V electrical potential difference exists; this large difference again points to the utility of permanganate as an oxidant. Additionally, this oxidant with carbonate has been shown to be a better extractor of uranium from some of the Oak Ridge Y-12 soils compared to extractions with peroxide or hypochlorite as oxidants.

	E°, volts	
$UO_2(CO_3)_3^{-4} + 2e^- = UO_2 + 3CO_3^{-2}$	− 0.32	(1)
$MnO_4^{-1} + 2H_2O + 3e^{-1} = MnO_2 + 4OH^-$	0.59	(2)

By combining Eqs. (1) and (2) and making the appropriate material balances, Eq. (3) results.

$$3UO_2 + 2MnO_4^{-1} + 9CO_3^{-2} + 4H_2O = 3UO_2(CO_3^{-2})_3^{-4} + 2MnO_2 + 8OH^{-1}. \quad (3)$$

As shown in the reaction above, hydroxides are produced and if unchecked can react with soluble uranium, resulting in the unwanted precipitation of the uranium from solution. Other sources of hydroxide in solution will also function similarly to promote hydrolysis and premature precipitation if the pH is not controlled. The uranium may simply precipitate, as a result of hydrolysis, in the form of $(UO_2)_2CO_3(OH)_2 \bullet H_2O$, or if the pH were to rise as high as 12 it might also be precipitated as the diuranate, generally represented as $Na_2U_2O_7$; many polymers of both such precipitates also form.

Selected ratios of sodium bicarbonate, which functions as a weak acid, and sodium carbonate are used to stabilize the pH of the reaction and to avoid precipitation of uranium as the reaction becomes more alkaline as a consequence of the oxidation of UO_2 to the uranyl form by permanganate. The overall equation when both carbonate and bicarbonate are present is as follows:

$$3UO_2 + 2MnO_4^{-1} + 9CO_3^{-2} + 8HCO_3^{-1} = 3UO_2(CO_3^{-2})_3^{-4} + 4H_2O + 8CO_3^{-1} + 2MnO_2 \quad (4)$$

The general approach will be to emphasize the extraction of uranium from Fernald soils by carbonate-based extractions (because of their less destructive characteristics on the layer silicates of soils than acid extractions). Also, because the initial leaching studies conducted by Lee and Marsh (1992) indicated high removal rates of uranium from some of the soils using citric acid, leaching with citric acid, by itself and in conjunction with carbonate extractions, will also be investigated. General relationships such as the effect of carbonate and citrate concentrations, pH, oxidants such as $KMnO_4$, temperature, and extraction time will be investigated.

2. METHODS AND MATERIALS

2.1 SOILS AND SOIL PREPARATION

Three soils and a sediment sampled from a storm sewer sediment trap at the Oak Ridge Y-12 Plant were used in this study. Two of the soils were obtained from the FEMP Uranium in Soils Integrated Demonstration (UID) program.

2.1.1 FEMP Soils

The FEMP soils were sampled and mixed by FEMP personnel and are being used in treatability tests for the decontamination task group of the UID (Kneff et al. 1992). One of the samples (B-16, Drum 6) was taken from near the Plant 1 Storage Pad Area within the FEMP production area. The other sample (A-14, Drum 12) was taken from near the Waste Incinerator located a few hundred yards east of the FEMP production area (see Figs. 1 and 2). Each excavated area was about 25 by 20 ft, with an excavation depth of 6 to 8 in. The storage pad sample (B-16) was taken within the same area where Lee and Marsh (1992) took 2-in.-diam cores SP3 and SP4 (represented in Table 1 as SP4-1A/2A). Likewise, the incinerator sample (A-14) was taken within the same area where Lee and Marsh (1992) took 2-in.-diam cores SP9 and SP10 (represented in Table 1 as SP9-1A/3A). At FEMP, each of the excavated soils was sifted through a 3/4-in.-diam screen to remove large debris and blended in a large concrete mixer. The soils were then loaded directly from the mixer into sets of 55-gal drums. Sixteen drums of soil were collected and blended from the storage pad area and 15 drums from the incinerator area. In this report, these soils will be referred to as storage pad and incinerator soils respectively.

On arrival of the FEMP samples at ORNL, aliquots were air-dried in a laboratory hood and then sieved through a 4.75-mm-diam screen (moisture contents, on an oven-dry basis, of drummed-shipped soil were 20.1 and 14.0%, respectively, for A-14 and B-16). Visually, the soils appeared moist and dark colored (indicative of a relatively high organic matter content) and both samples had a good granular aggregate structure. The soil sampled from near the waste incinerator (A-14) contained 3% material >4.75 mm while soil sampled near the plant 1 pad (B-16) contained 0.8% material >4.75 mm. The material >4.75 was discarded and not used in the leaching studies. The air-dried samples contained approximately 1.8 and 2.1% water (samples A-14 and B-16 respectively), based on an oven-dry weight. These air-dried samples passing a 4.75 mm sieve were used for the leaching studies; thus, all leaching data on the FEMP soils are expressed on an air-dried basis and soil passing a 4.75-mm sieve.

2.1.2 Y-12 Samples

Y-12 landfarm samples (S92 and S93) were received in sealed, large (approx. 1.5 L) widemouth glass jars. The soils looked as if they were near saturation with respect to water content and did not possess any sort of a granular structure (e.g., they had a dispersed clayey paste-like appearance). Moisture contents of the samples were 35 and 37% (S92 and S93 respectively) on an oven-dry weight basis. On air drying in the hood, the samples remained in a clayey, cloddy form. Because of this clayey, cloddy form, the soils had to be crushed by hand

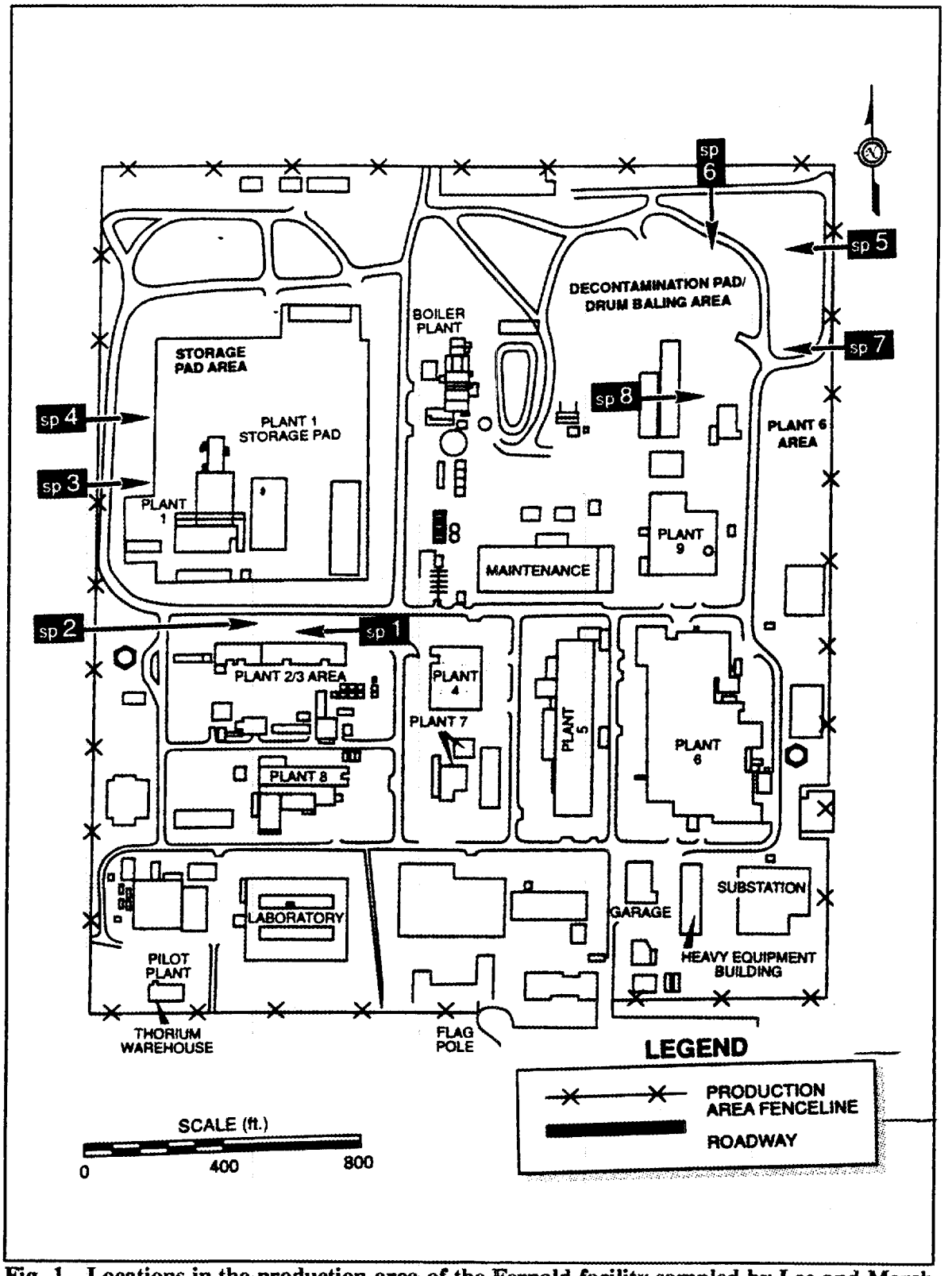


Fig. 1. Locations in the production area of the Fernald facility sampled by Lee and Marsh 1992.

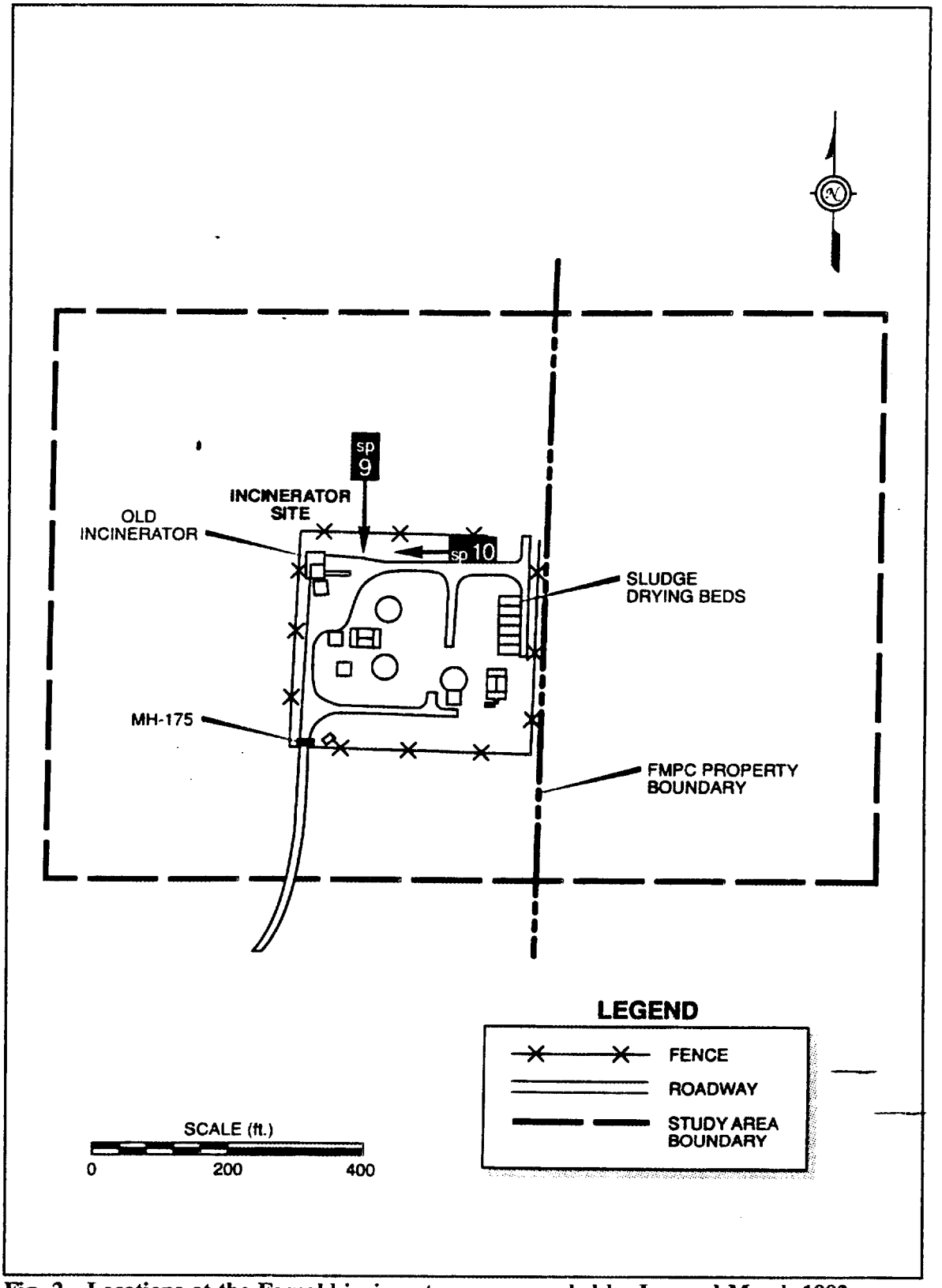


Fig. 2. Locations at the Fernald incinerator area sampled by Lee and Marsh 1992.

using an iron pistol and mortar. For the Y-12 landfarm samples, leaching was conducted on this air-dried crushed form.

Y-12 storm sewer sediment (SSS) samples contained a large quantity of stones and rocks which would require a very large sample size to correctly characterize particle size distribution. Since the interest at this time was the leachability of the uranium, assumed to be distributed in the smaller sized particulate, the sample was air-dried, sieved through a 1.18 mm sieve (No. 16), blended in a V-blender, and split into ~400 g aliquots. Leaching was conducted on this fraction (< 1.18 mm diam).

2.2 SOIL CHARACTERISTICS

2.2.1 Concentration and Distribution of Uranium in Soils

The objective of this report is to describe progress in the ongoing leaching studies of the FEMP and Y-12 soils. Characterization data presented here will be generally limited to total uranium analyses (by various analytical procedures), a description of the distribution of uranium within the particle size fractions of soil, and some limited microscopic studies. S. Y. Lee and M. P. Elless will be reporting in more detail the characteristics (and methodology used) of the soils at a later date.

