



ELSEVIER

Journal of Hazardous Materials 66 (1999) 67–87

**Journal of
Hazardous
Materials**

Bench- and pilot-scale studies relating to the removal of uranium from uranium-contaminated soils using carbonate and citrate lixiviants

C.W. Francis ^{a,*}, M.E. Timpson ^b, J.H. Wilson ^c

^a *Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS-6038, Oak Ridge, TN 37831-6038, USA*

^b *Oak Ridge Associated Universities, Oak Ridge, TN, USA*

^c *Chemical Technology Division, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS-6038, Oak Ridge, TN 37831-6038, USA*

Abstract

Development of the nuclear industry has resulted in soil becoming contaminated with uranium from a variety of sources. To avoid the disposal of these soils in conventional low-level radwaste burial sites, a 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. Two lixiviants, carbonate and citrate, were evaluated as to their ability to extract uranium from soil in a soil washing engineering process. The objective was to use a washing/extracting process to selectively remove the uranium from soil without seriously degrading the soil's physicochemical characteristics or generating a secondary waste form that is difficult to manage and/or dispose. Both carbonate and citric acid lixiviants were observed to be effective extractants to remove uranium from the soils tested. Carbonate, because of its ability to be recycled and its tendency to be more selective for uranium, is preferred for most soils. A major obstacle for using citric acid as well as mineral-based acids is their generation of waste streams from which it is difficult to remove uranium and manage (and dispose of any residual waste water sludges) in an environmentally acceptable manner. The removal of uranium was examined for three soils sampled from two US Department of Energy sites. Two soils were from the facility formerly called the Feed Materials Production Center at Fernald, Ohio and the other soil was from the Oak Ridge Tennessee Y-12 Plant. In the bench-scale studies, general relationships, such as the effect of

* Corresponding author. Fax: +1 423 458 6277; e-mail: chetfrancis@compuserve.com

carbonate and citrate concentrations, pH, the presence of oxidants, such as KMnO_4 , temperature, and extraction time were investigated. The best pilot-scale treatment consisted of three successive extractions with 0.25 M carbonate–bicarbonate (in presence of KMnO_4 as an oxidant) at 40°C followed with two water rinses. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Uranium removal; Carbonate lixiviant; Citrate lixiviant

1. Introduction

Uranium in soils consists of several natural long-lived alpha-emitting radioisotopes (^{238}U , ^{235}U , and ^{234}U) whose total concentration seldom exceeds 10 mg kg^{-1} ([1]). Uranium-238 dominates the natural distribution of uranium on a weight basis (i.e., it constitutes 99.27 wt.% while ^{234}U and ^{235}U make up 0.0055 and 0.72 wt.%, respectively). However, with respect to activity, because of the higher specific activity of ^{234}U ($6.13 \times 10^9 \text{ pCi g}_{\text{U-234}}^{-1}$) as compared to ^{238}U ($3.3 \times 10^5 \text{ pCi g}_{\text{U-238}}^{-1}$), ^{234}U actually contributes slightly more on an activity basis than ^{238}U (49.60, 48.13, and 2.27%, respectively, for ^{234}U , ^{238}U , and ^{235}U). Elevated uranium levels in soil may constitute a human health concern from the standpoint of leading to increased levels of alpha-emitting radioisotopes in drinking water and their uptake in plants and transport through the food chain to man. Uranium is also a known toxic metal that may lead to kidney damage and other health disorders in humans [2].

Production of enriched uranium for development of a nuclear industry has resulted in soils becoming contaminated with uranium from a variety of sources. Presently, there is an ongoing effort to determine how, and to what extent these sites will be cleaned up [3]. These sources include deposition of uranium airborne particles coming from stacks of facilities as well as leaks and spills of uranium-rich solvents and process effluents generated in a wide assortment of aqueous and nonaqueous extraction/treatment processes. One such production site that has experienced considerable contamination of soils with uranium is the United States Department of Energy (USDOE) facility formerly called the Feed Materials Production Center (FMPC) at Fernald, OH. 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, OH. 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 $\sim 10,000$ metric tons of uranium) and began a decline in 1964 to a low of about 1230 metric tons in 1975. In the mid-80's, production increased slightly but was terminated in 1989 due to decreased demand. The exact quantity of soil contaminated with uranium is not clearly resolved. Some estimates are as high as $2,000,000 \text{ m}^3$ of soil containing unacceptable levels of uranium. Another USDOE facility that has considerable quantities of uranium-contaminated soil is the Oak Ridge Y-12 Plant. In this instance, the quantity of contaminated soil is considerable less (probably less than 2000 m^3) resulting largely from land farming of waste oils containing uranium and collection of sediment from storm sewers within the Y-12 Plant production area. 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.

The objective of this research is to use a washing/extraction process to selectively remove the uranium from the soil without seriously degrading the soil's physico-chemical characteristics or generating a secondary uranium waste form that is difficult to manage and/or dispose. As a guide to assist in the evaluation of potential removal processes that may be applicable in a clean up technology, a screening level of 52 mg kg^{-1} of uranium (dry weight basis) was established. This concentration of uranium is equivalent to 35 pCi g^{-1} of the ^{238}U isotope. Several approaches will be taken to achieve these objectives. They include: (1) the use of conventional soil washing practices, (2) the deployment of methods used to extract uranium in the mining and milling industries, and (3) the utilization of the selective dissolution techniques developed in soil science to characterize and/or selectively remove the various primary and secondary minerals found in soils.

The definition of 'soil washing' is perplexing because it represents different processes to different people. Early development and implementation of soil-washing technology was based primarily on the use of water as the extraction solvent ([4]) and is basically a physical separation process. Methods of physical separation, such as screening, classification (separation of soil particulate based on their settling velocities), and flotation, are effective for soils in which a large proportion of the contamination is concentrated in the fine-grain fraction, which in turn occupies only a small percentage of the soil volume. This process is only applicable in remediation of soils containing highly water soluble constituents or soils containing very low concentrations of silt and/or clay particles (usually $< 15\%$ smaller than 0.050 mm in diameter). As a consequence, soil washing that uses water as the only extraction media has very limited application. For example, such soil-washing systems characteristically are not effective in removing contaminants from heavy textured soils [soils containing high concentrations of clays ($< 0.002 \text{ mm}$) and silts (0.050 to 0.002 mm)] as an appreciable proportion of the contaminants are often contained in the clay and silt fraction. This appears to be the case for the Fernald uranium-contaminated soils. For example, initial soil characterization studies of samples collected at Fernald by Lee and Marsh ([5]) indicated that the particle-size distribution in three of the six soil samples contained $> 66\%$ clay and silt fractions and that these fractions contained $\sim 50\%$ of the uranium. Most importantly, all of the size fractions contained uranium concentrations $> 52 \text{ mg kg}^{-1}$, the proposed screening level for applicable cleanup technologies. In three of the six samples, the most highly contaminated fraction was the sand fraction (2.00 – 0.053 mm particle-size range), indicating that a simple physical separation process would not be an effective cleanup technology. Thus, any successful soil-washing approach will likely depend on a chemical extraction or dissolution process.

