

SELECTIVE LEACHING OF URANIUM FROM URANIUM CONTAMINATED SOILS*

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ABSTRACT

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. 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 $\mu\text{g U/g}$ of soil while the samples from the Y-12 Plant ranged from 150 to 200 $\mu\text{g U/g}$ 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 ~40 to ~75%). Very small amounts of uranium could be extracted (<8%) from the storm sewer sediment. The most effective leaching rates (>90% from both Fernald soils) were obtained using a citrate/dithionite extraction procedure designed to remove 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, ~90 and ~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 waste form that is difficult to manage and/or to dispose.

INTRODUCTION

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 project is called the Fernald Environmental Management Project (FEMP) consisting of 1050 acres in a rural area approximately 18 miles northwest of downtown Cincinnati, Ohio. As a consequence of these production efforts, soils at this site have become contaminated with uranium from a variety of sources. These sources include deposition of uranium airborne particulate 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 $2 \times 10^6 \text{ yd}^3$ 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.

The objective of this research is to selectively extract uranium from soils 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 (<2 μ) and silts (50 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 (1) 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. Most importantly, all of the size

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fractions contained uranium concentrations $>50 \mu\text{g/g}$, the highest level of uranium established for evaluating potential clean-up technologies. In three of the six samples, the most highly contaminated fraction was the sand fraction (2000 to 53μ particle size range) indicating that a simple physical separation processes would not be an effective clean up technology. Thus, any successful soil washing approach will likely depend on a chemical extraction process (2).

Several conditions must be met to achieve adequate extraction of uranium from uranium contaminated soils:

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 solution chemistry must be controlled to insure that an adequate supply of complexing anions such as carbonate are available to complex and stabilize uranium in solution. Additionally, chemical environments or conditions which promote premature, unwanted precipitation of uranium must be avoided.
3. If carbonate is the selected complexing agent for uranium, the uranium must be oxidized to the hexavalent state, if not already oxidized.

The general approach has been 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 (1) 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, was also investigated. General relationships such as the effect of carbonate and citrate concentrations, pH, oxidants such as KMnO_4 , temperature, and extraction time were determined.

METHODS AND MATERIALS

Soils

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 three soils were obtained from the FEMP Uranium in Soils Integrated Demonstration (UID) program. The third soil was one sampled from the Y-12 landfarm, an area used in the late 1970's for treatment and disposal of waste oils containing elevated levels of uranium.

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. 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. Each excavated area was about 25 by 20 ft, with an excavation depth of 6 to 8 inches. In this report, these soils will be referred to as storage pad and incinerator soils, respectively.

The concentrations and distributions of uranium among particle size fractions of the soils varied. In the case of the Fernald incinerator soil, the highest concentrations of uranium ($\sim 1000 \mu\text{g/g}$) were observed in the sand size (2-

0.053 mm) and clay (<0.002 mm) fractions, while the silt fraction (which contained lower total uranium concentrations $\sim 300 \mu\text{g/g}$) constituted approximately 45% of the total uranium burden because of the high fraction of silt size particles ($\sim 75\%$). Clay in the storage pad soil contained the highest uranium concentration, $\sim 1000 \mu\text{g/g}$ as compared to approximately 240 and $120 \mu\text{g/g}$, in the silt and sand size fractions, respectively. Uranium concentrations in the particle size fractions of the Y-12 landfarm were generally uniform (ranging between 180 to $440 \mu\text{g/g}$) except for the fine sand and coarse silt fraction which only contained $\sim 30 \mu\text{g/g}$. Approximately 60% of the uranium in the Y-12 storm sediment was contained in the silt and clay fractions making up only 10% of the sediment meaning simple removal of these fractions would be a significant step in remediation of this material. The major difference between the samples from the Oak Ridge Y-12 plant and the Fernald samples was that the concentrations of uranium in the Y-12 samples were lower (ranging from 150 to $200 \mu\text{g/g}$ compared to 450 to $550 \mu\text{g/g}$ in the Fernald samples).

Leaching Designs

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

Most of the leaching tests conducted at the low-solution-to-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 any uranium (IV) to the uranyl (VI) state to form the stable uranyl tricarbonate complex, $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$. Potassium permanganate is a very strong oxidant in this pH range. 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. A similar experimental design was used to test the influence of citrate and pH on uranium extraction from the four soils. In this case, 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. For the Fernald soils, a bisequential leaching test was conducted by first leaching the soils with 0.1 M citric acid (20 g of soil in 200 mL) 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.