The methods used to separate particle size fractions are based on wet sieving and centrifugation techniques described in Jackson (1969). Listed in Tables 2 through 5 are the concentrations and distribution of uranium among particle fractions of the four soils leached in this study. For the Fernald soils (A-14 and B-16) and the Y-12 storm sewer sediment (SSS), the > 2-mm-diam fractions were not analyzed for uranium content. This size range constituted a rather small fraction of the total mass of these soils (1.2, 4.7, and 5.3%, respectably, for SSS, A-14, and B-16). The concentration of uranium (538 μg/g) in the incinerator soil (Table 2) is considerably less than that measured in the top 3 in. of the soil cores (5469 μg/g) taken from this area by Lee and Marsh (see Table 1), indicating considerable dilution in uranium concentration of the bulk sample on removing soil for treatability studies. However, the whole soil or any of its particle size fractions were not below the proposed screening criteria [35 pCi/g or 52 μg U/g, see Appendix A for a discussion on converting radioactivity of uranium (pCi/g) to units of μg U/g of soil], indicating that simple physical separation procedures will not generate a clean fraction from this soil.

The treatability sample taken from near the plant 1 storage pad (Table 3) also contained much less total uranium (446 μg/g) than that observed (4355 μg/g) in the top 7 in. of the soil core taken at this site (Table 1, sample SP4-1A/2A), again indicating considerable dilution in uranium concentration on taking bulk samples of soil. Here an even greater difference in distribution and concentration of uranium within particle size fractions of cored samples (Table 1) and bulk treatability samples (Table 3) was observed than the soil from the incinerator site. For example, the sand fraction (2–0.053 mm) of the cored sample contained the highest uranium concentration (15,900 μg/g), constituting ~48% of the uranium in the sample. On the other hand, the clay fraction (< 2μ) of the bulk treatability sample (Table 3) contained the highest uranium concentration (983 μg/g), making up over 56% of the uranium contribution compared

Table 2. Concentration and distribution of uranium in soil from near the Fernald waste incinerator (A-14)

Size fraction (mm)	Particle size distribution[a] (%)	Uranium concentration[b] (μg/g)	Particle Size load (μg U/g Soil)	Uranium contribution by size fraction (%)
Whole soil	NA[c]	538	NA	NA
Sand 2–0.053	12.5	1033	130	27
Silt 0.053–0.002	73.9	286	211	44
Clay <0.002	13.6	1019	138	29

[a]Based on particles <2mm diam.
[b]Determined by neutron activation analyses.
[c]Not applicable.

Table 3. Concentration and distribution of uranium in soil from near the Fernald plant 1 storage pad (B-16)

Size fraction (mm)	Particle size distribution[a] (%)	Uranium concentration[b] (μg/g)	Particle Size load (μg U/g soil)	Uranium contribution by size fraction (%)
Whole soil	NA[c]	446	NA	NA
Sand 2–0.053	22.6	117	26	7
Silt 0.053–0.002	56.5	239	135	37
Clay <0.002	20.9	983	205	56

[a]Based on particles <2 mm diam.
[b]Determined by neutron activation analyses.
[c]Not applicable.

to ~15% for the core sample taken at the storage pad site. The difference in total concentration of uranium between the bulk treatability samples and the cored samples is not surprising (i.e., a dilution effect in the treatability samples as a consequence of taking a sample over a larger area and depth); however, the difference in distribution of uranium among particle size fractions is!

The concentrations and distributions of uranium among particle size fractions of the Y-12 landfarm soil and storm sewer sediment are presented in Tables 4 and 5. The major difference between the samples from the Oak Ridge Y-12 Plant and the Fernald samples is that concentrations of uranium in the Y-12 samples were lower (ranging from 150 to 200 μg/g compared to 450 to 550 μg/g in the Fernald samples).

2.2.2 Microscopic Characteristics of Soils

A small amount of dry whole soil samples and size-fractionated samples from Fernald (A-14 and B-16) and Y-12 (S93 and SSS) was embedded in epoxy resin under vacuum to allow the resin to move into the soil micropores. After resin polymerization, microscopic specimens that have approximately 1 to 4 cm^2 cross-sectional areas were prepared by sanding the soil resin blocks and later polishing with very fine diamond powder. Scanning electron microscopy (SEM), utilizing both secondary electron imaging and backscattered electron imaging coupled with energy dispersive X-ray analysis (EDX), was used for analysis of morphology, particle size, and elemental distributions.

Table 4. The concentration and distribution of uranium in the Y-12 landfarm soil (S93)

Size fraction (mm)	Particle size distribution (%)	Uranium concentration[a] (μg/g)	Particle Size load (μg U/g soil)	Uranium contribution by size fraction (%)
Whole soil	NA[b]	177	NA	NA
>2	1.8	442	8.0	4.3
2–0.075	17.5	361	63.1	33.8
0.075–0.020	34.1	31	10.7	5.8
0.020–0.002	30.4	180	54.8	29.3
<0.002	16.1	312	50.2	26.9

[a]Determined by gamma energy spectroscopy using 3.03 times pCi/g activity.
[b]Not applicable.

Table 5. Concentration and distribution of uranium in Y-12 storm sewer sediment (SSS).

Size fraction (mm)	Particle size distribution[a] (%)	Uranium concentration[b] (μg/g)	Particle Size load (μg U/g soil)	Uranium contribution by size fraction (%)
Whole soil	NA[c]	149	NA	NA
Sand 2–0.053	90.3	60	54	41
Silt 0.053–0.002	5.7	923	53	40
Clay <0.002	3.9	604	24	18

[a]Based on particles < 2mm diam.
[b]Determined by neutron activation analyses.
[c]Not applicable.

The SEM micrographs of A-14 sand fraction show a wide variety of sizes and shapes of minerals (Fig. 3). Some minerals occur as a stable, large-sized aggregate. The unusually high stability of the aggregates is expected to develop during the incinerating process. The aggregates contained uranium particles as well as other heavy minerals. Uranium occurred also as a microfracture-filling mineral in the aggregate. Quartz was the dominant mineral in the sand fraction. Uranium-containing particles were typically composed of calcium, silicon, or phosphorus. A cerium phosphate mineral was also found in the sample. In the B-16 silt fraction (Fig. 4), some uranium particles were composed entirely of uranium and others had calcium and/or silicon. In future analytical determinations, detailed microscopic analyses will be performed after heavy liquid separation in order to examine concentrated uranium-bearing fractions.

Uranium particles in the Y-12 landfarm samples (S92) were relatively small (< 0.02 mm) and had irregular shapes (Fig. 5). Most of the uranium particles contained no other elements, except oxygen. Quantitative elemental composition of the uranium particles will be determined by microprobe analysis using a UO_2 mineral standard. Cerium phosphate minerals (monazite) containing lanthanum or thorium were frequently depicted. The Y-12 storm sewer sediment had uranium particles as well as mercury and lead particles (Fig. 6). Uranium particles in the storm sewer sediment were small but had a smooth surface and unweathered appearance. The storm sewer sediment contains a variety of materials such as mercury, mercury sulfide, thorium-rich mineral, lead, dolomite, and other man-made calcium/magnesium-rich silicates. Detailed mineralogical analyses will be performed after size, density, and magnetic separations.

Table 6. Comparison of analytical methods to determine total uranium in Fernald soil samples

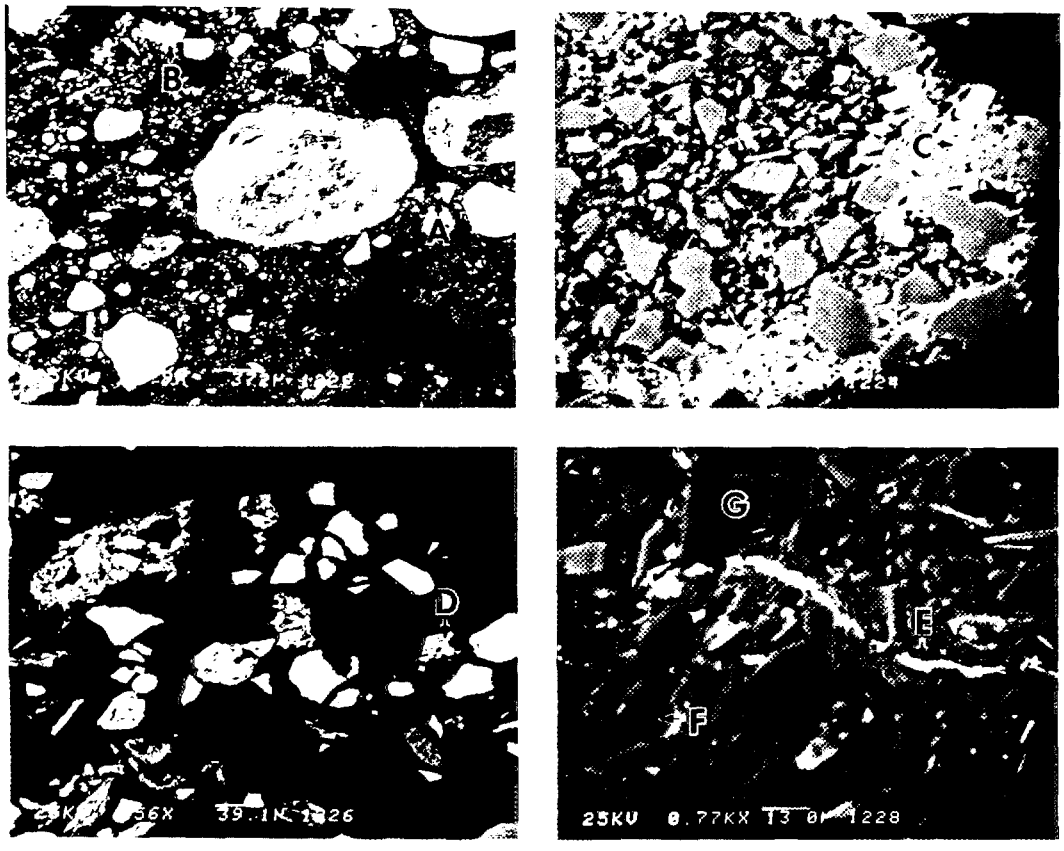
Method of analyses	A-14	B-16
Neutron activation		
Av conc (μg/g)	538	446
% Coeff variance	7.2	8.3
Number of samples	2	2
Wet digestion		
Av conc (μg/g)	470	387
% Coeff variance	4.0	9.5
Number of samples	4	4
Radiocounting		
Av conc (μg/g)	543	421
% Coeff variance	5.0	4.7
Number of samples	10	10

2.3 METHOD OF URANIUM ANALYSES

2.3.1 Total Uranium in Soils

The Fernald samples (A-14 and B-16) were analyzed for total uranium content using neutron activation, wet digestion, and radiocounting procedures. The results of these analyses are presented in Table 6. The neutron activation analyses were conducted by the Neutron Activation Analysis Laboratory at the ORNL High Flux Isotopes Reactor (Wade et al. 1992). In this method, count rates determined for the soil samples were compared to count rates for standards that contain know quantities of uranium. The neutron flux was approximately 5×10^{13}n/cm^2/sec. Gamma spectra of the activated samples were analyzed using the Nuclear Data ACCUSPEC system software and two programs developed at ORNL.

The wet digestion procedure (Kingston and Jassie 1988) consisted of acid digestion (using HNO_3, and HF) in a Parr microwave acid digestion bomb (model 4782) and was conducted in the Chemical Technology Division (ORNL). The bomb capacity was 45 mL and the digestion receipt used 2 g of dry soil, 5 mL of deionized water, 5 mL of concentrated hydrofluoric acid, and 5 mL of concentrated, ultrapure nitric acid. The samples were microwaved in a 700-W microwave oven for 1 min, cooled and microwaved twice again, making a total of three. During operation of these Parr bombs, temperature of 250°C and pressure of 1200 psi are achieved.



These four SEM micrographs were taken from the sand fraction of the Fernald incinerator soil (A-14). Particle A has uranium as a major component with a very small amount of oxygen. Particles B and D have uranium and lesser amounts of calcium, phosphous, and oxygen. Particle C has phosphorus, cerium, neodymium, and lesser amounts of thorium and oxygen. The microfracture-filling mineral (marked E) has uranium and silicon with smaller amounts of calcium and phosphorus. The matrix of the aggregate is aluminosilicate clays (marked F) and silt-size quartz (marked G).

Fig. 3. Four scanning electron micrographs of the sand fraction of the Fernald incinerator soil.

The radiocounting procedure was conducted in the Environmental Sciences Division using the procedure outlined in Lee and Marsh (1992) and using the conversion factor of 3.03 to convert activities of ^{238}U in pCi/g to $\mu g/g$ (see Appendix A). The results from neutron activation and radiocounting are similar (Table 6). Concentrations of uranium by the wet digestion method were ~12% lower than by the neutron activation or radiocounting procedures. To clarify if these differences are valid, total digestion of the samples by a lithium metaborate fusion technique has been conducted but results have not been received.

2.3.2 Uranium in Soil Leachates

Uranium in leachates was determined using two methods [method Y/P65-7165 by the Y-12 Plant Environmental Analysis Laboratory (MMES 1991) and EPA method 200.8 by ORNL's Analytical Chemistry Division]. Method Y/P65-7165 is an isotope dilution mass spectrometric method used to determine concentrations of isotopic and total uranium in potable and industrial water. The samples are acidified, spiked with a ^{233}U internal standard, and extracted. The mass spectrometer is calibrated to determine the correction factor for each isotope, and an aliquot is analyzed for the $^{238}U/^{233}U$ and $^{235}U/^{233}U$ ratios. Method 200.8 is an inductive coupled plasma–mass spectrometry (ICP-MS) method applicable to a large number of elements in water and wastes after digestion to determine total values.

