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INFLUENCE OF ATTRITION SCRUBBING, ULTRASONIC TREATMENT, AND OXIDANT ADDITIONS ON URANIUM REMOVAL FROM CONTAMINATED SOILS

M. E. Timpson, M. P. Elless, and C. W. Francis

Bldg 3504, MS-6317, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6317

ABSTRACT

As part of the Uranium in Soils Integrated Demonstration Project being conducted by the U.S. Department of Energy, bench-scale investigations of selective leaching of uranium from soils at the Fernald Environmental Management Project site in Ohio were conducted at Oak Ridge National Laboratory. Two soils (storage pad soil and incinerator soil), representing the major contaminant sources at the site, were extracted using carbonate- and citric acid-based lixiviants. Physical and chemical processes were used in combination with the two extractants to increase the rate of uranium release from these soils. Attrition scrubbing and ultrasonic dispersion were the two physical processes utilized. Potassium permanganate was used as an oxidizing agent to transform tetravalent uranium to the hexavalent state. Hexavalent uranium is easily complexed in solution by the carbonate radical. Attrition scrubbing increased the rate of uranium release from both soils when compared with rotary shaking. At equivalent extraction times and solids loadings, however, attrition scrubbing proved effective only on the incinerator soil. Ultrasonic treatments on the incinerator soil removed 71% of the uranium contamination in a single extraction. Multiple extractions of the same sample removed up to 90% of the uranium. Additions of potassium permanganate to the carbonate extractant resulted in significant changes in the extractability of uranium from the incinerator soil but had no effect on the storage pad soil.

INTRODUCTION

Chemical and metallurgical processing of uranium metal at the U.S. Department of Energy (DOE) production facility at Fernald, Ohio (~18 miles northwest of Cincinnati) has resulted in contamination of an estimated 2 million m³ of soil. Contamination stemmed from a variety of sources, including airborne incinerator particulates and bag-house dusts, uranium-rich solvent leaks, and spillage of aqueous and nonaqueous process effluents.

As part of the environmental restoration activities conducted by DOE, a pilot program, the Uranium in Soils Integrated Demonstration (USID), was established to investigate technologies that would allow DOE to remediate uranium-contaminated sites faster, safer, and more economically than traditional low-level radioactive waste disposal methods. A cleanup technology was sought that would (1) selectively remove the uranium without appreciably affecting the soil's physicochemical properties (allowing it to be reclaimed on-site) and (2) not result in production of a waste product that would be difficult to dispose of and manage.

Initial experiments that used end-over-end shaking in combination with carbonate and citric acid extractants (to simulate a batch reactor), indicated that the technology target level of uranium removal ($52 \mu\text{g U/g soil}$) was probably not achievable with this approach (1). Therefore, a different method of mixing the soil with the extractants was required. Soil "decon" operations based on a selective leaching process typically require longer residence times than traditional "soil washing" techniques. Long residence times, however, require either unacceptably large reaction vessels or very slow loading factors. Thus, a method that increased the rate of uranium removal from the Fernald soils was sought. Attrition scrubbing and ultrasonic dispersion techniques (both physical processes) were investigated for this purpose. A chemical method, requiring addition of an oxidant to the carbonate extracts, was also investigated.

Attrition scrubbing is a physical process that abrades particles through collision in a closed chamber at high solids loadings (typically 50 to 70% solids). Particle abrasion is accomplished by a set of propeller blades pitched in opposite directions. This design allows particles at the top and bottom of the chamber to collide at the center of the chamber (Fig. 1). The abrasive action reduces the size of the scrubbed particles (increasing the total surface area) and exposes fresh surfaces on the abraded particles. The overall effect of this process is to increase the extractability of the target contaminant.

Place Fig.1 here.

Ultrasonic treatment of soils is commonly utilized to achieve a dispersed soil suspension for particle-size analysis (2). The technique is based on the transmission of sound waves through a solution containing soil materials. The collapse of microscopic bubbles produced by the sonic vibrations results in cavitation. Release of the energy of cavitation "blasts the soil aggregates apart," resulting in the separation of the soil into primary particles (i.e., sand, silt, and clay-sized components) (3). Physical separation of the soil aggregates into their primary components results in increased total surface area (increasing chemical reactivity) and also releases particulate forms of uranium that may have been occluded in the soil aggregates.