RESULTS

The leaching of uranium from the Fernald incinerator soil appeared to be more dependent on time and temperature than leaching of uranium from soil near the storage pad area. 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 on the leaching of uranium from the storage 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. 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.

The most effective leaching rates (>90% from both Fernald soils) were obtained using a citrate/dithionite pretreatment extraction procedure (Table I). This extraction procedure is designed to remove amorphous iron/aluminum sesquioxides from the surfaces of clay minerals (3). The high reducing effect (theoretical redox potential of -1.12 V) of the dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) 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 any U(IV) to the uranyl form (VI) and subsequent extraction. The data in Table I imply that future research using a similar reducing environment at shorter leaching intervals may prove to be useful.

TABLE I

Removal of Uranium from the Fernald Soils Using a Citrate/dithionite Pretreatment Extraction Procedure

Soil	Uranium ($\mu\text{g/g}$ soil)		Fraction of uranium leached (%)
	Initial	Residual	
Plant 1 storage pad	387	12	97
Waste incinerator	470	37	92

Leaching with citric acid/citrate was limited to Fernald soils. The extraction of uranium from the two Fernald soils was strongly influenced by the pH of the citrate extractions (Fig. 1). 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.

SUMMARY AND CONCLUSIONS

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 to acceptable regulatory levels. 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

EXTRACTION OF URANIUM FROM A FERNALD SOIL

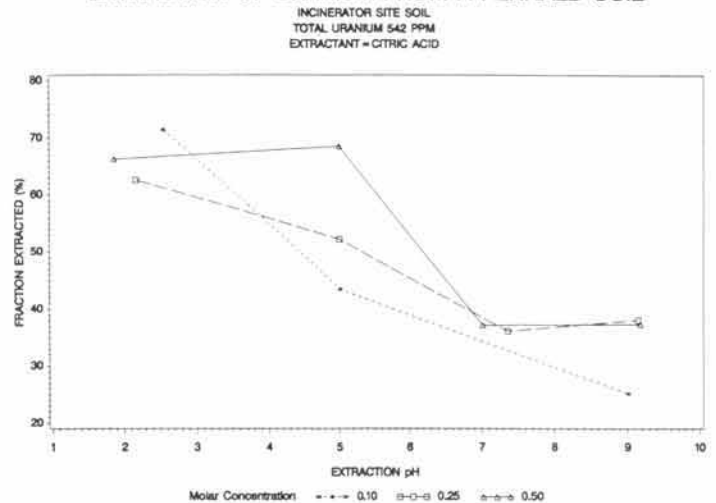


Fig. 1. The influence of pH on the effectiveness of citric/citrate concentrations to extract uranium from the incinerator soil at Fernald.

or generating a secondary uranium waste form that is difficult to manage and/or to dispose of. Carbonate extractions (total carbonate/bicarbonate concentration ranging from 0.1 to 0.5 M, over pH ranges of ~8 to slightly less than 10) generally removed from 70 to 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 ~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°C to 40°C for the sodium carbonate extractions of the Fernald waste incinerator soil increased the fraction of uranium leached from ~40 to ~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 μm) of soil than clay size fractions (< 2 μm).

Citric acid also proved to be a very good extractant for uranium. At pH values < 5, ~90% and ~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.

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. This extraction procedure uses sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) with a sodium citrate/ NaHCO_3 buffer (pH ~7.3) and elevated temperatures (75-80°C) to generate a high reducing effect 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.

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 phys-

ical 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.). Future work will focus on the establishment acceptable engineering residence times for a soil washing/leaching operation at Fernald. 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).

REFERENCES

1. LEE, S. Y., and J. D. MARSH, JR. 1992 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, Tennessee.
2. GOMBERT, D., and J. B. BOSELY. 1992. Soil Washing and Radioactive Contamination. pp. 366-370. In Proc. Nuclear and Hazardous Waste Management, Spectrum 92. Aug. 23-27, 1992. Boise, Idaho, Amer. Nuclear Soc., La Grange Park, Illinois.
3. JACKSON, M. L., C. H. LIM, and L. W. ZELAZY. 1986. Oxides, Hydroxides, and Aluminosilicates. pp. 101-150. In Methods of Soil Analysis, Part 1, Physical and Mineralogical Methods, 2nd Edition, Arnold Klute (ed), Soil Science Society of America, Inc. Madison, Wisconsin.