2.3.3 Other Analytical Methods Used

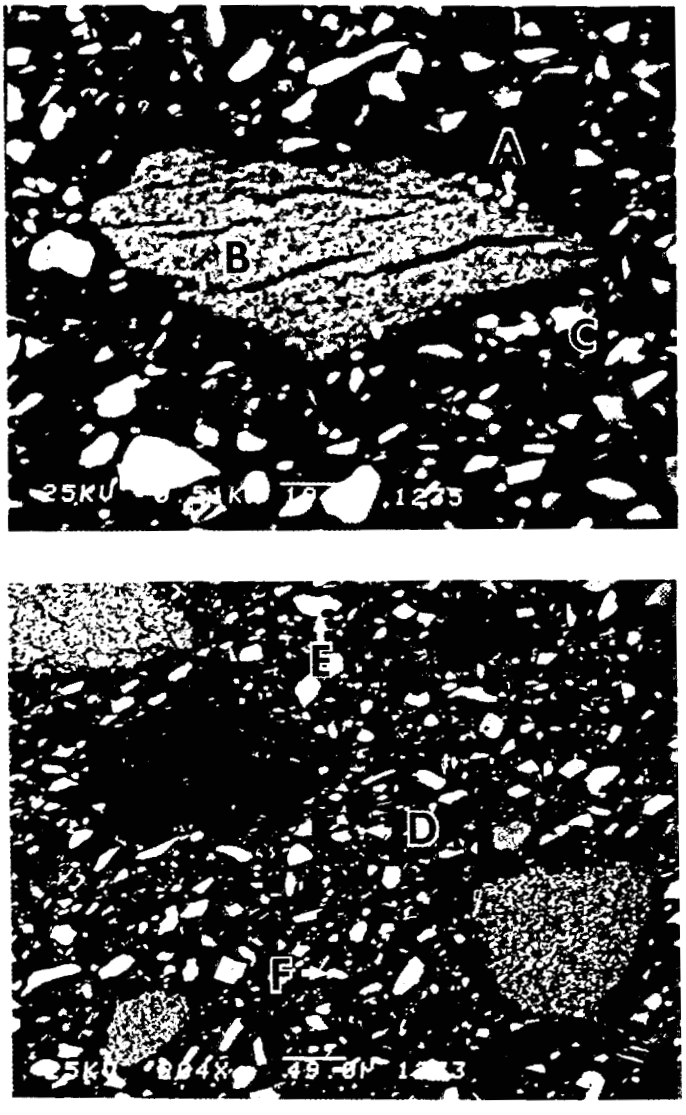
Total organic carbon in the Y-12 landfarm soil (S93) and the total organic carbon in the carbonate extractions of this soil were determined using methods 221021 and 415.1 respectively (Analytical Chemistry Division, ORNL). Method 221021 is a dry combustion method utilizing a Leco Model 212 carbon analyzer. Method 415.1 is a wet chemical oxidation method utilized for waters and aqueous industrial wastes. The carbon dioxide is measured directly by an infrared detector or converted to methane gas and measured by a flame ionization detector. Leachate pH levels were determined using a portable pH meter equipped with a gel-filled combination electrode. The unit was calibrated with reference buffered pH solutions before readings of leachate pH were taken.

2.4 LEACHING DESIGNS

Two leaching designs were used: (1) leaching at a low solution-to-soil ratio (~1:1) using paddle mixers for attrition and mixing and (2) leaching at a high solution-to-soil ratio (10:1) using a rotary extractor for mixing.

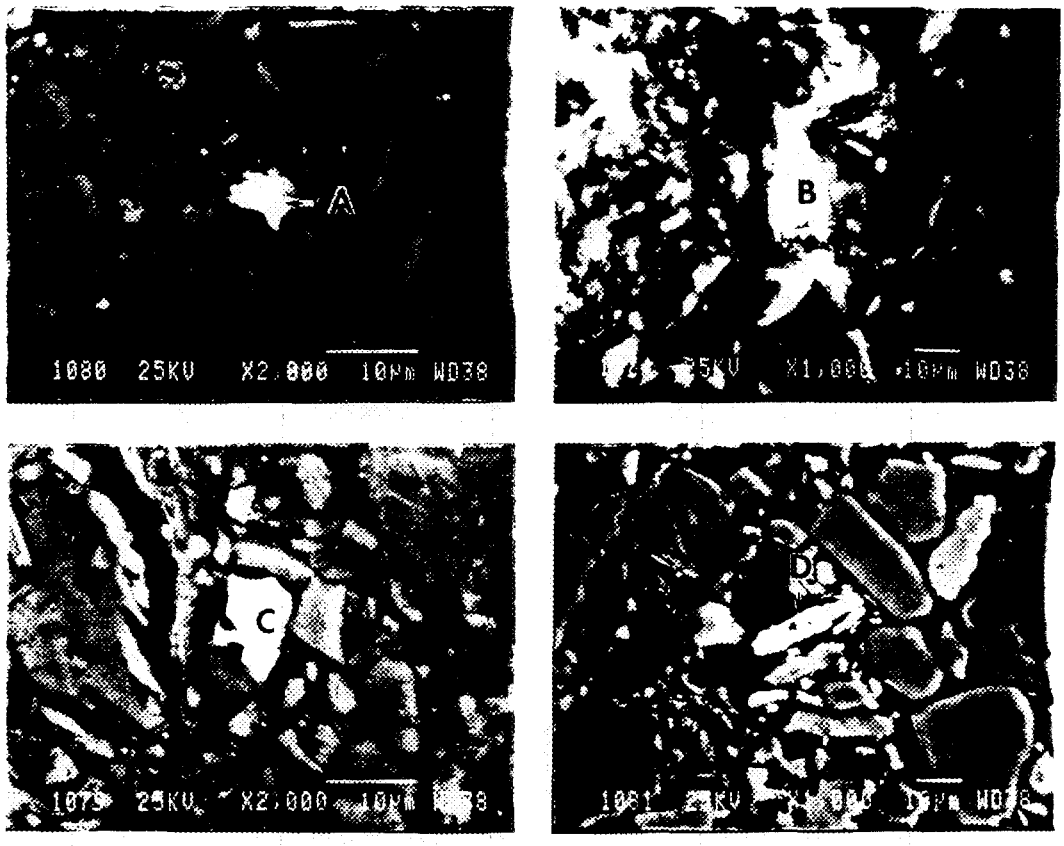
2.4.1 Low Solution-to-Soil Ratio Leaching

Low solution-to-solid ratio leaching tests were preformed to take advantage of the added physical attrition provided by the impaction of soil particles against each other during mixing to remove weathering products from their surfaces. Weathering products such as calcium carbonate



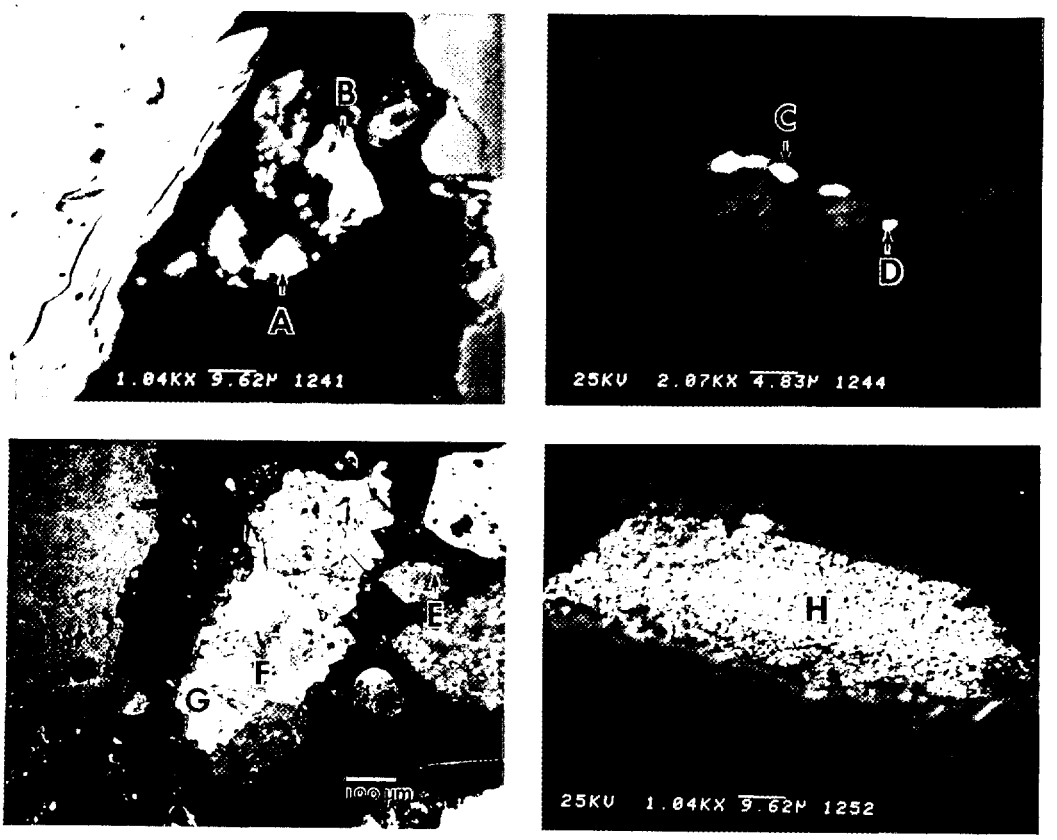
These two SEM micrographs were taken from the silt fraction of the Fernald storage pad soil (B-16). Particle A contains a high concentration of uranium as well as calcium, silicon, and alumium. The fine silty aggregrate is an aluminosilicate mineral (marked B). Particle C is an iron oxide mineral and particle D is a phosphate mineral that contains cerium, neodymium, and lanthanum (monazite). Particles E and F are an iron-titanium oxide (ilmenite) mineral. Other silt particles are quartz, dolomite (marked G), and feldspars.

Fig. 4. Two scanning electron micrographs of the silt fraction of the Fernald storage pad soil.



These four SEM micrographs show typical uranium particles and ceri particles conatined in the Y-12 landfarm samples (S93 and S92). T major component of particles A and B. Particle C is a cerium-lanth mineral and particle D is a cerium-thorium-calcium phosphate minera.

Fig. 5. Four scanning electron micrographs of typical uranium and cerium phosphate particles in the Y-12 landfarm samples.



These are four selected micrographs of Y-12 storm sewer sediment that i' presence of uranium particles (marked A, C, and E), metallic iron mercury sulfide (marked D), dolomite (marked F), calcite (marked G) lead aggregate (marked H).

Fig. 6. Selected micrographs of Y-12 storm sewer sediment.

and complex alumino-silico-iron compounds, either amorphous or crystalline, can coat the uranium on soil particles thus inhibiting contact of the extraction fluid and uranium. This same principle is relied on in the uranium mining and milling industry to achieve a similar objective while minimizing the use of water and reagents. In the uranium industry, pulp densities (percent solids, solution-to-solid ratios) as high as 60% solids by weight are sometimes used.

2.4.1.1 Leaching media

Most of the leaching tests conducted at the low-solution-soil ratio were conducted using a sodium carbonate solution (25 g $NaHCO_3$ and 25 g Na_2CO_3 per liter). In contact with the soils, a pH ranging from 9.3 to 9.5 was obtained. In this pH range, the ratio of bicarbonate to carbonate is ~ 10 and a carbonate concentration ranging from 4.5×10^{-2} to 6.8×10^{-2} M. Potassium permanganate ($KMnO_4$) was added (0.02 g/g of soil) to oxidize uranium(IV) to the uranyl(VI) state to form the stable uranyl tricarbonate complex, $Na_4[UO_2(CO_3)_3]$. Potassium permanganate is a very strong oxidant in this pH range.

2.4.1.2 Leaching equipment and methods

Leaching tests using the low solution-to-soil ratios were conducted in standard 1-L glass resin kettles immersed in a temperature controlled water bath. For most tests, 400 mL of the sodium carbonate was added to 400 g of soil and agitated with a motor and shaft arrangement which was used at a speed such that all solids were suspended off the bottom of the kettle during the leaching.

Upon completion of the leaching, the suspension was filtered through a Whatman 40 paper filter using a 24-cm Buchner filter funnel. The filtered solids were then resuspended with ~ 400 mL of wash solution in the resin kettle and mixed for 5 min before being filtered again. Three washing stages were employed for each test; the chemistry of the wash solution matched that of the extraction media in most cases.

After washing, the solids were dried at 110°C (or in a microwave oven), blended by hand, and sampled (~ 25 g) for total uranium analysis. To ensure that a representative sample was taken for total uranium analyses, the 25-g sample was pulverized to the consistency of fine flour using a tungsten carbide impeller type pulverizer. Two grams of this material were then digested in the Parr microwave acid digestion bomb (see Sect. 2.3.1).

To investigate the influence of abrasion (removal of weathering products on soil surfaces that might inhibit contact of the leaching media and uranium) or particle size reduction on leaching of uranium from the Fernald soils, two pretreatment methods were used. Initially, soils were pulverized (12,000 rpm for 10 s) to a fine powder-like consistency in a Bel-Art micro mill equipped with a tungsten carbide blade. The leached suspensions were difficult to filter, so a less extreme method was used. This method (termed "milled" in this report) consisted of milling the soil sample with approximately 200 mL of extraction solution in a ceramic jar mill with 2-cm ceramic balls. After 30 min., the slurry was wet sieved (to remove the ceramic balls) into the glass resin kettles for leaching with the other 200 mL of extractant solution.

2.4.2 High Solution-to-Soil Ratio Leaching

2.4.2.1 Leaching equipment and methods

This leaching design was used to investigate the influence of carbonate and citrate concentrations at varying pH on removal of uranium from the four uranium contaminated soils. Twenty grams of soil were extracted in 200 mL of extractant using a rotary extractor rotating at 50 rpm. This is the type of extractor used to conduct the EP and TCLP leaching tests to meet compliance with RCRA/EP regulations (Francis and Maskarenic 1986). After each extraction period, the pH of the soil suspension is recorded and the liquid phase is separated from the solid phase by centrifugation in a swinging bucket rotor (Damon/IEC model PR-J centrifuge with a No. 599 rotor) for 45 min at 2400 rpm. According to Stokes' law, this configuration is enough centrifugal force and time to settle particles $>0.2\ \mu$ and density of 2.5. If sequential extraction tests were conducted, the centrifuge bottles were weighed before and after changing extraction media. Aliquots of supernatant were removed and acidified to pH <2 with ultrapure nitric acid and sent to the analytical laboratory for uranium analyses. The efficiency of leaching was determined by expressing the quantity of uranium measured in the supernatant as a percentage of the total uranium determined in the soil sample.

2.4.2.2 Carbonate leaching tests

To test the influence of carbonate and pH on extraction of uranium from the four soils, a factorial-designed experiment using three levels of total carbonate/bicarbonate (0.10, 0.25, and 0.50 *M*) at three pH levels (8, 9, 10) and two replicates was conducted. These were 4-h tests conducted at a liquid-to-soil ratio of 10:1 (200 mL of extractant and 20 g of soil) in a rotary extractor.

2.4.2.3 Citric acid/citrate leaching tests

To test the influence of citrate and pH on uranium extraction from the four soils, a factorial-designed experiment using three levels of citrate (0.10, 0.25, and 0.50 *M*) at four pH levels (unadjusted, 5, 7, and 9) and two replicates was conducted. These were 4-h tests conducted at a liquid-to-soil ratio of 10:1 (200 mL of extractant and 20 g of soil) in a rotary extractor.