Removal of hexavalent uranium from ores/sediments using carbonate lixiviants is relatively easy and produces $[\text{UO}_2(\text{CO}_3)_3]^{-4}$, a highly stable, water-soluble, anionic complex. Leaching tetravalent uranium is more difficult and generally requires the addition of an oxidant to convert uranium (IV) to uranium (VI), which can then be complexed by the carbonate radical in solution. A number of oxidants are utilized in the uranium industry for this purpose; however, in this study we examined only potassium permanganate (KMnO_4).

The objectives of this study were to (1) examine the impact of attrition scrubbing and ultrasonic treatments in combination with carbonate- and citric acid-based lixiviants on uranium extraction from soils at the Fernald site and (2) investigate the influence of an oxidizing agent in combination with carbonate-based extractants on improving the release of uranium from these soils.

APPROACH

Two soils sampled from the production area of the Fernald facility were examined in this investigation. The samples were collected from two areas, each representing different uranium contamination sources. The storage pad soil represented contamination from spills of spent process solvents, whereas the incinerator soil represented particulate contamination from incinerator stack emissions. Earlier characterization studies indicated that these soils were representative of the major forms of contamination at the site (4).

Both soils had silt loam textures. The incinerator soil contained an average of 89% silt plus clay (particles $< 53 \mu\text{m}$) and the storage pad soil contained an average of 76% silt plus clay. Lee and Marsh (4) indicated that uranium in these soils was distributed throughout each particle-size fraction. Mineralogical characterization of these soils showed that both soils contained carbonates that were anthropogenic in nature. The incinerator soil contained 22% carbonates (mostly calcite), whereas the storage pad contained nearly equal amounts of calcite and dolomite (34% total carbonate) (5).

Various extractants were utilized to remove uranium from the contaminated soils, however, only two will be discussed in this paper: 3.13 *M* citric acid and 0.5 *M* (total carbonate) Na-carbonate/bicarbonate. Carbonate-based extractants are commonly employed in the uranium mining industry. Citric acid was chosen because the citrate anion is an effective chelator of polyvalent metals and earlier studies (1, 4) demonstrated its usefulness in extracting uranium from the Fernald soils.

Attrition scrubbing was conducted at two times (3 and 15 min) and two solids loadings (33 and 55%). Particle-size analyses of postattrition samples were made using a combination of wet sieving and elutriation. The particle-size fractions chosen were a compromise between traditional soil particle fractions and engineering-based size fractions. Uranium contents of the particle-size separates following treatment were determined using neutron activation analysis. The uranium in the soil extracts was analyzed by means of ICP-mass spectrometry.

Ultrasonic agitation was carried out at ~ 175 watts for 12 min. A solids loading of 10% was utilized. Three sequential leachings were performed on the incinerator soil with a 0.5 *M* total carbonate solution. The incinerator soil was chosen for this treatment because it contained the greatest quantity of refractory uranium phases.

In the oxidant experiments, 0.5 *M* total carbonate solutions were used at a solids loading of 10%. Potassium permanganate was added at a loading of 0.4 g KMnO_4 per gram of soil. Extractions were carried out with both soils. The soil/solution mixtures were shaken on a rotary extractor for 4 h prior to centrifugal separation of the solids and liquids.

RESULTS AND DISCUSSION

One of the aims of the USID program is to develop decontamination strategies that will allow the "cleaned" soils to be returned to their original location and reclaimed. Because of this, treatment technologies that have minimal impacts on soil physicochemical properties were sought. Citric acid removed up to 10% of the total soil mass from the incinerator soil and 20% of the mass in the storage pad soil (Fig. 2). The loss of mass in both soils resulted from acid attack on the carbonate minerals. Conversely, the carbonate-based extractant had no effect on the original mass of either soil. These results are important if the goal of the treatment is to remove the uranium without appreciably affecting the original soil properties.

Place Fig. 2 here.

Attrition scrubbing with carbonate- and citric acid-based lixiviants increased the rate of release of uranium from both soils relative to end-over-end shaking (Table I). Although the attrition extractions did not remove significantly more total uranium, the amounts extracted were removed in as little as 3 min. The increased uranium removal rate will provide advantages when scaling-up to a final engineering design. In addition, attrition scrubbing was performed at a solids loading of 55%, whereas the end-over-end shaking was performed at 10% solids. The reduction in extractant volume provided by attrition scrubbing also offers engineering advantages because it reduces the volume of secondary waste that must be treated.