Uranium is characteristically leached from uranium ores by acid- and carbonate-based extractants. In acid extraction of uranium ores, sulfuric acid, being less expensive than nitric acid, was used most often. Combined with milling the ore to pass a 200-mesh sieve ($< 0.075 \text{ mm}$), sulfuric acid can remove 90–98% of the uranium. Highly stable soluble complexes of uranyl sulfates are formed if the ores contained uranium in the

hexavalent state [uranium(VI)]. For ores containing uranium in the tetravalent state [uranium(IV)], oxidizing agents (e.g., sodium perchlorate and pyrolusite) were often added to convert the uranium to the hexavalent state. Compared with acid leaching systems, however, relatively few uranium milling operations employed carbonate leaching processes. The major disadvantage of the carbonate leaching process was the slower dissolution kinetics associated with the alkaline process as compared with acid leaching. The use of carbonates became attractive in cases where the uranium grade was high or where the excessive content of carbonate bearing minerals in the ore made the use of acid leaching uneconomical. The alkaline leaching process also produced a clean separation of uranium from its ores without solubilizing other metals because many metals are not soluble in alkaline solutions; an additional advantage when leaching soils that may contain hazardous metals. Acid leaching is also highly destructive of layer silicates in soils. The efficiency of carbonate–bicarbonate extractions to remove uranium from soils is based on the formation of the very stable water-soluble uranyl di- and tri-carbonates.



Ammonium carbonate extractions generally extract less silica than sodium carbonate extractions; however, the ammonium extractions are often not as effective in uranium removal and the ammonium constitutes a potential pollutant in the environment. Oxidants, such as potassium permanganate, and catalysts, such as ferrocyanide or copper salts, are often used to increase the efficiency of carbonate–bicarbonate in extracting uranium(IV) contained in primary minerals.

It is important to recognize that there are some very major obstacles in the direct employment of acid and carbonate leaching processes that have been successfully used in the uranium mining and milling industry to the remediation of uranium-contaminated soils. First of all and likely the most important difference in the mining and milling of uranium, the ore of concern usually contains a discrete known mineral form of uranium (e.g., pitchblende, uraninite, and carnotite) in relatively high concentration (0.1–1.0 wt.%) compared to clean up levels of uranium in soil (usually $< 50 \text{ mg kg}^{-1}$). In soil remediation, uranium forms in the soil result as a secondary reaction between the source term of the contaminant (air-borne or sedimentary particulate of various chemical forms or solubilized uranium in aqueous and nonaqueous effluents) that interact with mineral and biological constituents in soils. These interactions are highly time-dependent and the mobility or extractability of uranium from soils decreases rapidly with time. For example, it is known that uranium strongly partitions to Fe and Mn oxide surfaces of soils and subsurface materials. Subsurface biogeochemical processes including diffusion, oxidation/reduction and cycles of dissolution and precipitation cause the uranium to become fixed within the structure of Fe and Mn oxides and other soil components over time. High selectivity of uranium in soils, slow desorption kinetics, and fixation are the primary reasons why mining and milling operations for uranium are not directly applicable to the remediation of uranium-contaminated soils. Equally important is that the generation of large volumes of waste often encountered in mining and milling operations will not be tolerated in soil remediation processes.

However, as in the uranium mining and milling industry, leaching of uranium from uranium-contaminated soils require a few important prerequisites. These can be summarized as follows.

(1) The uranium must be exposed to the solution so that solubilization can occur. Effective soil remediation is a *dissolution process*. Simple additions of strong chelators for uranium to form water-soluble complexes with uranium will not be adequate for final clean up of uranium from most soils, as the slow desorption kinetics will not be compatible with most engineering processing facilities. It will be necessary to use oxidative/reductive dissolution processes to liberate uranium from surface oxide coatings or physical attrition methods to remove particulate forms of uranium from soils.

(2) Tetravalent uranium forms must be oxidized to the hexavalent state to be effectively removed by either the carbonate or sulfuric acid leaching process.

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

The general approach will be to investigate the extraction of uranium from soils by carbonate-based extractions (because of their high selectivity for uranyl and their less destructive characteristics on carbonate and layer silicate minerals of soils compared to acid extractions). Also, because the initial citric acid leaching studies conducted by Lee and Marsh [5] indicated high removal rates of uranium from the Fernald soils, leaching with citric acid, by itself and in conjunction with a reductive dissolution scheme in the presence of carbonate, will also be investigated. Citrate forms strong water-soluble complexes with uranyl over a wide range in pH. It also forms soluble complexes with tetravalent uranium which makes it especially valuable in reductive dissolution extractions in the removal of Fe, Mn, and Al sesquioxides from soil surfaces. General relationships, such as the effect of carbonate and citrate concentrations, pH, the presence of oxidants, such as KMnO_4 , temperature, and extraction time will also be investigated.

2. Soil characteristics

Two soil samples were used from the Fernald facility: (1) a sample adjacent to the low temperature waste incinerator used to burn contaminated debris (called in this report the Fernald 'incinerator soil'), and (2) a sample near the plant 1 storage pad (called in this report the Fernald 'storage pad soil'). The incinerator soil was selected as to represent soil contaminated from air borne deposits of 'low temperature' particulates while the storage pad soil was sampled to represent soil contaminated as a consequence of water-soluble forms of uranium interacting with the soil. The methods used for sampling and preparation are described by Francis et. al. [6]. The Fernald incinerator soil contained approximately 3 wt.% material > 4.75 mm and the storage pad soil contained 0.8 wt.% material > 4.75 mm. Material > 4.75 mm was discarded and not used in the leaching studies. Quantitative estimates of the carbonate minerals and quartz in the Fernald incinerator soil were 20 wt.% calcite, 2 wt.% dolomite, 65 wt.% quartz, and 13 wt.% clay minerals ([7]). The storage pad soil contained considerably more dolomite (15

wt.% calcite, 19 wt.% dolomite, 46 wt.% quartz, and 20 wt.% clay minerals). Kaolinite and illite are the two most dominant clay-size minerals of both soils. The carbonate minerals (calcite and dolomite) are anthropogenic artifacts because these two minerals are not present in the nearby off-site soils at this depth. This apparently occurred because of their application as road gravels to soils for erosion control and road construction activities.

The Y-12 landfarm soil was received in sealed, large widemouth glass jars and appeared to be near saturation with respect to water content. Moisture contents of the soil was near 35% 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 using an iron pestal and mortar. Leaching was conducted on this air-dried crushed form.

The concentrations and distribution of uranium in the particle size fractions of the three soils after wet-sieving and separation of the clay fractions (< 0.002 mm diameter by the methods according to Jackson [8]) are presented in Table 1. Only one fraction (the 0.075–0.020 mm size fraction of the Y-12 landfarm soil) contained uranium levels below the targeted screening level of 52 mg kg^{-1} . None of the size fractions separated from the Fernald soils approached the screening level. The sand (2.00–0.053 mm) and clay (< 0.002 mm) fractions of the Fernald incinerator soil contained uranium concentrations in excess of 1000 mg kg^{-1} (nearly twice that measured in the bulk sample). The clay fraction of the Fernald storage pad soil also contained uranium concentrations approaching 1000 mg kg^{-1} (approximately twice that measured in the bulk sample). These data conclusively demonstrate that a simple physical separation process would not be an effective clean up technology and the logical approach will depend on a chemical extraction process.

Table 1
Concentrations (dry weight basis) and distribution of uranium in soils

Soil uranium concentration (mg kg^{-1})	Size fraction (mm)	Particle size distribution (wt.%)	Uranium concentration (mg kg^{-1})	Uranium contribution by size fraction (wt.%)
Y-12 landfarm soil (177)	> 2.00	1.8	442	4.3
	2.00–0.075	17.5	361	33.8
	0.075–0.020	34.1	31	5.8
	0.020–0.002	30.4	180	29.3
	< 0.002	16.2	312	26.9
Fernald incinerator soil (538)	2.00–0.053	12.5	1033	27
	0.53–0.002	73.9	286	44
	< 0.002	13.6	1019	29
Fernald storage pad soil (446)	2.00–0.053	22.6	117	7
	0.053–0.002	56.5	239	37
	< 0.002	20.9	983	56

3. Bench-scale studies

A series of bench-scale studies were conducted to evaluate the influence of time, temperature, attrition scrubbing, pH and reagent concentrations, and the effects of oxidizing and reducing chemical environments on the removal of uranium from the three soils.