2.4.2.4 Bisequential citric acid/carbonate leaching tests

For the Fernald soils (A-14 and B-16), a bisequential leaching test was conducted by first leaching the soils with 0.1 *M* citric acid (20 g of soil in 200 mL of water) followed with two (200 mL) extractions with 0.1 *M* sodium carbonate/bicarbonate, pH 9. The effect of extraction time (0.5, 1, and 2 h) and use of $KMnO_4$ (0.02 g/g of soil) in the carbonate extractions were investigated. All treatments were conducted in duplicate.

2.4.2.5 Nitric acid leaching tests

To evaluate the influence of pH on the extraction of uranium in the absence of a strong chelator (such as citrate for uranium and iron), the Fernald storage pad soil (B-16) was extracted with dilute concentrations of nitric acid (0.1 to 0.15 *M*). This was done by adding concentrated ultrapure nitric acid to a suspension of 20 g of soil in 200 mL of water to a pH of 2.0 before extraction in the rotary extractor. A control (using 20 g of soil in 200 mL of deionized-distilled water) was also carried out. Both of these treatments (nitric acid and deionized-distilled water extractions) were conducted in triplicate.

3. RESULTS

3.1 LOW SOLUTION-TO-SOIL RATIO LEACHING

The leaching of uranium from the incinerator soil appears to be more dependent on time and temperature than leaching of uranium from soil near the storage pad area (see Tables 7 and 8). For example, increasing the extraction time from 4 to 23 h increased the fraction of uranium leached from the incinerator soil from 38 to 80% but had no influence on the leaching of uranium from the storage pad soil. Also, with the incinerator soil, increasing the temperature from 22 to 40°C (at 2 and 4 h leaching) increased the fraction of uranium removed to ~80% (compared to 40 to 50% at 22°C) but had no effect of the leaching of uranium from the storage

Table 7. The influence of pretreatment, temperature, and time on leaching of uranium from soil near the Fernald waste incinerator (A-14) using sodium carbonate extractions

Pretreatment	Temperature (°C)	Time (hr)	Uranium in residual[a] (μg/g)	Fraction of uranium leached (%)
None	22	2	238	49
None	22	4	290	38
None	22	6	95	80
None	22	23	95	80
None	40	2	78	83
None	40	4	88	81
None	40	6	14	97
None	40	23	112	76
None	60	2	148	68
None	60	4	106	78
None	60	6	70	85
None	60	23	63	87
Pulverized	60	23	74	84
Milled	60	23	49	90

[a]Initial uranium concentration was 470 μg U/g of soil.

Table 8. The influence of pretreatment, temperature, and time on leaching of uranium from soil near the Fernald plant 1 storage pad

Pretreatment	Temperature (°C)	Time (hr)	Uranium in residual[a] (μg/g)	Fraction of uranium leached (%)
None	22	2	68	82
None	22	4	56	86
None	22	6	71	82
None	22	23	59	85
None	40	2	32	92
None	40	4	54	86
None	40	6	44	89
None	40	23	40	90
None	60	2	46	88
None	60	4	56	86
None	60	6	30	92
None	60	23	37	91
Pulverized	60	23	39	90
Milled	60	23	31	92

[a]Initial concentration was 387 μg U/g of soil.

pad soil. An increase in temperature from 40 to 60°C had little influence on leaching of uranium from either soil. For example, the average fractions of uranium extracted at 40 and 60°C were 84 and 79%, respectively for the incinerator soil and 89 and 89%, respectively for the storage pad soil. The general patterns of how extraction efficiency was influenced by time and temperature of extraction are illustrated in Figs. 7 and 8. Pretreatment, by pulverizing and milling the samples, coupled with a long leaching time (23 h) and an elevated temperature (60°C) did not release additional uranium. High leaching efficiencies (>85% removal rates) were observed with all treatments in the case of the storage pad soil (Table 8). In the case of the soil from the storage pad area, future research needs to be directed at determining the leaching effectiveness at shorter leaching times. The influence of pulverization and/or milling of the soil samples also needs to be reinvestigated at shorter leaching times and nonelevated temperatures.

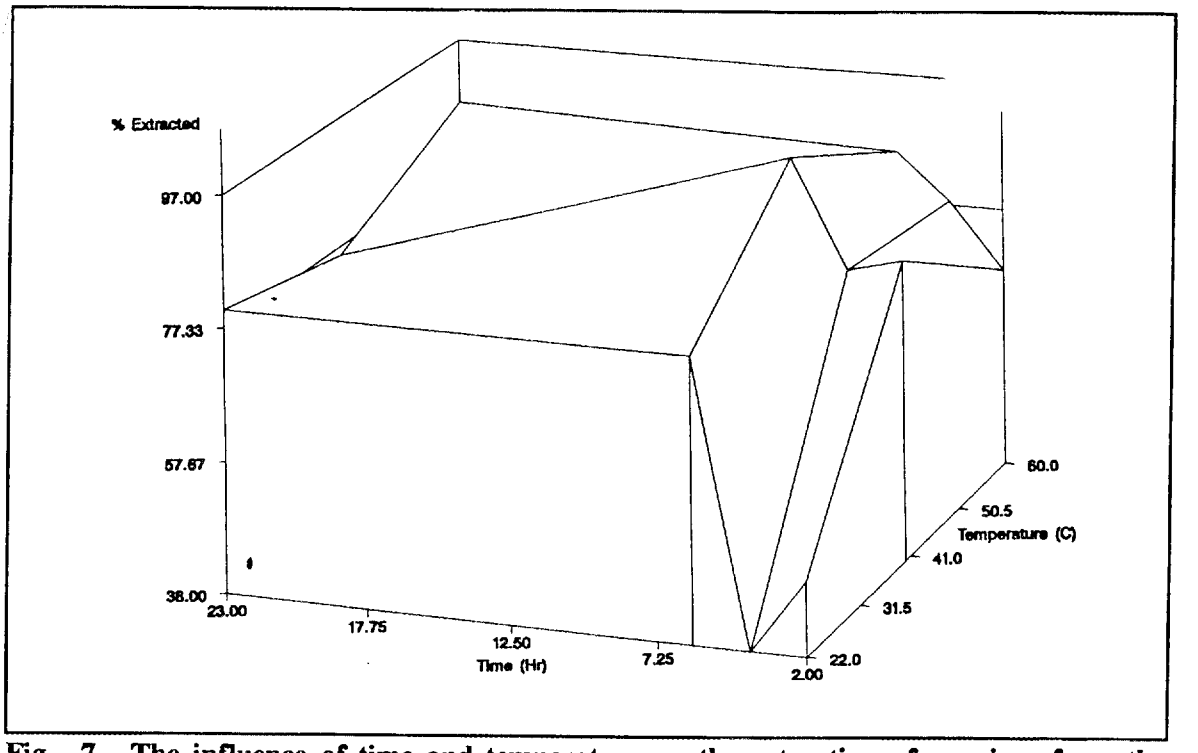


Fig. 7. The influence of time and temperature on the extraction of uranium from the Fernald incinerator soil (A-14) by sodium carbonate extractions, pH 9.5.

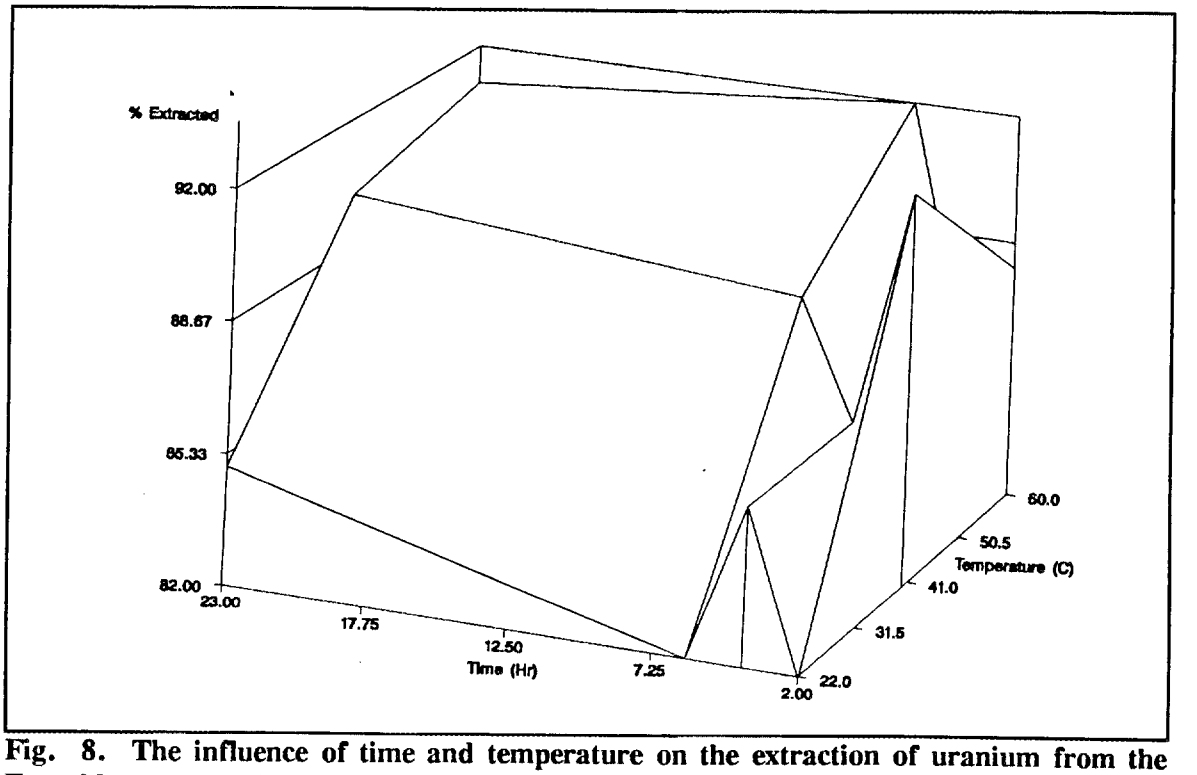


Fig. 8. The influence of time and temperature on the extraction of uranium from the Fernald storage pad soil (B-16) by sodium carbonate extractions, pH 9.5.

The most effective leaching rates (>90% from both Fernald soils) were obtained using a citrate/dithionite extraction procedure (Table 9). This extraction procedure is designed to remove amorphous iron/aluminum sesquioxides from the surfaces of clay minerals (Jackson 1969 and Jackson et al. 1986). The high reducing effect (theoretical redox potential of −1.12 V) of the dithionite ($Na_2S_2O_4$) in the presence of $NaHCO_3$ (pH >7.3) and elevated temperature (75–80°C) reduces noncrystalline iron (III) to iron (II) which is readily chelated by the citrate and removed from the soil's surface. After reaction with the dithionite at elevated temperatures an excess of $KMnO_4$ was added to the suspension to oxidize U(IV) to the uranyl form (VI) and subsequent extraction. These data imply that future research using a similar reducing environment at shorter leaching intervals may prove to be useful.

3.2 HIGH SOLUTION-TO-SOIL RATIO LEACHING

3.2.1 Carbonate Leaching Tests

The removal of uranium from the four soils (A-14, the Fernald incinerator soil; B-16, the Fernald storage pad soil; S93, the Y-12 landfarm soil; and SSS, the Y-12 storm sewer sediment) by sodium carbonate leaching at varying pH and total carbonate/bicarbonate is illustrated in Figs. 9–11. The experiment was designed to test the extraction efficiency of sodium carbonate extractions. Buffer solutions were made of $NaCO_3$ and $NaHCO_3$ at pH values of 8, 9, and 10 and total bicarbonate and carbonate concentrations of 0.1, 0.25, and 0.5 *M* using the dissociation constant of

$$\frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} = 10^{-10.33}.$$

The Fernald storage pad soil showed the highest and the Y-12 storm sewer sediment the lowest removal rates of uranium by carbonate extraction (Figs. 9–11). Removal ranged between 75 and 87% for the Fernald storage pad soil and there appeared to be little influence with respect to total bicarbonate and carbonate concentrations or pH (see Appendix B for tabular leach data).

Table 9. Removal of uranium from the Fernald soils using a citrate/dithionite extraction

Soil	Uranium (μg/g soil)		Fraction of uranium leached (%)
	Initial	Residual	
Plant 1 storage pad (B-16)	387	12	97
Waste incinerator (A-14)	470	37	92

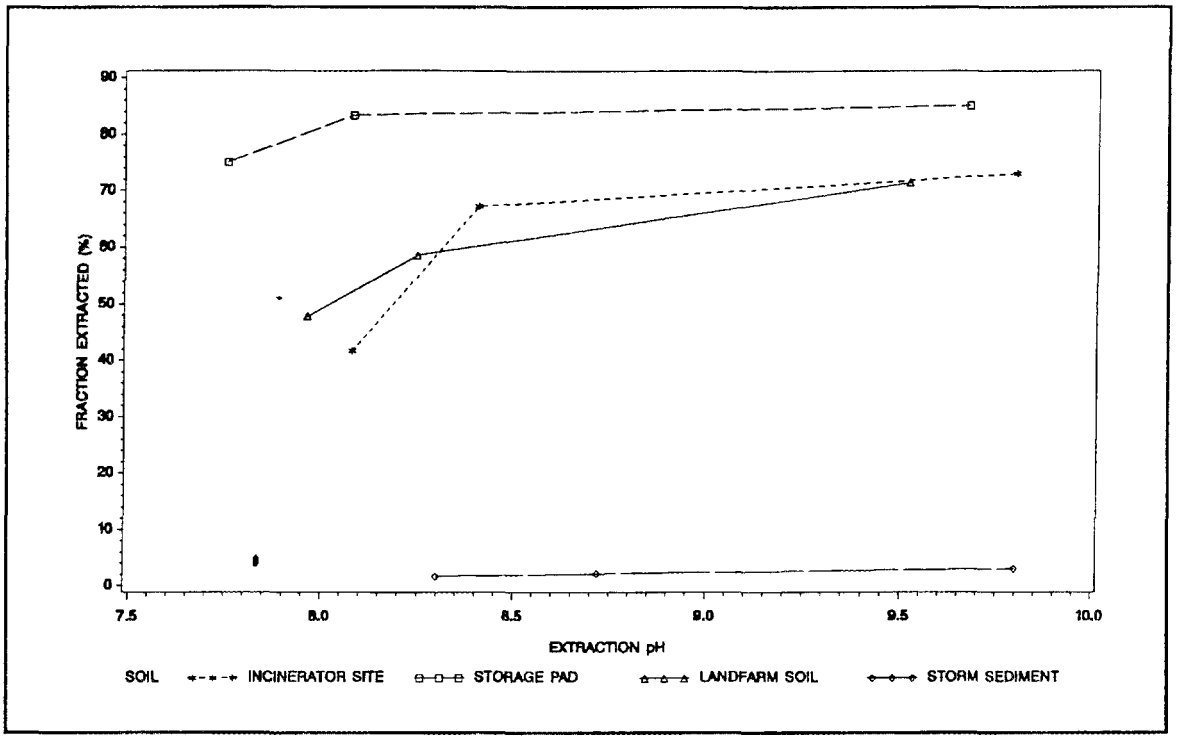


Fig. 9. The extraction of uranium from four soils using a carbonate leach (total carbonate/bicarbonate conc. = 0.1 *M*).