To further test the effectiveness of attrition scrubbing versus end-over-end shaking in removing uranium from these soils, a second experiment was performed in which equal solids loadings and extraction times (55% solids and 15 min) were used. Attrition scrubbing was found to improve uranium removal from the incinerator soil, but in general, it had little effect on the storage pad soil (Table II). The poor performance of citric acid in extracting uranium from the storage pad soil was the result of the extraction conditions used in the end-over-end shaking: to achieve a 55% solids loading, 80 mL of citric acid solution was added to 100 g of soil. This created a moist soil mass that did not agitate well. The low solution volume combined with limited agitation yielded extremely low uranium extraction. The difference in the effectiveness of attrition scrubbing between the two soils is related to the form of contamination. The incinerator stack particulates are relatively refractory compounds that are not easily leached, whereas uranium compounds resulting from spent solvents are more readily removed.

Attrition scrubbing commonly requires high solid loadings and is usually performed on coarse particles (generally $> 50 \mu\text{m}$). The soils in the Fernald area are loess-derived and contain virtually no coarse fragments and very little sand. Particles $> 50 \mu\text{m}$ constituted up to 24% by weight of the two soils from the plant. It would have been impractical to separate a sufficient quantity of the coarse particles to allow a traditional use of attrition scrubbing. Consequently, the entire soil was attrition scrubbed. Table III shows the results of attrition scrubbing tests performed at 55% and 33% solids loadings. Contrary to traditional thinking,

these results suggest that if the whole soil is used, attrition scrubbing at lower solids loadings is more effective in removing uranium from these relatively fine-textured soils.

Figure 3 shows the posttreatment uranium content of each particle-size fraction. The uranium content of the coarsest particle fraction from the incinerator soil was not determined because this particle fraction generally composed $< 1\%$ of the total soil mass. Results from the other size fractions indicate that the technology target level ($52 \mu\text{g/g}$) was met in only one size class from the citric acid treatment (Fig. 3A). Residual uranium concentrations in this soil demonstrate the refractory nature of the particulate contaminants from the incinerator stack. Posttreatment uranium concentrations in the storage pad soil (Fig. 3B) were below the $52 \mu\text{g/g}$ technology target level in most particle-size fractions, demonstrating the ease with which this soil can be decontaminated. A comparison of the residual uranium concentrations in the two soils demonstrates the differences in the extractability of the two forms of contamination.

Place Fig. 3 here.

As much as 90% of the uranium was removed from the incinerator soil as a result of sequential carbonate extractions combined with ultrasound treatments (Table IV). As might be expected, the greatest amount of uranium was removed by the first extraction. Successive extractions leached lesser quantities of uranium. The decreasing quantities of extractable uranium in this soil further indicate the refractory nature of the incinerator stack particulates. Further evidence of the difficulty in extracting uranium from the incinerator soil is provided in Table V. Single sodium carbonate extractions removed nearly equal amounts of uranium from this soil regardless of the method of mixing or time of extraction.

Oxidizing agents are frequently used in uranium mining processes to increase the extractability of the ore. To investigate the effect of such agents on the extractability of uranium in the Fernald soils, potassium permanganate (KMnO_4) was utilized in combination with sodium carbonate solutions. The use of KMnO_4 significantly increased the extraction of uranium from the incinerator soil, but had no effect on the storage pad soil (Table VI). Earlier studies, conducted at Los Alamos (6), demonstrated that the majority of the uranium in the Fernald soils was in the hexavalent state. Data from Argonne National Laboratory (7) have indicated the presence of residual uranium (IV)-containing compounds in samples of carbonate- and citric acid-treated soils from the incinerator area. The Argonne samples were extracted without an oxidizing agent. The increase in uranium extractability noted in the incinerator soil when a combination of sodium carbonate and KMnO_4 was used suggests that the tetravalent uranium compounds in the incinerator soil were being oxidized to the hexavalent state and then complexed by the carbonate radical, forming uranyl carbonate. The lack of an effect observed in the storage pad soil suggests that the majority of the uranium contamination in that soil consisted of hexavalent compounds.