3.1. Influence of time and temperature on removal of uranium from the Fernald soils

Uranium was extracted from the two Fernald soils using a loading of 33 wt.% solids in a sodium carbonate solution (25 g NaHCO_3 and 25 g Na_2CO_3 l^{-1}). In contact with the soils, a pH range from 9.3 to 9.5 was obtained with the ratio of bicarbonate to carbonate of ~ 10 and a carbonate concentration ranging from 4.5×10^{-2} to 6.8×10^{-2} M. Potassium permanganate (KMnO_4), a very strong oxidant in this pH range, was added (20 mg g^{-1} of soil) to oxidize uranium(IV) to the uranyl(VI) state.

The leaching of uranium from the Fernald incinerator soil appeared to be more dependent on time and temperature than the leaching of uranium from the storage pad soil (see Figs. 1 and 2). 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 little 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 $\sim 80\%$ (compared to 40 and 50% at 22°C) but had little effect on the leaching of uranium from the storage pad soil. An increase in temperature from 40 to 60°C had little effect on uranium removal 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. Pretreatment of the soil samples by pulverizing and milling, coupled with a long leaching time (23 h), and an elevated temperature (60°C), did not release additional uranium from either soil ([6]).

3.2. The influence of pH and reagent concentration on the extraction of uranium by carbonate and citric acid

Factorial-designed experiments were used to determine the influence of pH and reagent concentration on the extraction of uranium from the three soils (Y-12 landfarm soil, Fernald incinerator soil, and the Fernald storage pad soil). These were 4-h end-over-end shaking tests conducted at a liquid-to-soil ratio of 10:1 (200 ml of extractant and 20 g of soil) in a rotary extractor([6]). For the carbonate leaching tests, two replicates of three levels of carbonate/bicarbonate (0.10, 0.25, and 0.50 M) and three pH levels (8, 9, 10—pH of the extractants before adding to the soils) were used. For the citric acid/citrate leaching tests, two replicates of three levels of citrate (0.10, 0.25, and 0.50 M) and four pH levels (unadjusted, 5, 7, and 9—pH of the extractants before adding to the soils) were used. After the designated extraction time, the pH of the soil suspension was recorded and the liquid phase of the suspension separated by centrifugation([6]).

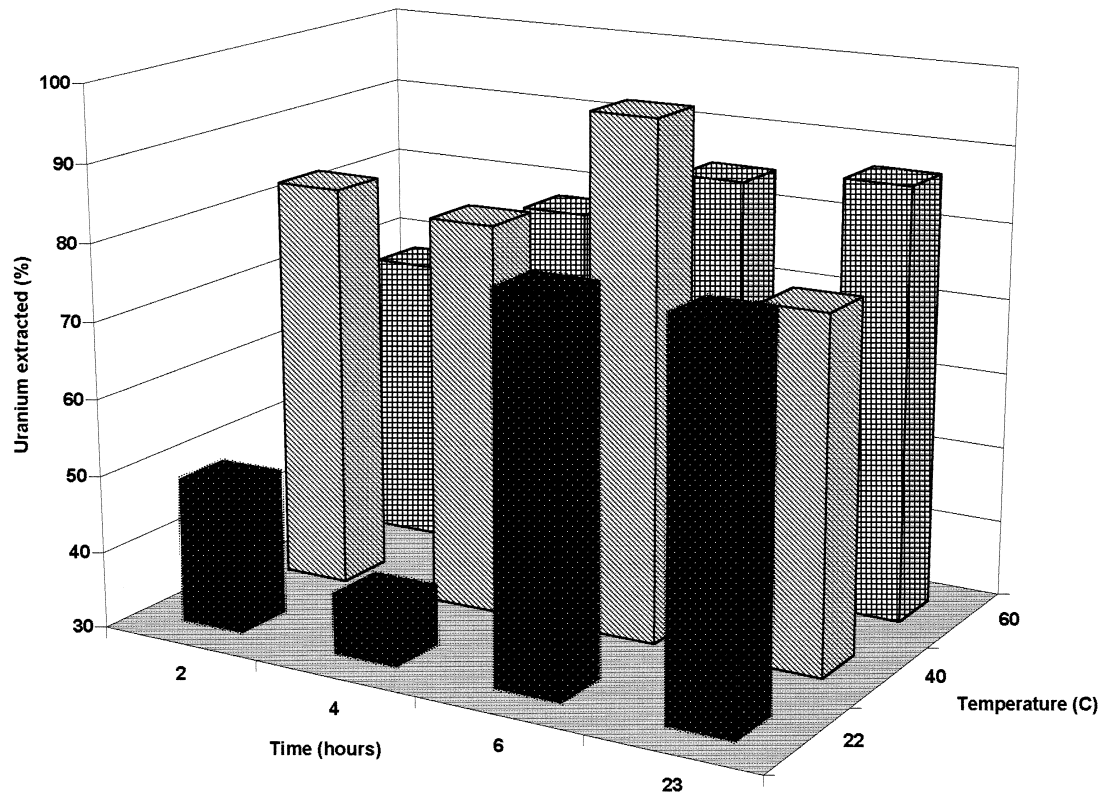


Fig. 1. The influence of time and temperature on the extraction of uranium from the Fernald incinerator soil.

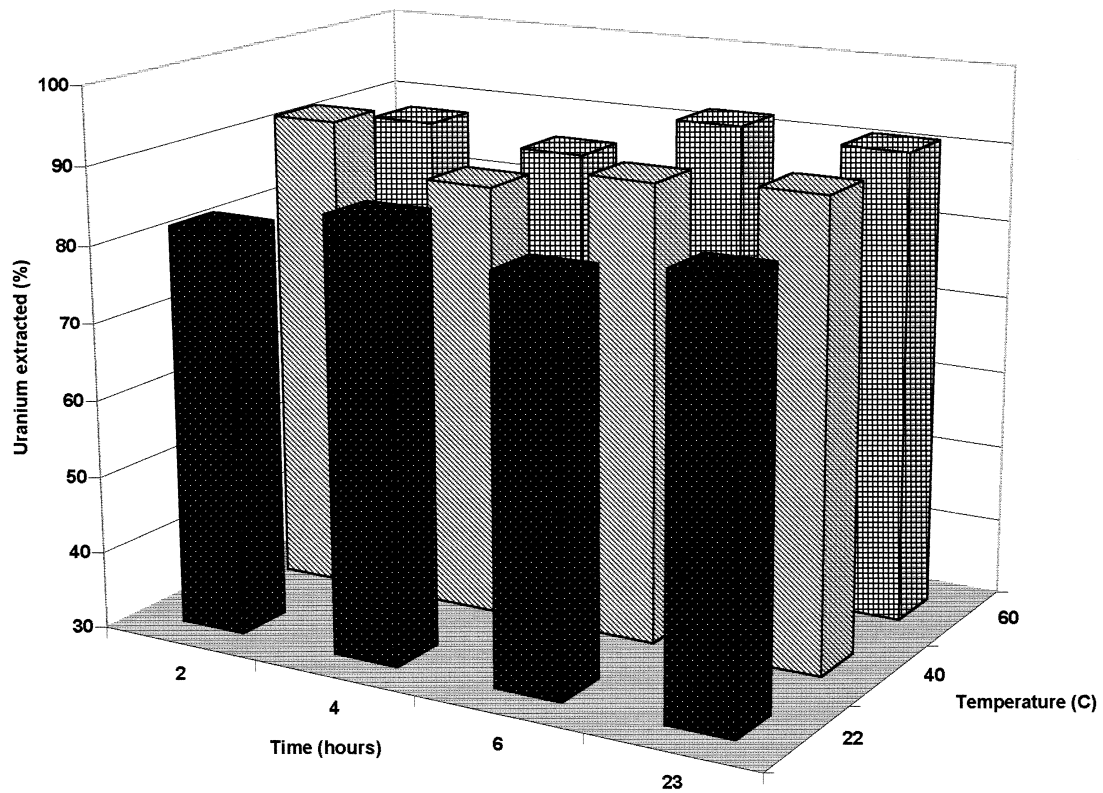


Fig. 2. The influence of time and temperature on the extraction of uranium from the Fernald storage pad soil.