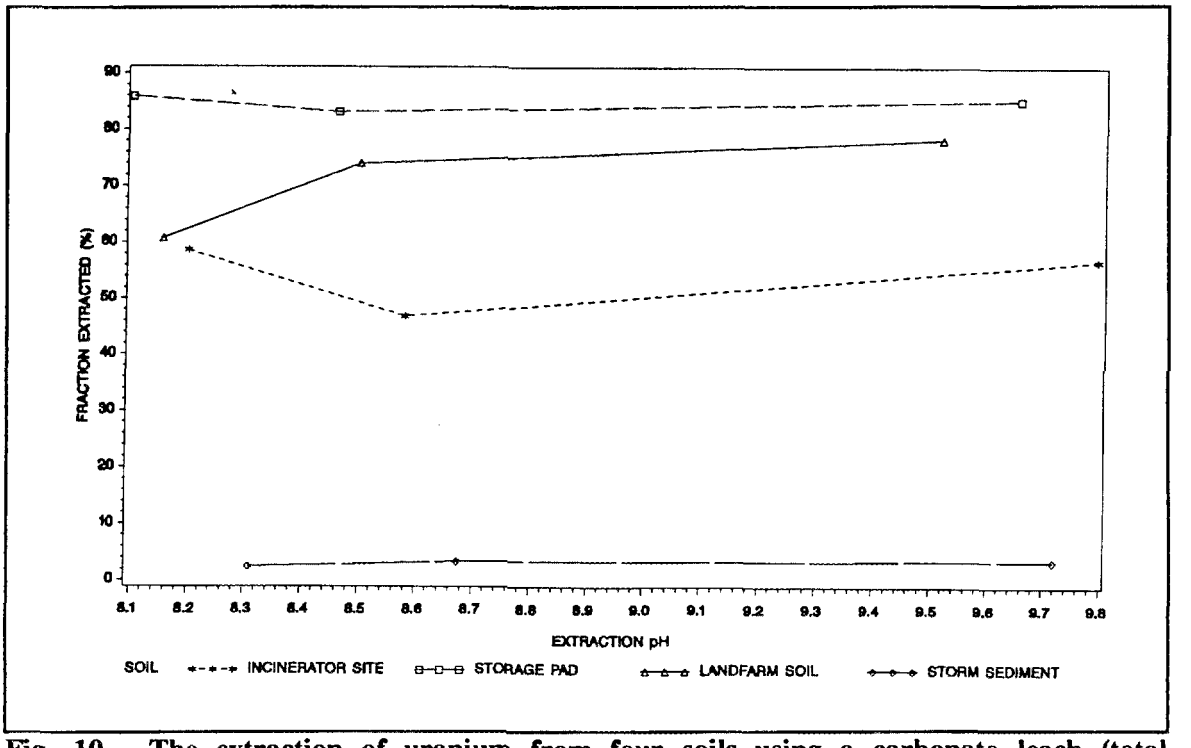


Fig. 10. The extraction of uranium from four soils using a carbonate leach (total carbonate/bicarbonate conc. = 0.25 *M*).

Leaching efficiencies of uranium from the Fernald incinerator soil and the Y-12 landfarm soils were approximately the same (generally ranged from 40 to 75%). However, for these soils increasing pH and increasing total bicarbonate and carbonate appeared to improve extraction effectiveness. Very small quantities of uranium were extracted from the Y-12 storm sewer sediment by carbonate (generally <5%) indicating the presence of a very leach resistance uranium form in this material.

The basic principle in the use of carbonate leaching to remove uranium from uranium contaminated soils is the formation of the water-soluble stable uranyl tricarbonate $X_4[UO_2(CO_3)_3]$, where X is the sodium or ammonium cation. Concentrations of CO_3^{-2} in the carbonate leaching tests (as determined by the pH of the resulting suspension after the 4-h extraction period) ranged from $\sim 2.0 \times 10^{-4}$ to 0.1 *M*, but appeared to have little influence in the effectiveness of extracting uranium (see Fig. 12). The single exception might be the extraction of uranium from the Y-12 landfarm soil (S93). In this case, simple linear regression analysis showed a highly significant regression ($P < 0.001$, $R^2 = 0.71$) with an intercept of 95.0 and regression coefficient of 12.3 (using PROC REG of SAS 1985). Linear regression coefficients for log carbonate concentrations versus the fraction uranium extracted for the other soils were 5.9, 2.8, and 1.3, respectively, for A-14, B-16, and SSS (and $R^2 < 0.35$). The extraction of uranium from the Y-12 landfarm soil (S93) also showed a highly significant simple linear regression between uranium extracted and pH ($P < 0.001$, $R^2 = 0.58$) with an intercept of −41.4 and regression coefficient of 12.4. Multiple linear regression analyses of extracting uranium from the Y-12 landfarm soil (S93) revealed a highly significant relationship ($P < 0.001$, $R^2 = 0.71$) of the extraction efficiency with log carbonate concentration (regression coefficient of 12.5) and pH (regression coefficient of −0.31).

Total organic carbon (TOC) was determined in the carbonate extractions of the Y-12 landfarm soil. The quantities of organic matter extracted from this soil were highly dependent of the pH and level of total carbonate/bicarbonate in the extract (Fig. 13). The highest TOC (122 μg/mL) was observed in the 0.5 *M* extractions at a pH of ~9.4. The initial soil contained 2.37% total carbon (the pH of sample S93 by the soil/paste method was 3.9; therefore, the total carbon determined by the dry combustion method is assumed to be organic carbon). Thus, approximately 5% of the organic carbon was extracted from the soil using the 0.5 *M* extractant at a pH of 9.4. The quantities of organic carbon contained in the carbonate extractions will likely be >100 μg/mL for many surface soils. These concentrations may have a negative impact on methods used to recover uranium from the supernatant as well as the treatment of secondary wastes.

3.2.2 Citric Acid/Citrate Leaching Tests

Leaching with citric acid/citrate was limited to Fernald soils (A-14 and B-16). Initial leaching studies conducted by Lee and Marsh (1992) revealed that as much as 75% of the uranium in the soil collected near the plant 1 storage pad (sample SP-1A/2A, Table 1) could be removed in 2 h using 0.1 *M* citric acid at a solution-to-soil ratio of 8. This present study involved a complete factorial design utilizing three levels of citrate (0.10, 0.25, and 0.5 *M*) at four pH levels (unadjusted citric acid, and pHs of 5, 7, and 9 obtained by neutralizing citric acid with 50% NaOH). These were 4-h tests conducted at liquid-to-soil ratios of 10:1 (200 mL of

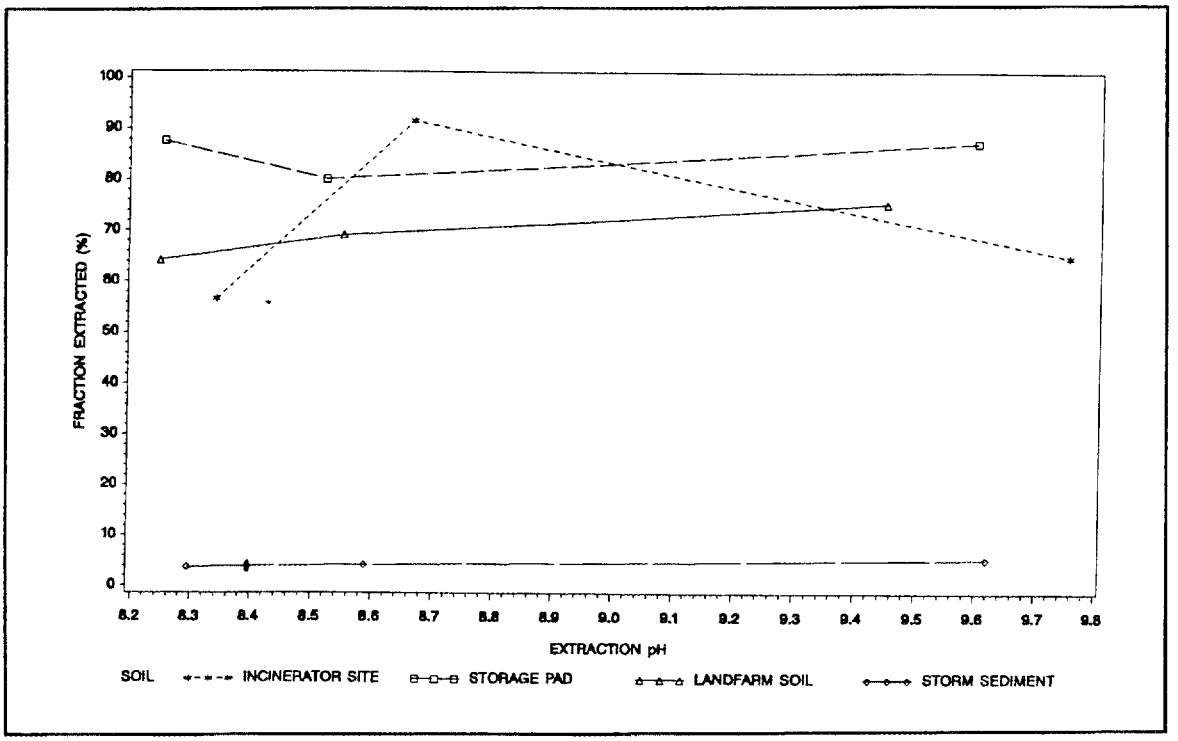


Fig. 11. The extraction of uranium from four soils using a carbonate leach (total carbonate/bicarbonate conc. = 0.50 *M*).

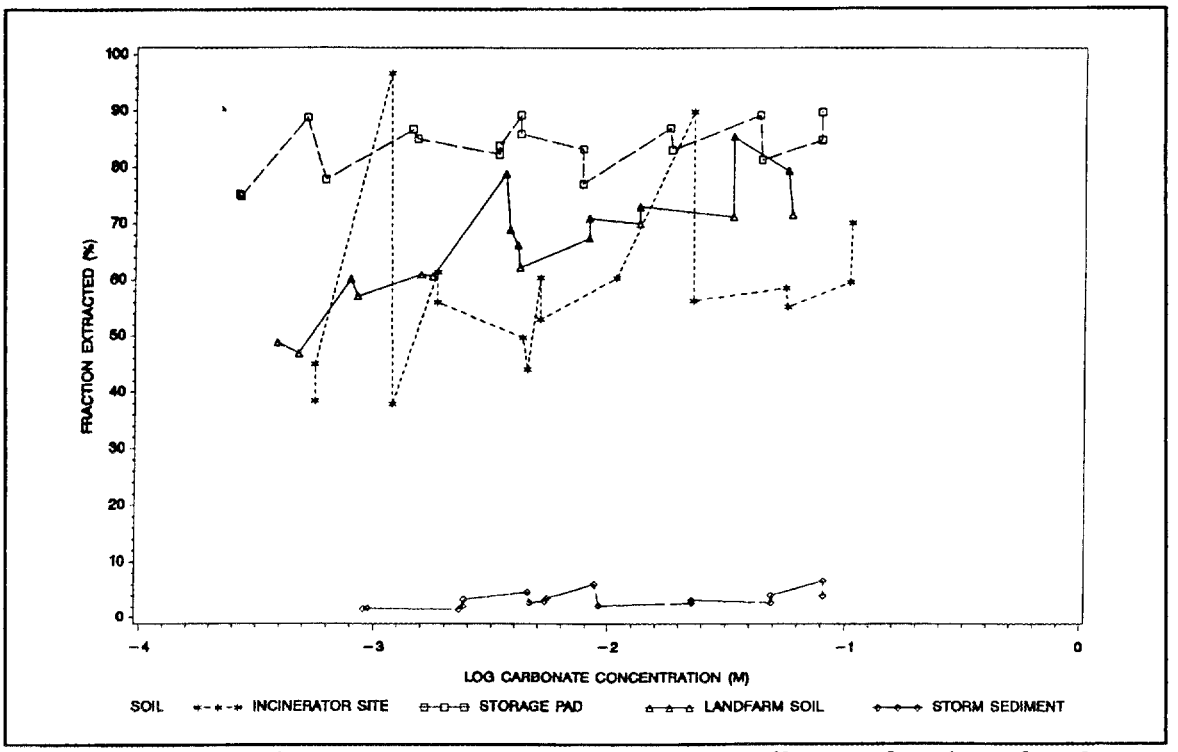


Fig. 12. Fraction of uranium extracted from the four soils as a function of carbonate concentration.