CONCLUSIONS

In comparison with end-over-end shaking, attrition scrubbing increased the rate of uranium removal from both Fernald soils. The attrition technique offered engineering advantages in terms of speed of uranium removal and volume of secondary waste produced. A comparison of attrition scrubbing versus end-over-end shaking at equal solid loadings and extraction times indicated that the use of this technique was only beneficial for the incinerator soil. This difference was related to the initial form of contamination. The particulate-based contamination from the incinerator stack effluent responded to physical abrasion processes in the attrition scrubber more readily than did the solvent-based contamination found in the storage pad soil. Attrition scrubbing at solids loadings lower than those typically used in this technique (i.e., 33%) was found to be beneficial when processing whole-soil material containing large quantities of fine particles ($< 50 \mu\text{m}$).

Sequential sodium carbonate extractions in combination with ultrasonic dispersion removed up to 90% of the uranium contamination from the Incinerator soil. However, when a single extraction was carried out with Na-carbonate solutions, approximately equivalent quantities of uranium were leached from the incinerator soil, regardless of the method of mixing or the extraction time employed. In addition, the use of an oxidizing agent (KMnO_4) increased the extractability of the incinerator soil but had no effect on the removal of uranium from the storage pad soil. This was probably the result of the presence of refractory tetravalent uranium compounds in the incinerator soil and their absence or lesser presence in the storage pad soil.

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Table I. Effect of attrition scrubbing versus end-over-end shaking on the percentage of uranium extracted from two Fernald soils.

Soil	Extractant	Treatment		
		AS3*	AS15	Shaking4**
Incinerator	Na-Carbonate	63	68	73
	Citric Acid	53	66	63
Storage Pad	Na-Carbonate	79	73	84
	Citric Acid	77	95	96

* AS = Attrition Scrubbing, 55% solids, 3 min. and 15 min.

** 10% solids, 4 h shaking time.

Table II. Comparison of the effect of attrition scrubbing versus end-over-end shaking on the percentage of uranium from Fernald soils by extraction under identical conditions with respect to solids loading (55%) and extraction time (15 min).

Extractant	No. of Analyses	Attrition	End-to-End
		----- % Removed -----	
Incinerator Soil			
Carbonate	2	68 ^{a*}	48 ^b
Citric	2	66 ^a	36 ^b
Storage Pad Soil			
Carbonate	3	73 ^a	75 ^a
Citric	3	95 ^a	9 ^b

*Means within extractants within a soil followed by the same letter are not significantly different at the 95% level.

Table III. Percentage of uranium removed from Fernald soils by combining sodium carbonate solution and attrition scrubbing for 30 min at room temperature.

SOIL	Solids Content	Estimated Removal
	----- % -----	
Incinerator	55	58
Storage Pad	55	66
Incinerator	33	71
Storage Pad	33	84

Table IV. Percentage of uranium removed from incinerator soil by sequential extraction that combined sodium carbonate solution and ultrasonic treatments.

Extraction	Mean*	Standard Dev.	Coeff. Var.
	----- % Removed -----		(%)
First	71.0	4.8	6.8
Second	11.8	0.63	5.3
Third	7.4	0.35	4.7

* Results are based on 4 replicates.

Table V. Percentage of uranium removed from the incinerator soil by carbonate extraction combined with various treatments.

Treatment	U Removed* (%)
Attrition	68
Ultrasound	71
End-to-end	60

* Attrition scrubbing at 55% solids, 15 min; ultrasound at 10% solids, 12 min; end-to-end shaking at 10% solids, 4 h.

Table VI. Comparison of the mean percentage of uranium removed from both Fernald soils when they were extracted with sodium carbonate in the presence or absence of an oxidant.

Soil	With KMnO_4	Without KMnO_4
Incinerator	81 ^{a*}	71 ^b
Storage Pad	89 ^a	87 ^a

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

Fig. 1. Bench-scale attrition scrubber used in this investigation.

Fig. 2. Post-leaching particle-size distributions of Fernald soils. Changes in the particle distributions of the citric acid treatments were the result of loss of mass through carbonate dissolution. The water treatment was used as a control.

Fig. 3. Post-treatment uranium concentrations by particle-size fraction. ND means not determined.

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