The impacts relating to the extractability of uranium from the three soils on changing pH and carbonate concentrations are illustrated in Figs. 3–5. The removal of uranium from the Y-12 landfarm soil appears to increase on increasing pH for all carbonate concentrations (Fig. 3). For the Fernald soils, this relationship appears to be true for only for the 0.10 M carbonate concentration (Figs. 4 and 5). At carbonate concentrations of 0.25 and 0.50 M, uranium removal appears to be independent of pH (as long as the pH is maintained in the range from 8 to 10). Except for the Y-12 landfarm soil, the removal of uranium does not appear to be strongly influenced by carbonate concentration. Even for the Y-12 landfarm soil, removal by 0.25 M appeared to be equivalent to that by 0.50 M carbonate concentration. For the Fernald soils, uranium removal by the 0.10 M levels was equivalent to that by the 0.25 M levels. Only for the Fernald incinerator soil was the removal by the highest level of carbonate tested (0.50 M) appreciably higher than that by the 0.10 M carbonate concentration. Much higher uranium removal efficiencies were observed with the Fernald storage pad soil as compared to the Fernald incinerator and Y-12 landfarm soils (see Fig. 6).

Uranium removal by citrate from the Fernald soils was strongly related to pH; e.g., removal was much higher at low pH values (see Figs. 7 and 8). At pH values of approximately 3, uranium removal also appears to be independent of citrate concentration; only at pH values > 4 did there appear to be more uranium extracted with increasing citrate concentration. This was especially the case for the Fernald storage pad soil (see Fig. 8). Like carbonate extractions, considerably higher uranium extraction

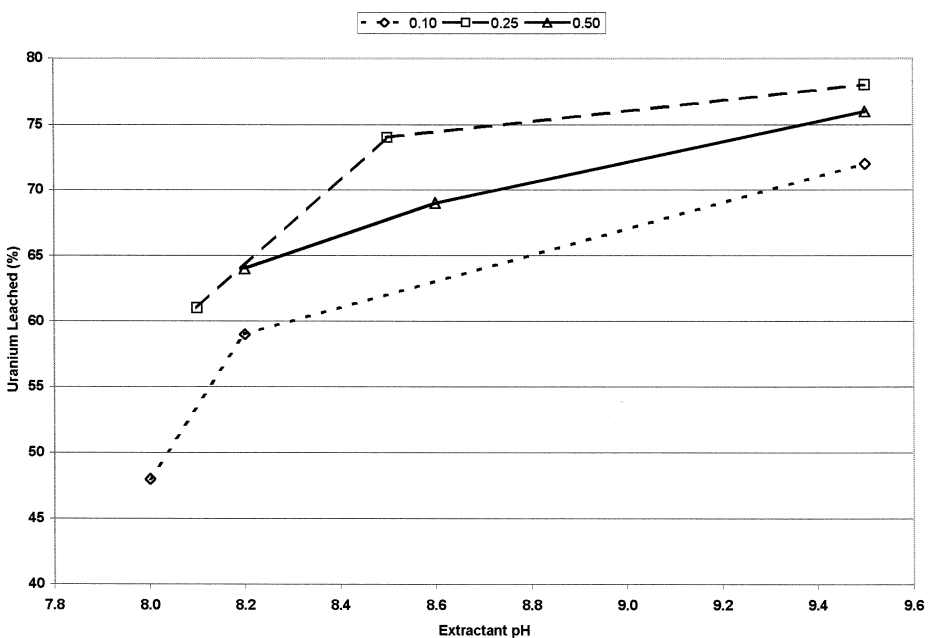


Fig. 3. The extraction of uranium from the Y-12 landfarm soil as a function of carbonate concentration (0.10, 0.25, and 0.50 M) and pH. Each data point is a mean of two replicated treatments.

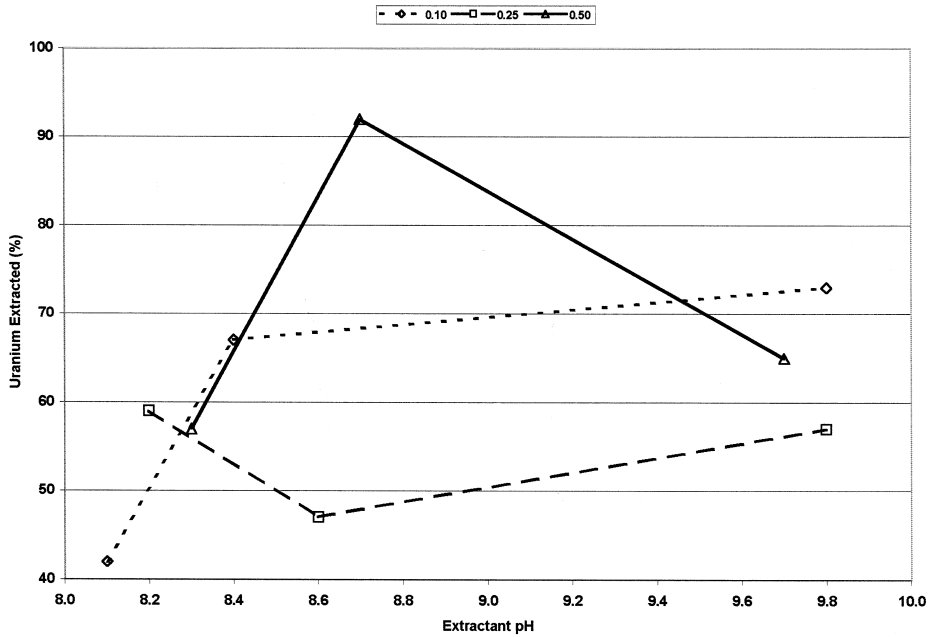


Fig. 4. The extraction of uranium from the Fernald incinerator soil as a function of carbonate concentration (0.10, 0.25, 0.50 M) and pH. Each data point is a mean of two replicated treatments.

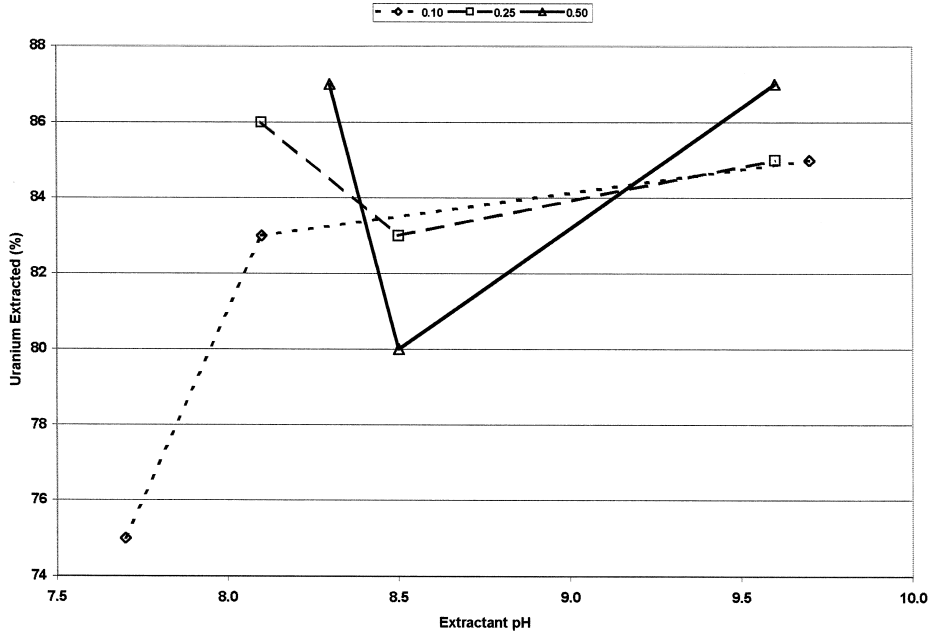


Fig. 5. The extraction of uranium from the Fernald storage pad soil as a function of carbonate concentration (0.10, 0.25, 0.50 M) and pH. Each data point is a mean of two replicated treatments.

