

URANIUM REMOVAL FROM SOILS: AN OVERVIEW FROM THE URANIUM IN SOILS INTEGRATED DEMONSTRATION PROGRAM

C. W. Francis
Oak Ridge National Laboratory

J. R. Brainard and D. A. York
Los Alamos National Laboratory

Gretchen Matthern
Idaho National Engineering Laboratory

D. J. Chaiko
Argonne National Laboratory

ABSTRACT

An integrated approach to remove uranium from uranium-contaminated soils is being conducted by four of the U.S. Department of Energy national laboratories. In this approach, managed through the Uranium in Soils Integrated Demonstration program at the Fernald Environmental Management Project, Fernald, Ohio, these laboratories are developing processes that selectively remove uranium from soil without seriously degrading the soil's physicochemical characteristics or generating waste that is difficult to manage or dispose of. These processes include traditional uranium extractions that use carbonate as well as some nontraditional extraction techniques that use citric acid and complex organic chelating agents such as naturally occurring microbial siderophores. A bench-scale engineering design for heap leaching; a process that uses carbonate leaching media shows that >90% of the uranium can be removed from the Fernald soils. Other work involves amending soils with cultures of sulfur and ferrous oxidizing microbes or cultures of fungi whose role is to generate mycorrhiza that excrete strong complexers for uranium. Aqueous biphasic extraction, a physical separation technology, is also being evaluated because of its ability to segregate fine particulate, a fundamental requirement for soils containing high levels of silt and clay. Interactions among participating scientists have produced some significant progress not only in evaluating the feasibility of uranium removal but also in understanding some important technical aspects of the task.

INTRODUCTION

The development of a nuclear industry in the United States required the mining, milling, and fabrication of a large variety of uranium products. One of these products was purified uranium metal, such as ingot feed materials, for use in the Savannah River and Hanford site reactors. Most of this ingot feed material was produced at the U.S. Department of Energy (DOE) facility formerly called the Feed Materials Production Center at Fernald, Ohio. Currently this facility is called the Fernald Environmental Management Project (FEMP) and consists of 1050 acres in a rural area ~18 miles northwest of downtown Cincinnati. During the operation of this facility, soils have become contaminated with uranium from a variety of sources. These sources include deposition of airborne uranium particulate coming from facility stacks 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. The exact quantity of soil contaminated with uranium is unknown. Some estimates of soil containing unacceptable levels of uranium are as high as 2,000,000 yd³. Many other DOE sites also have significant quantities of uranium-contaminated soils. To avoid the disposal of these soils in conventional low-level radwaste burial sites, a specific technology is needed to extract, or leach, uranium from the soil, concentrate it into small volumes of acceptable form, and return the soil to its original place.

APPROACH

To address the management of uranium-contaminated soils at Fernald and other DOE sites, the DOE Office of Technology Development formed the Uranium in Soils Integrated Demonstration (USID) program. The USID has five

major tasks. These include the development and demonstration of technologies that can 1) characterize the uranium in soil, 2) decontaminate or remove uranium from the soil, 3) treat the soil and dispose of any waste, 4) establish performance assessments, and 5) meet necessary state and federal regulations. Groups have been formed within USID to address each of these tasks. This report deals with soil decontamination, or more specifically, the removal of uranium from contaminated soils. It summarizes some of the ongoing research by the USID soils decon group.

The fundamental goal of the soils decon task group is to selectively extract, or leach, uranium from soil faster, cheaper, and safer than current conventional technologies. The objective is to selectively remove uranium from soil without seriously degrading the soil's physicochemical characteristics or generating waste that is difficult to manage or dispose of. The research emphasis was on chemical extraction techniques more than physical extraction techniques. This strategy was taken because most of the highly contaminated uranium soils are in the eastern United States (predominantly Fernald and the Oak Ridge Y-12 Plant, Oak Ridge, Tennessee) and, consequently, contain high levels of fine-textured materials (i.e., silt and clay) that are not directly amenable to physical separation techniques such as soil washing with water. Chemical extraction techniques under evaluation involved traditional uranium extractions that use sulfuric acid and carbonate as well as some nontraditional extraction techniques that use citric acid and complex organic chelating agents such as naturally occurring microbial siderophores. A project using carbonate leaching media in an engineering design for heap leaching has recently been implemented. Other work involves amending soils with cultures of sulfur and ferrous oxidizing

microbes [to enhance dissolution of uranium(IV) forms] or cultures of fungi whose role is to generate mycorrhiza that excrete *strong complexers* for uranium that can solubilize insoluble uranium(VI) secondary minerals. One physical separation technology (aqueous biphasic extraction) is also being evaluated because of its ability to segregate fine particulate, a fundamental requirement for soils containing high levels of silt and clay (i.e., Fernald soils contained >85% by weight <50 μ m diameter particles). Aqueous biphasic extraction involves the selective partitioning of either solutes or colloid-sized particles between two immiscible aqueous phases.