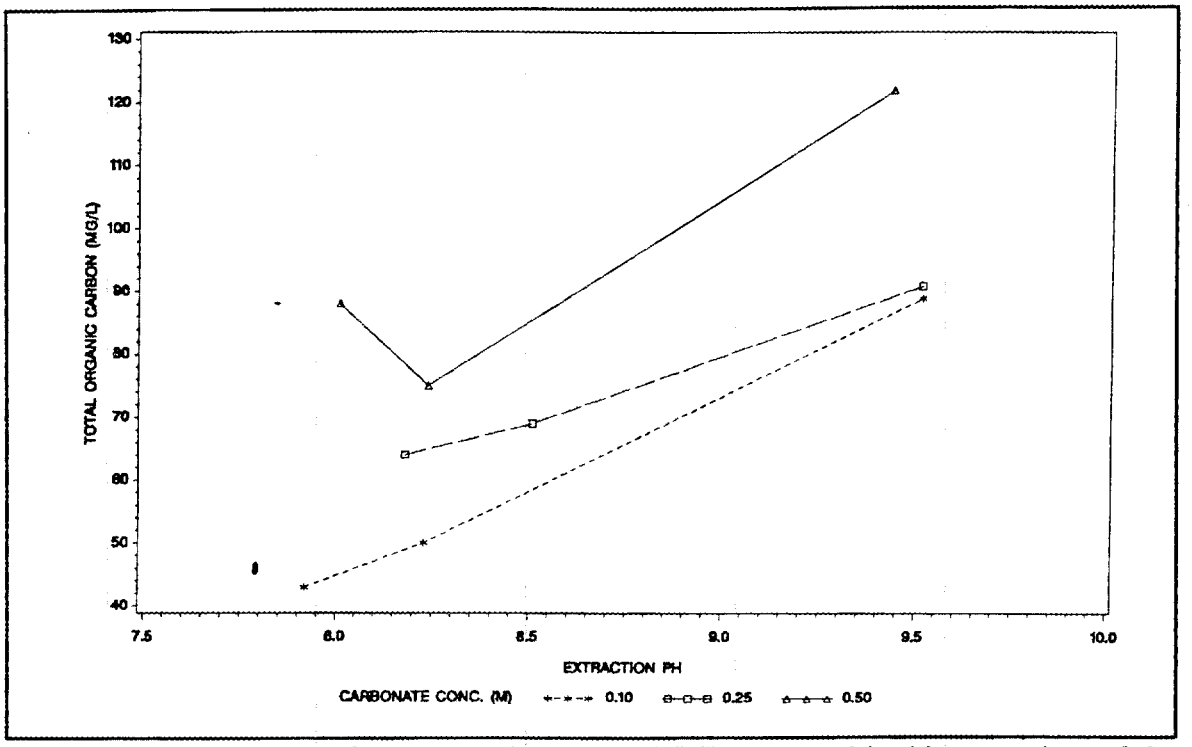


Fig. 13. Concentrations of total organic carbon (TOC) measured in 4-h extractions of the Y-12 landfarm soil as a function of extraction pH and total carbonate/bicarbonate concentration.

extractant and 20 g of soil) in a rotary extractor (with duplicate samples for each treatment). Extraction effectiveness was determined by analyzing the quantities of uranium extracted in the supernatants and expressed as the fraction of that initially analyzed in the soil. The basic objective was to determine the influence of pH and concentration of citrate on removal of uranium from the two soils.

The extraction of uranium from the two Fernald soils was strongly influenced by the pH of the citrate extractions (Figs. 14–16). Using unadjusted citric acid (average pH of the three citrate concentrations was 3.4 and 2.2 for the storage pad and incinerator soil respectively), an average of ~99 and ~68% of the uranium was extracted from the storage pad and incinerator soil respectively. (Note that the fraction of uranium extracted should not be taken as an absolute value as considerable error may be involved by determining extraction effectiveness by difference. The main points to consider here are the differences in the extraction of uranium from the two soils and the relative effects of pH and concentrations of citrate on the extraction of uranium. As work progresses, concentrations of uranium remaining in the residuals of selected extractions will be performed to identify more clearly the absolute quantities of uranium remaining after leaching.)

The higher concentration of citrate (0.5 compared to 0.1 *M*) significantly ($P < 0.01$) increased the extraction of uranium from the Fernald storage pad soil (B-16) but not the incinerator soil (A-14). Extraction pH was the most important of the two variables, pH and concentration of citrate. For example, simple linear regression analyses of the extraction

effectiveness as a function of pH at each level of citrate for each of the two soils showed a highly significant regression ($P<0.01$) except for the incinerator soil leached with 0.50 *M* citrate (see Table 10). Also, multiple linear regression analyses revealed that the extraction effectiveness of uranium from either of the two soils could be reasonably well estimated (R^2 of 0.86 and 0.74, respectively for the storage pad and incinerator soil, $P<0.01$) using pH and citrate concentration (Table 11).

The efficiency of uranium extraction is dependent on the stability of the complexes formed between citric acid and the uranyl ion. In the pH range of 2–4, the uranyl ion is in equilibrium with mononuclear and binuclear citrate chelates, with a preponderance of binuclear complexes (Rajan and Martell 1965). Above pH 4, the binuclear chelates tend to react with hydroxide ions and polymerize into larger complex molecules. These larger molecules tend to become less water-soluble and as the pH of the suspension is increased the molecules likely form similar hydroxide bonding to the hydroxy groups of clay surfaces and become sorbed on clays. Proposed 1:1 formation constants of uranyl citrate chelates are $10^{-2.79}$, $10^{-4.30}$, and $10^{-5.35}$ for the K_1, K_2, and K_3 dissociation constants, respectively (Rajan and Martell 1965). Analyses of the leaching efficiency for uranium in the pH ranges of <2.79, 2.79 to 4.30, 4.3 to 5.35, and >5.35 revealed significantly higher percentages ($P < 0.01$) of uranium were leached from both soils at pH values <2.79 and 2.79–4.30 than at pH values >5.35. Citric acid also forms stable water-soluble complexes with iron and aluminum; thus, the enhanced extraction of uranium at the lower pH values is also likely due to the removal of amorphous iron and aluminum sesquioxides from the soils' surfaces, thus exposing uranium compounds to citric acid extraction. In this respect, the citric acid extraction functions in a fashion similar to the dithionite/citrate

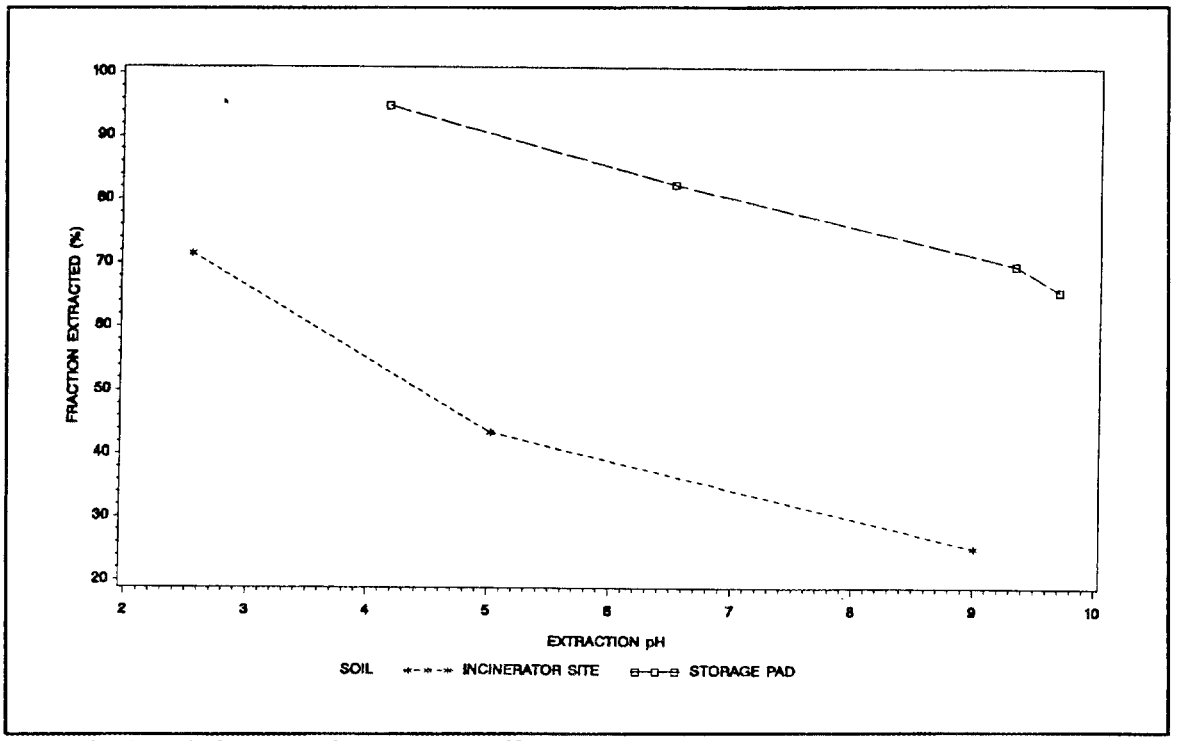


Fig. 14. The influence of pH on the effectiveness of citric acid/citrate to extract uranium from the storage pad and incinerator soils at Fernald (citrate conc. of 0.1 *M*).

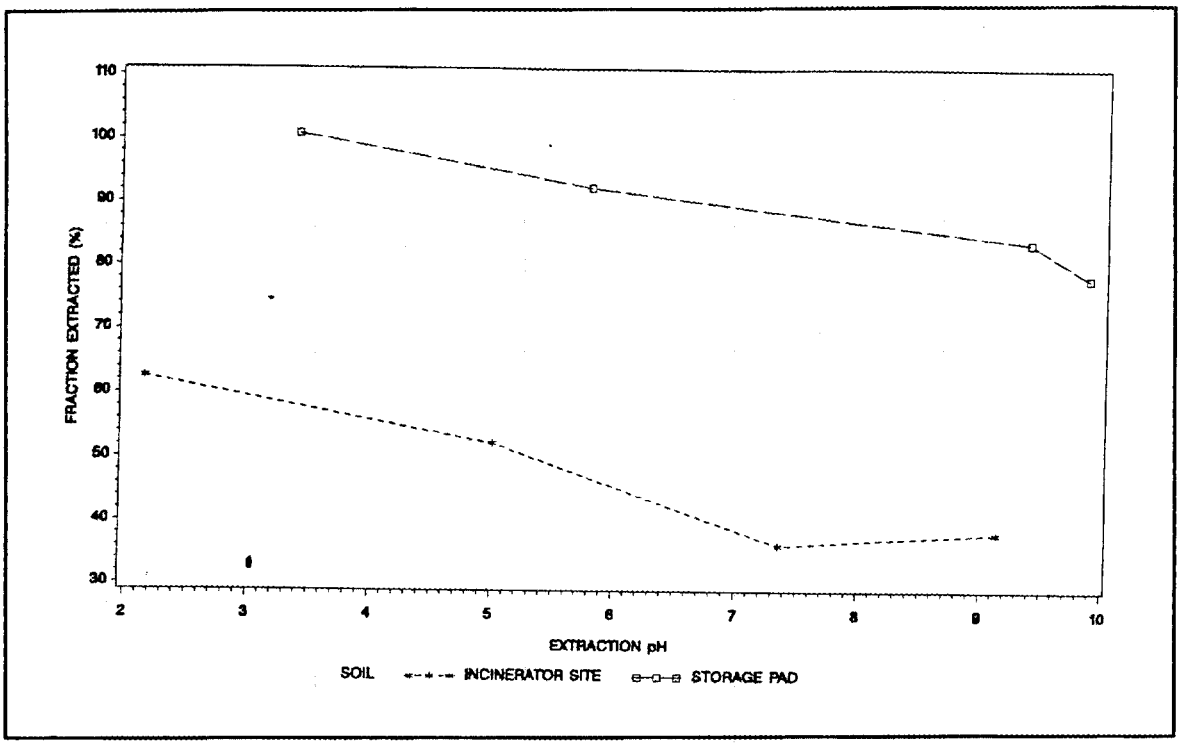


Fig. 15. The influence of pH on the effectiveness of citric acid/citrate to extract uranium from the storage pad and incinerator soils at Fernald (citrate conc. of 0.25 *M*).

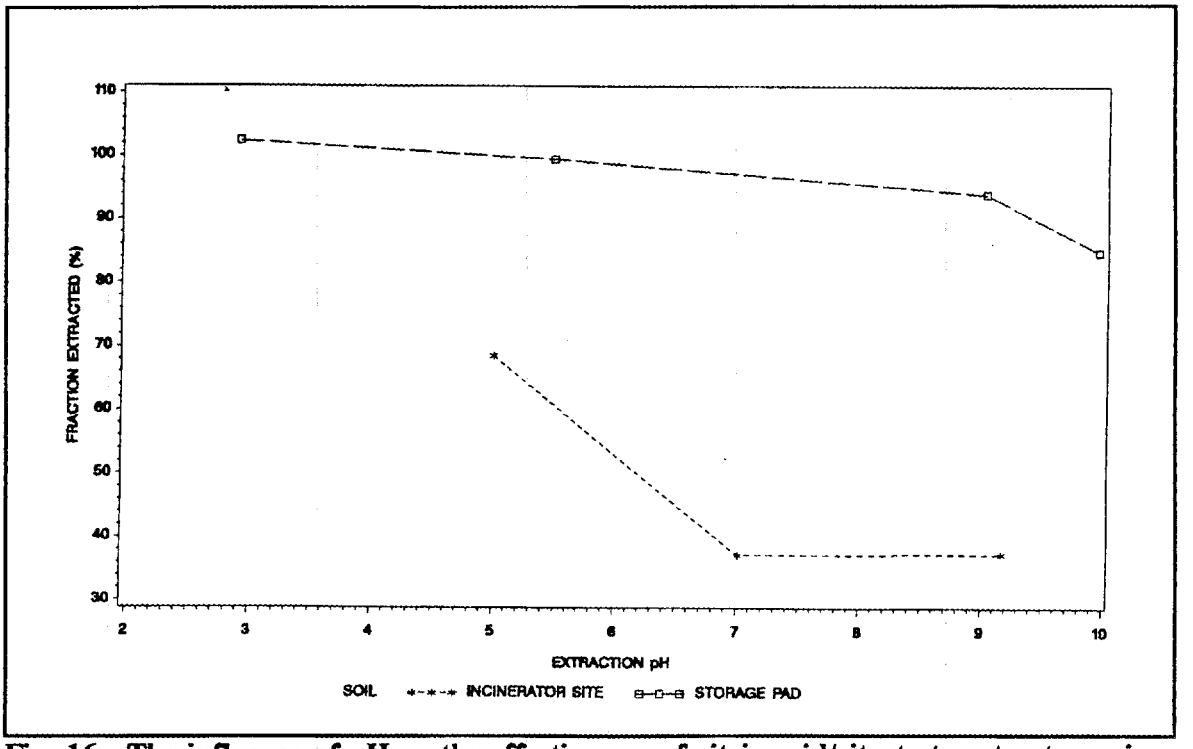


Fig. 16. The influence of pH on the effectiveness of citric acid/citrate to extract uranium from the storage pad and incinerator soils at Fernald (citrate conc. of 0.50 *M*).

Table 10. Linear regression analyses of extraction effectiveness as a function of pH of the citrate leaching solution (for each soil and citrate concentration)

Soil	Citrate conc (M)	R^2	Probability	Intercept	Regression coefficient
Storage pad	0.10	0.96	<0.01	115	-5.08
	0.25	0.94	<0.01	111	-3.20
	0.50	0.81	<0.01	109	-2.16
Incinerator	0.10	0.93	<0.01	85	-6.92
	0.25	0.86	<0.01	70	-3.92
	0.50	0.56	<0.05	79	-4.71

extraction which was shown to be very effective in the removal of uranium (see Sect. 4.1).