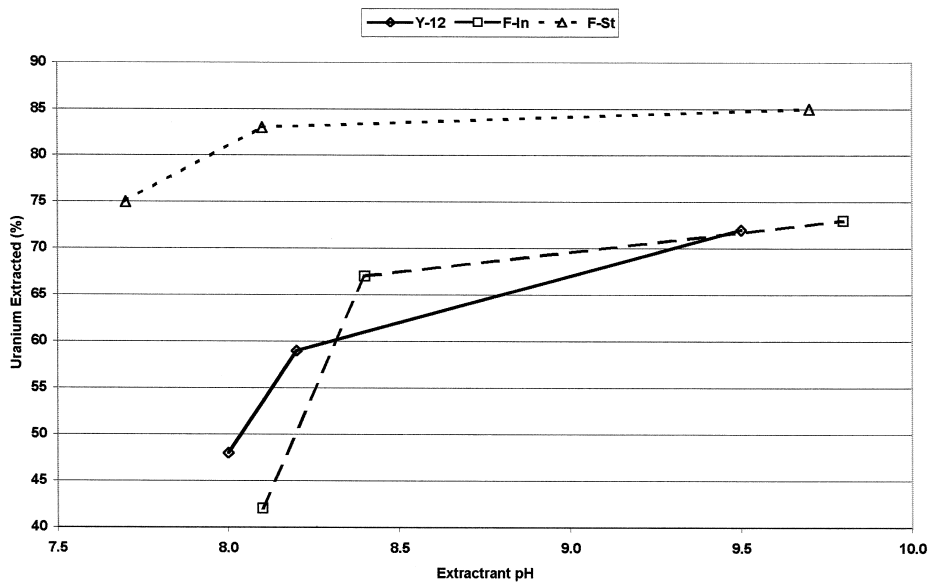


Fig. 6. The extraction of uranium from all three soils [Y-12 landfarm soil (Y-12), Fernald incinerator soil (F-In), and the Fernald storage pad soil (F-St) as a function of pH at a carbonate concentration of 0.10 M.

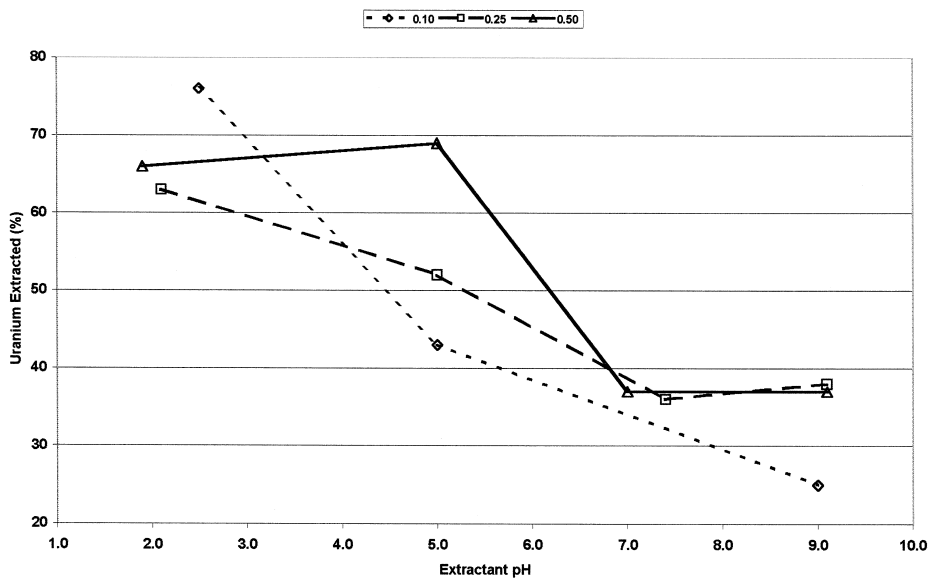


Fig. 7. The extraction of uranium from the Fernald incinerator soil as a function of citrate concentration (0.10, 0.25, 0.50 M) and pH. Each data point is a mean of two replicated treatments.

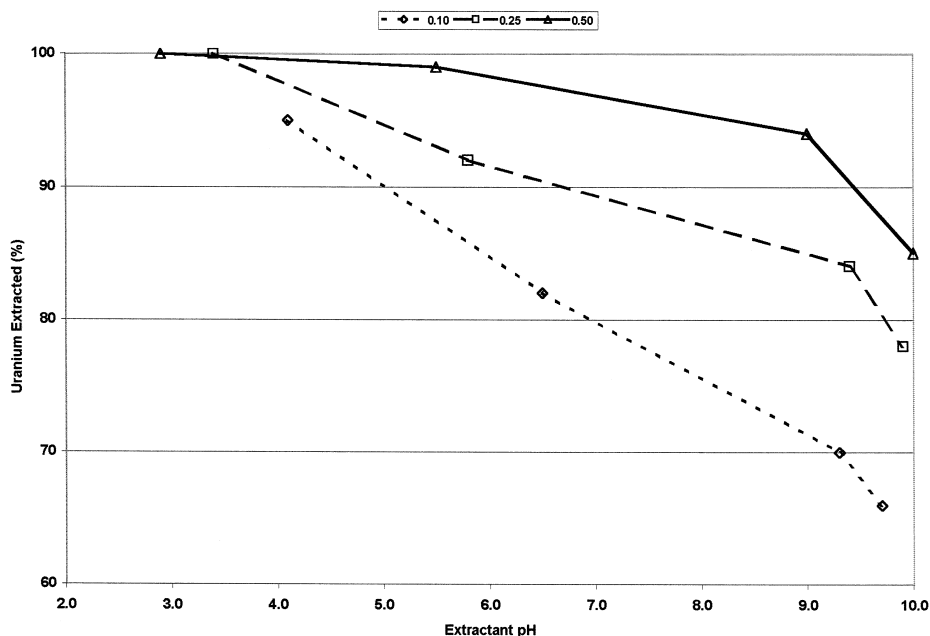


Fig. 8. The extraction of uranium from the Fernald storage pad soil as a function of citrate concentration (0.10, 0.25, 0.50 M) and pH. Each data point is a mean of two replicated treatments.

efficiencies were obtained from the Fernald storage pad soil as compared to the Fernald incinerator soil.

3.3. Influence of $KMnO_4$ amendments to remove uranium in carbonate extractions

Leaching soils that contain uranium in the tetravalent state is more difficult, and the addition of oxidizing agents may enhance removal efficiency. To test the influence of an oxidizing agent in the presence of carbonate extractions, each of the Fernald soils were leached with 0.50 M carbonate solution with and without $KMnO_4$ using the same leaching procedure as stated above (20 mg of $KMnO_4$ g^{-1} of soil were added as the $KMnO_4$ amendment). Amendments of $KMnO_4$ significantly increased the removal efficiency of uranium from the Fernald incinerator soil but not the storage pad soil (Table 2).