CARBONATE AND CITRIC ACID EXTRACTION

Carbonate-based solutions appeared to be a logical and pragmatic approach to extracting uranium from uranium-contaminated soils. However, little data existed relating to its effectiveness in decontaminating soils. Carbonate-based solutions had been used successfully in the uranium mining and milling industry to extract uranium, but there are major differences between their use in the uranium mining and milling industry and their effectiveness in removing uranium from uranium-contaminated soils. First, a subtle but very important difference is that in the mining and milling industry the material being mined and treated with carbonate has traditionally been coarse textured sedimentary deposits containing the mineral carotite [most uranium ores containing the primary mineral uraninite are treated with sulfuric acid in the presence of a strong oxidant to convert the uranium(IV) to uranium(VI)]. These secondary deposits often contain large quantities of calcite and dolomite, therefore treatment with sulfuric acid is not an economic option. These ores are often milled (80% passing a 200 mesh sieve, <75 μ m) to increase extractability. Care is taken not to mill them too much as material <50 μ m (called "slimes" in the mining industry) often have to be discarded as uranium is difficult to extract from them (due to their sorptive characteristics) and their painstaking filtering and dewatering characteristics. Uranium-contaminated soils, on the other hand, do not contain uranium in a single discrete mineral (such as carotite). Uranium in uranium-contaminated soils is present as insoluble reaction products of a uranium source material reacting with soil constituents under prevailing soil weathering conditions. The uranium source materials consist of a variety of particulate forms (ranging from metallic uranium as well as oxides and fluorides of processed uranium) and soluble uranium in liquid effluents. The characterization task group of the USID has made significant progress in identifying these forms (1).

Leaching data using carbonate- and citrate-based extraction media revealed significant differences in the extractability of uranium from two soils sampled from the Fernald site. Soil sampled near a waste incinerator contained considerably more recalcitrant uranium forms than soil sampled adjacent to a storage pad (Table I). For example, increased temperature and time increased the extractability of uranium from the incinerator soil but not the storage pad soil. Four-hour extractions using unadjusted citric acid removed >95% and ~68% of the uranium from the storage pad and incinerator soil, respectively (2). Attrition scrubbing the incinerator soil removed approx. 20% more uranium than extraction in simple stirred reactors (3). A similar treatment showed no increases in the removal of uranium from the storage pad soil. Also, the addition of an oxidant (KMnO₄) significantly increased (10 to 15%) the extractability of uranium from the incinerator soil but not the storage pad soil.

TABLE I
Sodium Carbonate Leaching of Fernald Soils as Influenced by Temperature and Extraction Time

Treatment	Waste Incinerator Soil (470 mg U/kg)	Storage Pad Soil (387 mg U/kg)
	Uranium conc. in residues (mg U/kg)	
Temperature (°C)		
22	180	63
40	73	42
60	97	42
Extraction Times (Hr)		
2	154	48
4	161	55
6	60	48
23	90	45

Experimental data accumulated to date indicate that the incinerator site soil is more representative of the Fernald soils than the storage pad site soil with respect to uranium leaching characteristics. Thus, the likelihood of removing uranium to concentrations <50 mg/kg (a technology screening level) using carbonate- or citrate-based extractants without prolonged extraction times is not good. Bench-scale studies are under way to evaluate a variety of engineering schemes coupling attrition scrubbing (at different percentages of solids and feed rates of varying particle-size), temperature, and type of oxidant. Other bench-scale studies have shown that uranium concentrations <50 mg/kg can be achieved using a citrate-bicarbonate-dithionite (CBD) reductive dissolution scheme developed to remove free oxides from soils and clays (4); however, like sulfuric acid extractions, significant quantities of iron as well as calcium are extracted generating copious quantities of secondary waste. Pilot-scale studies have begun at Fernald and have been encouraging in the removal of uranium from the storage pad soil. For example, uranium concentrations in excess of 2000 mg/kg were lowered to <60 mg/kg.

HEAP LEACHING OF URANIUM FROM SOIL

A new approach to uranium removal that also uses carbonate as a leaching media has proved highly effective in laboratory column experiments. This approach, being led by D. A. York at Los Alamos National Laboratory, is based upon existing heap leach mining technologies. In the laboratory tests, heap leaching of Fernald contaminated soils with carbonate salt solutions resulted in uranium removal efficiencies as high as 95%.

Historically, carbonate leaching has performed well in recovering uranium from ore. More than one-third of the U.S. uranium mills have employed carbonate leaching at one time or another. Ideally, carbonate leaching is applied in an integrated and closed-circuit process that recycles the leach solution to minimize the secondary waste stream. Carbonate leaching also has the advantages of being relatively noncorrosive and safe to handle. It generates a relatively pure leachate solution from which uranium can easily be precipitated.

Carbonate salt leach solutions successfully remediated the FEMP soils for two primary reasons.