3.2.3 Bisequential Citric Acid/Carbonate Leaching Tests

The bisequential citric acid/carbonate leaching tests were conducted by first leaching with 0.1 M citric acid (20 g of soil in 200 mL of extractant) followed with two leachings (200 mL each) with 0.1 M sodium carbonate/bicarbonate pH 9 buffer solutions. The effect of extraction time was investigated (e.g., each of the three extractions were carried out at 0.5, 1, and 2 h). The influence of adding $KMnO_4$ (0.017 g/g of soil) to oxidize uanium(IV) to uranium(VI) in the

Table 11. Multiple linear regression analyses of extraction effectiveness as a function of pH and citrate concentration

Soil	R^2	Intercept	Regression coefficient[a]	
			pH	Conc
Storage pad	0.86	100	$-3.3^{0.01}$	$36.1^{0.01}$
Incinerator	0.73	73	$-5.0^{0.01}$	17.1^{ns}

[a]Superscript indicates level of significance, $P<0.01$ and ns (not significant at $P<0.05$).

carbonate extractions were investigated. All treatments were conducted in duplicate at a liquid-to-soil ratio of 10:1 on a rotary extractor rotating at 50 rpm.

Between 50 and 60% of the uranium was removed from the incinerator soil (A-16) by the citric acid extractions. The first carbonate extractions removed an additional 20 to 30% and the second carbonate extraction removed considerably less, <5% (see Table 12). The addition of $KMnO_4$ appeared to increase the extraction of uranium ~5%. Extraction of uranium is time dependent and appears to be only related to the initial extractions with citric acid. For example, the 0.5-hr extractions with citric acid removed approximately 50% of the uranium while the 2-hr extractions removed an additional 10%. Increasing extraction time with the carbonate extractions did not result in greater removal of uranium, indicating that once the labile forms of uranium are removed from the soils' surface the dissolution of the more residual uranium forms is a slow process.

A similar phenomenon was observed in the citric acid/carbonate sequential extraction of the Fernald storage pad soil (B-16). However, in this case, a 0.5-h extraction with citric acid (0.1 *M*) was equivalent to a 2-h extraction (see Table 13) indicating that this soil contains a readily leachable fraction and a residual uranium fraction which was more difficult to extract. The first 2-h sodium carbonate extraction, with $KMnO_4$ added to oxidize uranium(IV), showed a much larger fraction of uranium extracted than the 0.5- or 1-h extractions. Also, other than the 2-h extraction times, the addition of $KMnO_4$ did not appear to increase the extraction of uranium from the Fernald storage pad soil. Thus, it appears that a large fraction (~70%) of the uranium in this soil is present in a labile form that is readily leached by citric acid. However, longer extraction times than 2 h are required to extract residual forms (see Fig. 17). Linear regression analyses of the fraction of uranium extracted as a function of extraction time revealed a very good fit with the incinerator soil (R^2 = 0.98, y-intercept of 48.2, and regression coefficient of 6.98). The fit for the storage pad soil was not as good (R^2 = 0.75 and a *y*-intercept of 65.1), but the regression coefficient was quite similar (6.61), indicating that the extraction kinetics of the residual uranium from the two soils were similar which may reflect dissolution of uranium from similar uranium forms.

The leached residual from the 2-hr extraction of the incinerator soil was analyzed for total uranium by neutron activation procedures (Wade et al. 1992). To determine the effectiveness of extraction with respect to the soil's particle size, the leached residual was fractionated into sand, silt, and clay fractions, and the concentration of uranium determined in each of these size fractions (Table 14). Direct uranium analyses of the leached soils by neutron activation indicated the fraction of uranium removed from the incinerator soil by this leaching method was less than that predicted by analyses of the leachate and calculation of the percent leached by difference (see Table 12). For example, by direct neutron activation analysis, ~75% of the uranium was calculated to be leached from the sample without using $KMnO_4$ with the carbonate extractions (Table 14). On the other hand, analyses of the supernatant for uranium by ICP-MS indicated ~86% of the initial uranium in the sample had been leached by the procedure (Table 12), a difference of nearly 10%. The leaching with $KMnO_4$ in the carbonate extractions did not show the differences in extraction efficiencies to be greatly different between the two analytical methods (89% leached by ICP-MS analyses of the leachate as compared to 85% leached by direct uranium analyses of the leached residual via neutron activation procedures). Uranium appears to be extracted more effectively from the smaller size fractions of soil (see Table 14). For example, over 80% of the uranium in the clay fraction was removed by this extraction process and only

Table 12. The removal of uranium from the Fernald incinerator soil (A-14) using sequential extractions of 0.1 *M* citric acid and 0.1 *M* sodium carbonate, pH 9.5 (w and w/o $KMnO_4$)

Time (h)	Oxidant with carbonate[a]	Percent uranium extracted[b]			
		Citric	1st carbonate	2nd carbonate	Total
0.5	None	49.7	23.8	4.8	78.3
	With	50.1	28.2	5.1	83.4
1.0	None	55.5	21.3	3.4	81.2
	With	58.9	24.4	4.6	87.9
2.0	None	62.6	20.0	3.8	86.2
	With	61.3	24.5	3.0	88.8

[a]0.017 g $KMnO_4$/g of soil.
[b]As determined by uranium measured in extracts (average of two replicates).

Table 13. The removal of uranium from the Fernald storage pad soil (B-16) using sequential extractions of 0.1 *M* citric acid and 0.1 *M* sodium carbonate, pH 9.5 (w and w/o $KMnO_4$)

Time (h)	Oxidant with carbonate[a]	Percent uranium extracted[b]			
		Citric	1st carbonate	2nd carbonate	Total
0.5	None	74	14	8.5	96
	With	69	8	4.5	82
1.0	None	75	12	4.7	92
	With	73	14	3.0	91
2.0	None	69	18	6.8	94
	With	70	31	4.2	106

[a]0.017 g $KMnO_4$/g of soil.
[b]As determined by uranium measured in extracts (an average of two replicates).

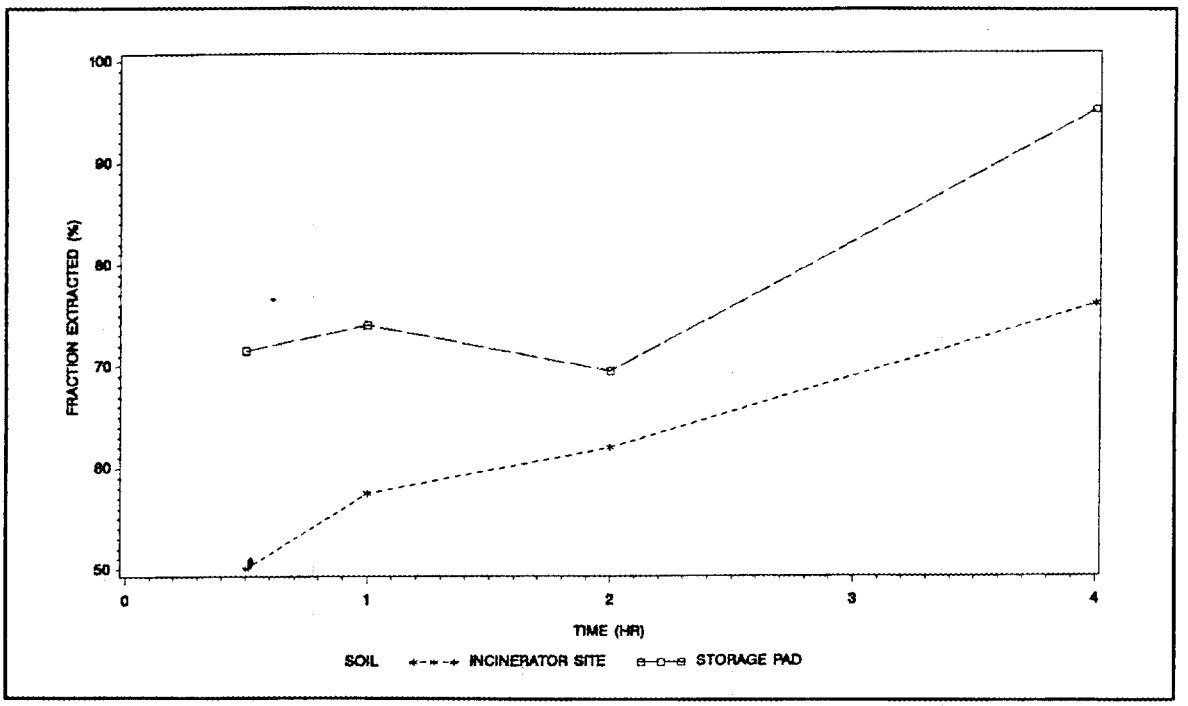


Fig. 17. The influence of extraction time on the extraction of uranium from the Fernald soils (A-14, the incinerator and B-16, the storage pad soil) using 0.1 *M* citric acid.

Table 14. Uranium concentrations in the leached residual of the 2-h sequential citric acid/carbonate extractions of the Fernald incinerator soil (A-14)

Size fraction	^{238}U $\mu g/g$	Treated			
		^{238}U $\mu g/g$		% Leached	
		Without $KMnO_4$	With $KMnO_4$	Without $KMnO_4$	With $KMnO_4$
Whole soil	538	136	94	75	82
Sand 2mm–53μm	1033	416	294	60	71
Silt 53–2μm	286	91	56	68	80
Clay $<2\mu$m	1019	171	152	83	85

60 to 70% was leached from the sand size fractions (2 mm to 53 μm fraction). Also, with respect to the use of $KMnO_4$ as an oxidant to convert uranium (IV) to (VI), smaller differences in the fraction of uranium leached were noted in the clay fraction as compared to the silt and sand fractions, indicating that the $KMnO_4$ was more effective in converting uranium (IV) to uranium (VI) in the larger particle ranges. It could also be implied that there were higher levels of uranium(IV) in the larger particle ranges than the smaller particle ranges. Such a relationship is entirely likely as uranium particulate deposited to the soil in particle ranges <2 μm diam would have a significantly larger surface area exposed and subject to oxidation reactions than uranium particulate >53 μm diam.

3.2.4 Nitric Acid Leaching Tests

Nitric acid leaching tests were conducted to evaluate the influence of pH on the extraction of uranium in the absence of a strong chelator such a citrate for uranium and iron. Citric acid appears to be a good extractant of uranium from the Fernald storage pad soil (extraction efficiencies $>80\%$ in single 4-h extractions). The effectiveness of citric acid may be due to its strong chelation capacity for uranium, or its ability to remove noncrystalline forms of sesquioxides from surfaces of soil particles; thus, exposing surfaces of uranium particulate to dissolution by citric acid.

To test this, 20 g of the Fernald storage pad soil (B-16) was extracted with 200 mL of water. Prior to extraction in the rotary extractor, the pH of the suspension was lowered to 2.0 using ~ 1.5 mL of ultrapure concentrated nitric acid. After 4 h, the pH of the suspension had risen to 5.60 ± 0.06 due to the dissolution of dolomite particulate. The pH in the control treatment (where nitric acid was not added) was 8.11 ± 0.01 after 4 hr. These extractants were carried out in triplicate.

In the soil suspensions acidified to pH 2 before extraction, $22.3 \pm 6.1\%$ of the uranium was extracted as determined by measuring the uranium concentration in the resulting supernatant. In the deionized-distilled water extractions, $6.29 \pm 2.3\%$ of the uranium was removed. In the pH range of 5.0–6.0, extractions with citric acid generally removed 80 to 90% of the uranium from this soil under the same extraction conditions (see Figs. 14, 15, and 16). Thus, these data strongly support the hypotheses that the extraction of uranium from soils by citric acid is not due to a simple acidification relationship, but is likely due to citric acid's ability to chelate strongly with uranium as well as to remove coatings of amorphous iron and aluminum sesquioxides from solid phase uranium particulate; thus, enhancing the dissolution and extraction of uranium.

4. SUMMARY, CONCLUSIONS, AND FUTURE DIRECTIONS

Three soils and a sediment contaminated with uranium were used in this study to determine the effectiveness of sodium carbonate and citric acid leaching to decontaminate or remove uranium from uranium contaminated soils. The objective was to selectively extract uranium using a soil washing/extraction process without seriously degrading the soil's physicochemical characteristics or generating a secondary waste form that would be difficult to manage and/or dispose of. Two of the soils were surface soils from the DOE facility formerly called the Feed Materials Production Center (FMPC) at Fernald, Ohio. This facility is presently called the Fernald Environmental Management Project (FEMP). The two soils collected at the Fernald facility are those being used in an interlaboratory treatability study sponsored by the FEMP Uranium in Soils Integrated Demonstration (UID) program. One of the soils is from near the Plant 1 storage pad and the other soil was taken from near a waste incinerator used to burn low-level contaminated trash. The third soil was a surface soil from an area formally used as a landfarm for the treatment of spent oils at the Oak Ridge Y-12 Plant. The sediment sample was material sampled from a storm sewer sediment trap at the Oak Ridge Y-12 Plant. Uranium concentrations in the Fernald soils ranged from 450 to 550 μg U/g of soil while the samples from the Y-12 Plant ranged from 150 to 200 μg U/g of soil (air-dried basis).

Carbonate extractions (total carbonate/bicarbonate conc ranging from 0.1–0.5 *M*, over pH ranges of ~ 8 to slightly less than 10) generally removed from 70–90% of the uranium from the Fernald storage pad soil. Uranium was slightly more difficult to extract, by carbonate extraction, from the Fernald incinerator and the Y-12 landfarm soils (extraction efficiencies ranged from ~ 40 to $\sim 75\%$). Very small amounts of uranium could be extracted ($< 8\%$) from the storm sewer sediment using sodium carbonate extractions. Increasing the extraction temperature from 22 to 40°C for the sodium carbonate extractions of the Fernald waste incinerator soil increased the fraction of uranium leached from ~ 40 to $\sim 80\%$. However, the increased extraction temperature did not appear to increase extraction effectiveness for the soil sampled near the Fernald storage pad. Extraction with carbonate at high solution-to-soil ratios were as effective as extractions at low solution-to-soil ratios, indicating attrition by the paddle mixer was not significantly different than that provided in a rotary extractor. Also, pretreatments such as milling or pulverizing the soil sample did not appear to increase extraction efficiency when carbonate extractions were carried out at elevated temperatures (60°C) or long extraction times (23 h). Adding $KMnO_4$ (to oxidize tetravalent uranium forms to hexavalent forms for extraction as the carbonate complex) in the carbonate extraction appeared to increase extraction efficiency from the Fernald incinerator soil but not the Fernald storage pad soil. Also, additions of $KMnO_4$ to the carbonate extractions, appeared to be more effective in removing uranium from the silt and sand size fractions ($> 2\mu$m) of soil than clay size fractions ($< 2\mu$m).