3.4. The effect of attrition scrubbing to remove uranium

Attrition scrubbing is a physical process intended to dislodge and remove or scarify finer size particulate from sand size particles. It is commonly used in uranium mining and milling industry to enhance extraction efficiencies. To determine the influence of attrition scrubbing to remove uranium, comparison tests were conducted using carbonate (0.50 M) and citric acid (3.13 M) extractants in an attrition scrubber (bench-top Denver

Table 2

Measured influence of KMnO_4 amendments to 0.50 M carbonate extractants for the removal of uranium from the Fernald soils

Soil	Uranium removal (%)	
	With KMnO_4	Without KMnO_4
Fernald incinerator soil	81 ^a	71 ^b
Fernald storage pad soil	89 ^a	87 ^a

Means ($n = 4$) within a soil followed by the same letter as a superscript are not significantly different at the 95% level.

model no. 5333000) to that of the end-over-end rotary extractor. Under equivalent conditions (extraction time of 15 min and a solids loading of 55%), attrition scrubbing appeared to enhance removal rates of uranium from both soils as compared to end-over-end shaking (Table 3). Uranium removal from both Fernald soils in an attrition scrubbing mode for 15 min using either carbonate or citric acid extracted equivalent quantities of uranium in an 4 h end-over-end shaking mode. Thus, attrition scrubbing offers several advantages in conducting the extraction over shorter extraction times and use of less extractant. Note the relatively poor extraction efficiencies for citric acid in the end-to-end test at the 15 min extraction time and a solids loading of 55%. Both of these soils contain appreciable quantities of carbonate minerals (22 and 34 wt.%, respectively for the incinerator and storage pad soils). Thus, in the use of citric acid as an extractant for these soils, the quantities of acid and length of extraction needs to be carefully evaluated before proceeding to a pilot-scale operation.

3.5. Effective management of the carbonate / bicarbonate lixiviant

To effectively manage the quantity and character of lixiviant to remove uranium from soils, it is necessary to determine the impact of successive extractions on a soil. To test this, the Fernald incinerator soil was extracted five times in succession with 0.10, 0.25, 0.50 M carbonate (pH 9.5, without KMnO_4 amendments). These were 16 h extractions in a rotary extractor at a solids loading of 33% (replicated in triplicate). At the higher

Table 3

Effect of attrition scrubbing vs. end-over-end shaking on uranium removal from the two Fernald soils

Soil	Extractant	Removal (%)			
		Attrition scrubbing		End-over-end	
		3 min	15 min	15 min	4 h
Fernald incinerator soil	Carbonate	63	68	48	73
	Citric acid	53	66	36	63
Fernald storage pad soil	Carbonate	79	73	75	84
	Citric acid	77	95	9	96

Attrition scrubbing was conducted at 55% solids. The 15 min end-over-end shaking was also conducted at 55% solids while the 4 hour end-over-end shaking was conducted at 33% solids.

carbonate concentrations (0.25 and 0.50 M), approximately 90% of the extractable uranium was removed in the initial extraction, and the remaining ~ 8 and $\sim 2\%$ extracted in the second and third extractions, respectively. Uranium removal in the initial extraction was statistically the same for the 0.25 and 0.50 M concentrations, and approximately 10% more effective than the 0.10 carbonate concentration (Fig. 9).

One of the important aspects in the management of an extraction technology is the ability to recycle the lixiviant. To test the ability to recycle the sodium carbonate lixiviant, extractant from a carbonate extraction (0.5 M) was used to extract uranium from fresh incinerator soil. This process was repeated through seven recycles (Fig. 10), with only fresh carbonate extractant added to make up for entrained losses during liquid-to-solid separation process (keeping the solids loading at 33% during the extraction stages). Extraction effectiveness was lowered to approximately 200 to 250 mg of uranium kg^{-1} of soil in the sixth and seventh recycles as compared to 300–350 mg of uranium kg^{-1} of soil in the initial two extractions. These data imply a slight decline in extraction effectiveness of uranium on continued recycle. However, uranium concentrations of 100 to 250 mg l^{-1} in the first and second recycle (Fig. 10) certainly did not significantly impact extraction efficiency, indicating that any recycled carbonate lixiviant containing these levels of uranium will not effect overall extraction effectiveness.

The ability to recycle the extractant is a very important advantage of carbonate as a lixiviant as opposed to citric acid (or sulfuric and nitric acids). Acid lixiviants require very low pH regimes (< 3) which can only be accomplished by continually adding fresh acid. Their use with soils containing large quantities of carbonate adds significantly to reagent costs. Leaching tests with mineral acids on the Fernald soils indicated that over 200 l of concentrated sulfuric acid would have to be used per metric ton of the storage pad soil to keep the pH < 2 ([9]). More important is the quantities of waste generated by the acid lixiviants. Carbonate extracted approximately the same quantities of uranium

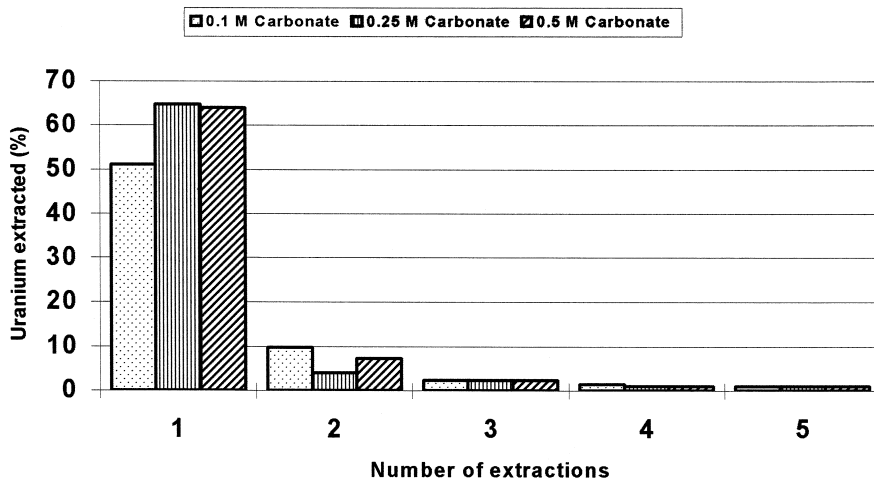


Fig. 9. The effect of successively extracting the Fernald incinerator soil with varies concentrations of carbonate to remove uranium.

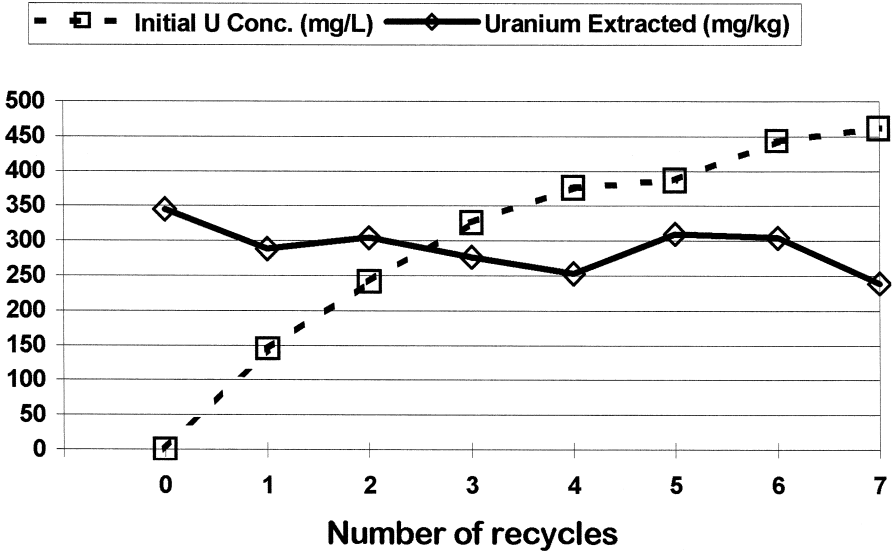


Fig. 10. The effect of recycling a carbonate lixiviant on uranium removal from the Fernald incinerator soil.

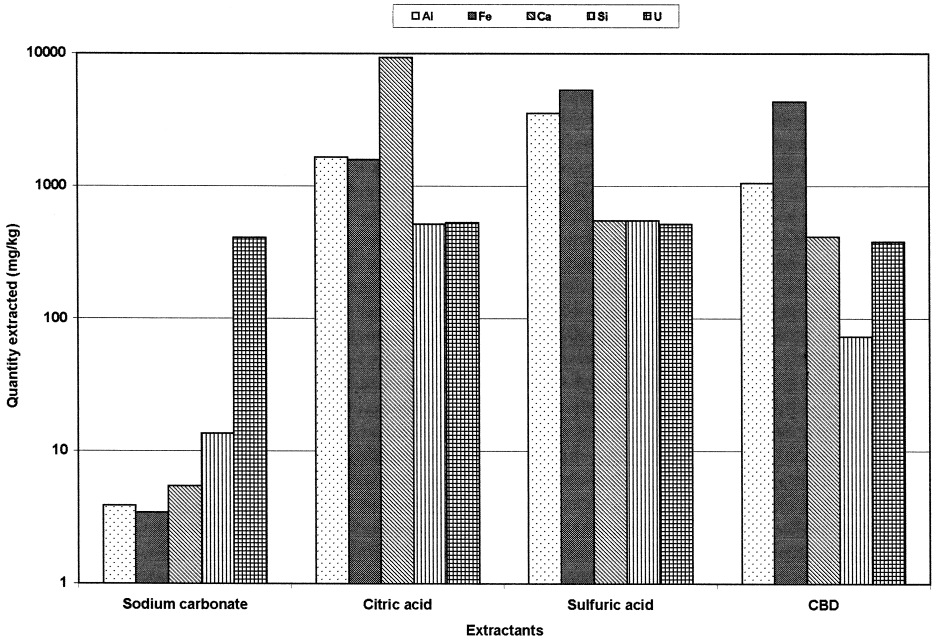


Fig. 11. Quantities of aluminium, iron, calcium, silica, and uranium removed from the Fernald storage pad soil by the four extractants (0.50 M carbonate, 3.13 M citric acid, 5 N sulfuric acid, CBD is a reductive dissolution process using sodium citrate, bicarbonate, and dithionate, and extractant) with a solids loading of approximately 50% in an attrition scrubber.

from the Fernald storage pad soil as the citric and sulfuric acid extractants, but the acid extractants removed on the order of 1000 mg kg^{-1} of Al, Fe, Ca, and Si in comparison to approximately 10 mg kg^{-1} for the carbonate extraction (see Fig. 11). These acid extractants also contain large quantities of sulfate and citrate, respectively. For example, on standing, a jelly-like white precipitate (Ca and Mg citrates) was formed in the citric acid extractant. The effective removal of uranium from these acid raffinate is much more difficult than removal from the carbonate extractant; consequently, the wastes that are generated with the acid extractants may be as much of a waste management problem with regards to clean up and disposal as the contaminated soils!

4. Pilot-scale studies

Pilot-scale studies were conducted at the Fernald facility in late 1993 and 1994 ([10]). The test unit (Fig. 12) was operated in a batch mode (approximately 150 kg) to demonstrate the removal of uranium from the Fernald incinerator and storage pad soils previously used in the bench-scale studies. The standard processing sequence involved: (1) the removal of coarse material from the soil in a trommel and a vibrating screen, (2) centrifuging the soil slurry to produce a nominal 0.020 mm size cut, (3) treating the coarse soil fraction in an attrition scrubber, and (4) recombining the two soil fractions and leaching with chemicals in a stirred reactor. Twenty-one tests were conducted [(11 with the incinerator soil, 10 with carbonate and 1 with citric acid as the lixiviant) and (10 with the storage pad soil, 9 with carbonate and 1 with citric acid as the lixiviant)] all with material balances for the amount of solids and uranium in each stream. The parameters investigated included the importance of attrition scrubbing (with and without separating the 0.020 mm size fraction as well as with and without the carbonate lixiviant at the attrition scrubbing stage) and temperature (elevated to 40°C). These tests were conducted in late fall of 1993 and early 1994. The final phase of testing (under 'optimum' operating conditions) was conducted in fall of 1994. The objective of these tests was to develop data on the efficiency and operability of the soil decontamination process that could be used for the design of a full-scale system that could produce a soil containing a uranium concentration equal to or less than 52 mg kg^{-1} , the initial technology screening level.

The results of the tests conducted in the fall of 1993 and early 1994 are presented in Table 4. The major conclusions based on these tests were as follows: (1) attrition scrubbing had no significant effect on decontamination efficiency, (2) increased reactor temperature increased uranium decontamination for the incinerator soil, and (3) citric acid was apparently not as effective as the carbonate lixiviant for leaching the incinerator soil (For the storage pad soil, there was no difference between the two lixiviant.). The final pilot-scale testing carried out in the fall of 1994 under 'optimum' conditions included the following: (1) attrition scrubbing was eliminated as a process step, (2) the soil underwent three 1-h leaching reactions followed by two rinsing steps, (3) KMnO_4 was used as an oxidant in the leaching procedure, and (4) the leaching reactor was operated at 40°C . Operating under these conditions, uranium removal was 84–88% for the incinerator soil and 87–90% for the storage pad soil. However, final uranium