The most effective leaching ($> 90\%$ from both Fernald soils) was obtained using a citrate/dithionite extraction procedure designed to remove amorphous (noncrystalline) iron/aluminum sesquioxides from surfaces of clay minerals. This extraction procedure uses sodium dithionite ($Na_2S_2O_4$) with a sodium citrate/$NaHCO_3$ buffer (pH ~ 7.3) and elevated temperatures (75–80°C) to generate a highly reducing condition that reduces noncrystalline iron(III) to iron(II) which is readily chelated by the citrate and removed from the soil's surface. After reaction with the dithionite at elevated temperatures, an excess of $KMnO_4$ was added to oxidize any U(IV) to the uranyl form and subsequent extraction as the carbonate complex.

Citric acid also proved to be a very good extractant for uranium. At pH values <5, $\sim 90\%$ and $\sim 50\%$ of the uranium could be extracted (in 4 h) from the Fernald storage pad and incinerator soils, respectively. A citric acid extraction (0.1 *M*) of the Fernald incinerator soil followed with two carbonate extractions containing $KMnO_4$ (three sequential 0.5-h extractions) removed $>80\%$ of the uranium indicating that a combination of citric acid and carbonate leaching procedures may be the best approach for soils containing residual forms of uranium. Extractions of soils with nitric acid indicated that the extraction of uranium by citric acid is not due to a simple acidification relationship. For example, extractions of the Fernald storage pad soil acidified to pH 2 with nitric acid (average pH of 5.6 after three 4-h extractions) removed only 22% of the uranium. Citric acid extractions (in the same pH range of 5 to 6) removed 80 to 90% of the uranium from the same soil, indicating that extraction by citric acid is due to its ability to chelate strongly with uranium as well as to remove coatings of amorphous iron and aluminum sesquioxides from solid phase uranium particulate; thus, enhancing the dissolution and extraction of uranium.

Research to date has shown that significant quantities of uranium can be extracted from the Fernald and Y-12 landfarm soils without seriously degrading the soil's physicochemical characteristics or generating a secondary uranium waste form that is difficult to manage and/or to dispose of. For the Fernald soils, residual concentrations after extraction with the citrate/dithionite procedure were below the UID proposed 52-μg U/g screening criteria. Meeting this proposed screening level will be much easier with the storage pad soil than the incinerator soil. For example, these levels were routinely observed in the extractions of the storage pad soil using citric acid (4 h using 0.1 *M* conc at room temperature) or carbonate (2 h at 40°C). The leaching characteristics of the storage pad soil are likely more representative of uranium soil contamination within the production area, while the incinerator soil represents a very small part of the uranium contaminated soil at Fernald. Uranium in the incinerator soil is concentrated in the very top surface of the soil and has mineralogical characteristics of a low temperature ash (Lee and Marsh 1992). The total volume of contaminated soil at the incinerator site is very low (probably <40 yd^3) and much of it has already been removed as part of a removal action.

Future research needs to be directed at speeding up the rates at which uranium is leached from the soils. Residence times in conventional soil washing operations (based on physical separation processes) are characteristically <5 min. Obviously, a soil washing/leaching operation (based on chemical leaching processes) will require longer residence times; however, long residence times, such as hours, will require unacceptably large reaction vessels or a very slow load factor (in terms of yd^3/hr, etc.). This coming year, work will focus on the establishment of acceptable engineering residence times for a soil washing/leaching operation at Fernald, and the leaching research aspect of the project will be directed at attaining acceptable leach rates. To do this, laboratory scale attrition scrubbers will be used in combination with elevated temperatures and a variety of leaching media (based on carbonate and citric acid).

Although research to date has centered on the use of sodium carbonate/bicarbonate as extraction media, the use of ammonium carbonate has certain advantages. For example, the use of ammonium carbonate permits the recovery of both the cation and anion of the salt from the uranium recovery solution. For example, the ammonium cation can be steam stripped from solution as ammonia gas and the carbonate anion can be removed as carbon dioxide. Both of these gases are readily recombined in a scrubber to form fresh ammonium carbonate solutions. During the steam stripping process (represented by the following equation), uranium can be

removed from the solution as $UO_3 \cdot 2H_2O$, providing a method to recycle the ammonium carbonate as well as recovery of the uranium in an acceptable small volume waste form (Langston et al. 1957 and Mattus 1980).

$$(NH_4)_4UO_2(CO_3)_3 + \text{heat} = 4NH_{3\,(gas)} + 3CO_{2\,(gas)} + UO_3 \cdot 2H_2O.$$

In addition, ammonium carbonate is less aggressive in the dissolution of soil layer silicates. Thus, for these reasons the ability of ammonium carbonate to extract uranium from the three soils and sediment will also be examined.

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APPENDIX A

CONVERSION FACTORS

Appendix A

CONVERSION FACTORS

Activities of Natural Uranium, Depleted Uranium and ^{238}U, to μg U/g of Soil

There is some confusion as to what conversion factors are appropriate in converting activities of uranium (usually expressed in pCi/g) to ppm uranium in soil (μg U/g of soil). The Fernald RI/FS studies have used the conversion factor of 1.48 (1.48 times the pCi/g of activity = ppm uranium in soil). Thus, the proposed screening level of 35 pCi/g is equilvalent to 51.8 ppm U in soil (51.8 μg U/g of soil). This conversion factor is determined from the natural distribution of the uranium isotopes (0.0055% ^{234}U, 0.72% ^{235}U, and 99.27% ^{238}U). The total activity in a gram of natural uranium (6.79×10^5 pCi/$g_{U\text{-}Total}$) is determined using the specific activities of 3.3×10^5 pCi/$g_{U\text{-}238}$, 2.14×10^6 pCi/$g_{U\text{-}235}$, and 6.13×10^9 pCi/$g_{U\text{-}234}$ and their respective mass fractions. Even though the mass fraction of ^{234}U is small, it constitutes slightly more activity (3.37×10^5 $pCi_{U\text{-}234}$) than the mass of ^{238}U (3.27×10^5 $pCi_{U\text{-}238}$). ^{235}U in natural uranium is a small contributor of activity (1.54×10^4 $pCi_{U\text{-}235}$). The specific activity of 1 gram of natural uranium (6.79×10^5 pCi/$g_{U\text{-}total}$) is equivalent to

$$1 \text{ pCi U}/g_{soil} = 1.48 \text{ ppm } U_{soil} = 1.48\times10^{-6}\ g_{U\text{-}total}/g_{soil}.$$

For depleted uranium (assuming a mass distribution of 0.0034, 0.3, and 99.7% respectively for ^{234}U, ^{235}U, and ^{238}U, the conversion factor from pCi to ppm is 1.84 rather than 1.48.

When gamma spectroscopy is used to determine ^{238}U (from the activity of ^{234m}Pa, $t_{1/2}$ = 1.14 min) the specific activity of ^{238}U (3.3×10^5 pCi/$g_{U\text{-}238}$) should be used giving a conversion factor of 3.03 (1 pCi U/g_{soil} = 3.03 ppm U_{soil} = 3.03 μg U/g of soil). The important point to keep in mind is that 35 pCi/g of soil determined by gamma spectroscopy for ^{238}U is not all the activity of the sample (assuming natural distribution of the uranium isotopes). Thus, it is not the same as the proposed 35 pCi/g screening level, but 3.03 times the pCi/g determined by gamma spectroscopy does represent >99% of the uranium mass in a sample.

APPENDIX B

TABULAR DATA

Table B1. The influence of extractant concentration and pH on the extraction of uranium from soil (A-14) from near the Fernald waste incinerator

Extractant			Fraction of uranium leached[a] (%)
Type	Concentration (*M*)	pH	
Carbonate	0.10	8.1	42
		8.4	67
		9.8	73
	0.25	8.2	59
		8.6	47
		9.8	57
	0.50	8.3	57
		8.7	92
		9.7	65
Citrate	0.10	2.5	76
		5.0	43
		8.4	ND[b]
		9.0	25
	0.25	2.1	63
		5.0	52
		7.4	36
		9.1	38
	0.50	1.9	66
		5.0	69
		7.0	37
		9.1	37

[a]As determined by concentrations of uranium in liquid extractions.
[b]Not determined.

Table B2. The influence of extractant concentration and pH on the extraction of uranium from soil (B-16) from near the Fernald plant 1 storage pad

Extractant			Fraction of uranium leached[a] (%)
Type	Concentration (*M*)	pH	
Carbonate	0.10	7.7	75
		8.1	83
		9.7	85
	0.25	8.1	86
		8.5	83
		9.6	85
	0.50	8.3	87
		8.5	80
		9.6	87
Citrate	0.10	4.1	95
		6.5	82
		9.3	70
		9.7	66
	0.25	3.4	101
		5.8	92
		9.4	84
		9.9	78
	0.50	2.9	102
		5.5	99
		9.0	94
		10.0	85

[a]As determined by concentrations of uranium in liquid extractions.

Table B3. The influence of extractant concentration and pH on the extraction of uranium from the Y-12 landfarm soil (S93)

Extractant			Fraction of uranium leached[a] (%)
Type	Concentration (*M*)	pH	
Carbonate	0.10	8.0	48
		8.2	59
		9.5	72
	0.25	8.1	61
		8.5	74
		9.5	78
	0.50	8.2	64
		8.6	69
		9.5	76

[a]As determined by concentrations of uranium in liquid extractions.

Table B4. The influence of extractant concentration and pH on the leaching of uranium from the Y-12 storm sewer sediment (SSS)

Extractant			Fraction of uranium leached[a] (%)
Type	Concentration (*M*)	pH	
Carbonate	0.10	8.3	1.6
		8.7	2.1
		9.8	2.9
	0.25	8.3	2.4
		8.7	3.3
		9.7	3.4
	0.50	8.3	3.7
		8.6	4.1
		9.6	5.3

[a]As determined by concentrations of uranium in liquid extractions.

Table B5. Concentrations of total organic carbon in carbonate extracts of the Y-12 landfarm soil (S93)[a]

Carbonate concentration (*M*)	Extract pH	Total organic carbon TOC (μg/mL)
0.10	7.92	43
0.10	8.23	50
0.10	9.52	89
0.25	8.18	64
0.25	8.51	69
0.25	9.52	91
0.50	8.01	88
0.50	8.24	75
0.50	9.44	122

[a]Extraction time = 4 h

Table B6. pH values of carbonate and citric acid extractions of the Y-12 and Fernald uranium contaminated soils

				1ST EXTRACTION	2ND EXTRACTION	3RD EXTRACTION
				MEAN	MEAN	MEAN
SOIL	EXTRACT	CONC	INITIAL PH			
A14	CARBONATE	0.10 M	8.43	8.08	8.42	8.47
			8.90	8.41	8.84	8.89
			9.70	9.80	9.92	9.98
		0.25 M	8.33	8.20	8.50	8.49
			8.79	8.59	8.83	8.86
			8.97	8.57	8.83	8.85
			9.60	9.80	9.84	9.86
		0.50 M	8.30	8.34	8.52	8.51
			8.67	8.66	8.75	8.68
			9.51	9.75	9.75	9.76
	CITRATE	0.10 M	2.26	2.53	2.24	2.14
			4.89	5.01	5.09	5.12
			7.16	8.37	9.15	8.59
			8.45	9.01	9.81	9.50
		0.25 M	1.82	2.16	1.91	1.94
			4.98	5.01	5.02	5.08
			6.89	7.36	7.42	7.30
			8.62	9.15	9.77	.
		0.50 M	1.61	1.86	1.71	1.79
			5.00	5.00	5.05	5.19
			6.87	7.01	6.96	6.98
			8.66	9.18	9.73	9.63

Table B6 (Continued)

				1ST EXTRACTION	2ND EXTRACTION	3RD EXTRACTION
				MEAN	MEAN	MEAN
SOIL	EXTRACT	CONC	INITIAL PH			
B16	CARBONATE	0.10 M	8.43	7.75	8.35	8.47
			8.90	8.08	8.76	8.79
			9.70	9.68	9.85	9.79
		0.25 M	8.33	8.10	8.49	8.53
			8.79	8.46	8.78	8.73
			8.97	8.46	8.78	8.73
			9.60	9.66	9.78	9.69
		0.50 M	8.30	8.25	8.49	8.61
			8.67	8.52	8.72	8.68
			9.51	9.60	9.71	9.61
	CITRATE	0.10 M	2.25	4.15	4.10	3.56
			5.20	6.53	6.44	6.08
			6.96	9.34	9.74	9.65
			8.96	9.70	10.19	10.09
		0.25 M	1.90	3.40	3.18	2.43
			5.20	5.80	5.60	5.50
			7.10	9.41	9.74	9.65
			9.28	9.90	10.34	10.40
		0.50 M	1.84	2.91	2.62	2.12
			5.00	5.49	5.46	5.34
			6.90	9.04	9.27	9.18
			9.03	9.97	10.34	10.40

Table B6 (Continued)

SOIL	EXTRACT	CONC	INITIAL PH	1ST EXTRACTION MEAN	2ND EXTRACTION MEAN	3RD EXTRACTION MEAN
S93	CARBONATE	0.10 M	8.43	7.96	8.43	8.59
			8.90	8.25	8.82	8.93
			9.70	9.52	9.72	9.74
		0.25 M	8.33	8.16	8.57	8.67
			8.79	8.51	8.80	8.84
			8.97	8.49	8.79	8.85
			9.60	9.52	9.61	9.66
		0.50 M	8.30	8.25	8.50	8.60
			8.67	8.55	8.72	8.77
			9.51	9.45	9.50	9.59
SSS	CARBONATE	0.10 M	8.43	8.30	8.38	8.54
			8.90	8.72	8.77	8.93
			9.70	9.80	9.75	9.90
		0.25 M	8.33	8.31	8.38	8.48
			8.79	8.68	8.70	8.79
			8.97	8.67	9.69	8.81
			9.60	9.72	9.69	9.81
		0.50 M	8.30	8.30	8.40	8.47
			8.67	8.59	8.62	8.74
			9.51	9.62	9.62	9.73

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