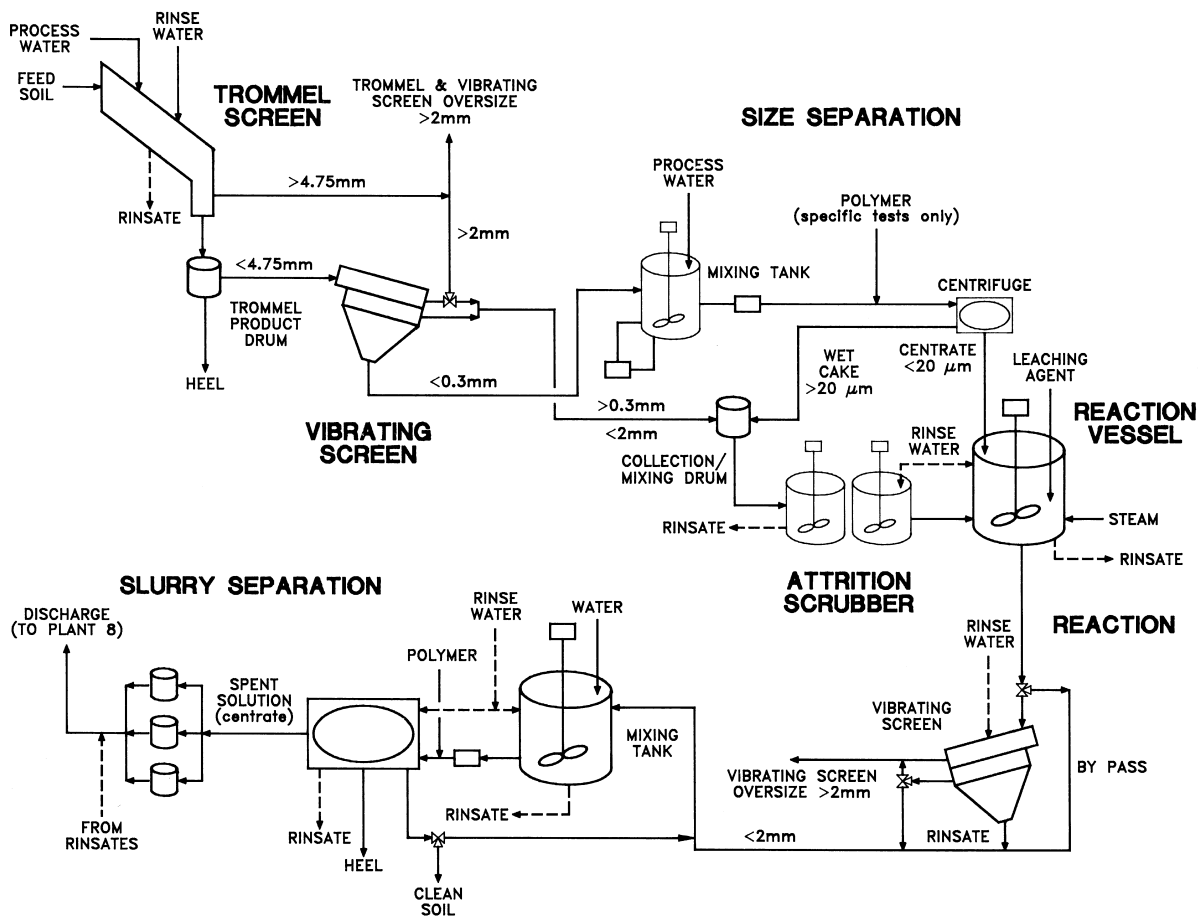


Fig. 12. Process flow diagram of pilot-scale test unit. ORNL DWG 95A-599 (NOT ON COMPUTER FILE).

Table 4
Operation conditions and results of pilot-scale testing

Lixiviant	Test no.	Operating conditions	Uranium in feed (mg kg ⁻¹)	Uranium in product (mg kg ⁻¹)	Removal (%)
<i>Storage pad soil</i>					
Carbonate	4	Attrition scrubbing in water (> 0.020 mm fraction only)	1484	108	93
	5	Replicate of test 4	1920	116	94
	6	Replicate of test 4	1810	129	93
	19	Replicate of test 4	1650	182	89
	16	Attrition scrubbing in carbonate (total soil)	1840	125	93
	17	Same as test 4 but at 40°C	1640	125	93
Citric acid	8	Replicate of test 4	1710	125	93
<i>Incinerator soil</i>					
Carbonate	0	Attrition scrubbing in water, 1 h (> 0.020 mm fraction only)	606	120	80
	2	Attrition scrubbing in water (> 0.020 mm fraction only)	690	130	81
	3	Replicate of test 2	723	116	84
	15	Replicate of test 2	697	168	75
	1	No attrition scrubbing	730	110	85
	13	Attrition scrubbing in carbonate, (> 0.020 mm fraction only)	791	159	80
	14	Attrition scrubbing in water (total soil)	756	168	76
	18	Same as test 2 but at 40°C	743	85	89
Citric acid	7	Replicate of test 2	1120	290	74

concentrations (84 and 88 mg kg⁻¹ for the incinerator soil and 50 and 114 mg kg⁻¹) were not consistently below the 52 mg kg⁻¹ technology screening level.

5. Conclusions

Both carbonate and citric acid lixiviants were observed to be effective extractants to remove uranium from the soils tested. Carbonate, because of its ability to be recycled and its tendency to be more selective for uranium, is preferred for most soils. A major obstacle for using citric acid as well as mineral-based acid is their generation of waste streams from which it is difficult to remove uranium and manage (and dispose of any residual waste water sludges) in an environmentally acceptable manner.

Experimental data on carbonate extraction of uranium from the Fernald soils indicated the following: (1) initial extraction was rapid (< 30 min) for 90% of extractable uranium, (2) increased extraction occurred when temperature was increased from 25°C to 40°C, but little effect was observed at > 40°C, (3) extraction efficiency at concentrations of 0.25 and 0.50 M (especially at 40 to 45°C) appeared to be equivalent, and both concentrations were more effective than the 0.10 M concentration, (4) the change in pH between 8 and 10 did not effect extraction efficiency, (5) attrition scrubbing showed little effect, (5) data indicated a possible > 10% but < 20% increase in extraction efficiency when an oxidant was used (only for the incinerator soil), and (6) approximately 85 to 90% of extractable uranium was removed in the initial extraction. The best pilot-scale treatment consisted of three successive extractions with 0.25 M carbonate–bicarbonate (in presence of KMnO₄ as an oxidant) at 40°C followed with two water rinses.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Technology Development and conducted by Oak Ridge National Laboratory, Oak Ridge, TN, managed by Lockheed Martin Energy Systems under contract DE-AC05-96OR22464. Appreciation is expressed to Kim Nuhfer, Program Coordinator for the Uranium in Soils Integrated Demonstration Program, for administrative support throughout the project.

References

- [1] E.R. Graham, 1964. Radioisotopes and Soils, in: F.E. Bear (Ed.), Chemistry of the Soil, American Chemical Society, Monograph Series, Reinhold Publishing, New York, pp. 445–473.
- [2] Agency for Toxic Substances and Disease Registry, Toxicological Profile for Uranium, TP-90-29, U.S. Department of Health and Human Services, Atlanta, GA, 1990.
- [3] D.W. Layton, A.Q. Armstrong, Methodological considerations for determining cleanup limits for uranium in treated and untreated soils, *J. Soil Contamination* 3 (4) (1994) 319–348.
- [4] T.J. Pollaert, Soil washing with water under high energy input: commercial experience with the lugri deconterra process, in: Fourth Forum on Innovative Hazardous Waste Treatment Technologies: Domestic

- and International, Abstract Proceedings, EPA/540/R-92/081, U.S. Environmental Protection Agency, Washington, DC, 1992.
- [5] S.Y. Lee, J.D. Marsh, Characterization of Uranium Contaminated Soil from DOE Fernald Environmental Management Project Site: Results of Phase I Characterization, ORNL/TM-11980, Oak Ridge National Laboratory, Oak Ridge, TN, 1992.
 - [6] C.W. Francis, A.J. Mattus, L.L. Farr, M.P. Elless, S.Y. Lee, Selective Leaching of Uranium from Uranium-Contaminated Soils: Progress Report, ORNL/TM-12177, Oak Ridge National Laboratory, Oak Ridge, TN.
 - [7] S.Y. Lee, M.P. Elless, F.M. Hoffman, Solubility Measurements of Uranium in Uranium-Contaminated Soils, ORNL/TM-12401, Oak Ridge National Laboratory, Oak Ridge, TN, 1993.
 - [8] M.L. Jackson. Soil Chemical Analysis—Advanced Course, 2nd edn., Madison, WI, 11th printing, 1985, published by author.
 - [9] C.W. Francis, A.J. Mattus, M.P. Elless, M.E. Timpson, Carbonate- and citrate-based selective leaching of uranium from uranium-contaminated soils, in: Removal of Uranium from Uranium-Contaminated Soils, Phase I: Bench-Scale Testing, ORNL-6762, Oak Ridge National Laboratory, Oak Ridge, TN, 1993.
 - [10] J.H. Wilson, R. Chernikoff, W.D. DeMarco, C.W. Francis, L.L. Stebbins, Carbonate and Citric Acid Leaching of Uranium from Uranium-Contaminated Soils: Pilot-Scale Studies (Phase II), Oak Ridge National Laboratory, Oak Ridge, TN.