- Application of the leach solution results in the formation of highly soluble, anionic, carbonate uranyl

species, including uranyl dicarbonate ($\text{UO}_2(\text{CO}_3)_2$ - and uranyl tricarbonate ($\text{UO}_2(\text{CO}_3)_3$ -). This allows high concentrations of uranium in the leachate solution.

- Carbonate salts are highly selective for dissolution of uranium from uranium-contaminated soils. Other compounds in the soil are relatively unaltered.

The column experiments (Fig. 1) demonstrated that higher molar strength carbonate solutions (~ 0.5 M) are more effective than lower molar strength solutions (~ 0.1 M). The application rate was approximately 1 L/d through 1 kg of soil (i.e., a liquid-to-solid ratio of 1:1). Chemical reaction rates (kinetics) are not critical in heap leaching applications. Uranium removal is also a function of the solution flow rate and the ratio of carbonate to bicarbonate. Uranium removal was slower, and less effective, when the Fernald soils were agglomerated with Portland cement.

The benefits of this form of soil remediation, when proved at field scale, would include 1) on-site cleanup; 2) conservation of repository space; and 3) elimination/reduction of long-term costs for monitoring, isolation, and habitat protection. Additionally, the method would provide the ability to examine, sort, treat, and verify that the soil meets and/or exceeds soil quality standards. This methodology will offer a permanent solution to the soil contamination problem, not just a relocation of the soil with a resultant increase in volume and expense for future care.

URANIUM EXTRACTION BY COMPLEX ORGANIC CHELATING AGENTS

Brainard et al. (5) are evaluating the efficiency of more complex organic chelating agents as extractants for uranium in contaminated soils. The primary focus of their efforts is on microbial siderophores and their biomimetic analogs. The selection of these particular chelators as potential extractants for uranium was based on 1) the extraordinarily high binding constants of siderophores and synthetic analogs for metal ions, 2) the natural role of siderophores in mobilizing and transporting insoluble forms of metals under very mild conditions, and 3) the availability of strategies for ready recovery of

bound metals from these chelators and for recycle of the chelators.

Siderophores are metal ion chelators which are produced by many microorganisms in order to obtain iron, an essential nutrient. Approximately 300 siderophores have been isolated and characterized; most characterized to date contain either catecholate and/or hydroxamate functionalities for metal binding. These chelators and their synthetic analogs have some of the highest known binding constants (up to 10^{49}) for hard Lewis acid metal ions such as Fe^{3+} , U^{4+} , Pu^{4+} .

Brainard et al. have evaluated natural siderophores, biomimetic analogs, and some amino carboxylates as potential extractants in two soil treatability samples obtained from the Fernald site. In addition, they have performed a limited number of experiments on pure uranium solid phases, in order to better understand some of the mechanisms operating during decontamination. Finally, they have examined the effects of extraction conditions such as pH, and liquids-to-solids ratio on the extraction effectiveness of Tiron (1,2 dihydroxy-2,5-benzenedisulfonic acid) the most successful chelator to date.

Results obtained by the USID characterization team have guided the strategy in the development and testing of these chelators. This technical team is responsible for characterizing the speciation of uranium in the soils at Fernald so that rational strategies for extraction of the uranium can be developed. Early in their investigation, the characterization team used X-ray absorption spectroscopy to show that the oxidation state found in both treatability samples from Fernald was predominantly U(VI). This finding was particularly important because the selection of siderophores and analogs was based largely on their high affinity for U(IV) and the expectation that these chelators might play a particularly important role at sites where the contamination was present as U(IV).

Because of the higher affinity of these chelators for U(IV) and the importance of redox changes in dissolution of many sparingly soluble mineral phases, it was hypothesized that the reduction of solid uranyl phases in the presence of a strong chelator for U(IV) might aid the effectiveness of uranium extraction. This strategy has indeed proved to be effective in decreasing the levels of residual uranium present in soils after treatment; results for Tiron extraction of uranium in the presence and absence of dithionite as a reductant are shown in Fig. 2.

Future plans are directed at treatment of the secondary waste stream for uranium recovery and chelator recycling. In

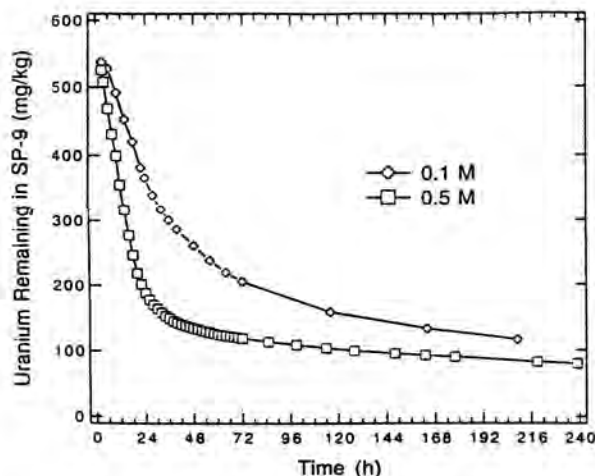


Fig. 1. The removal of uranium from the Fernald incinerator site soil by heap leaching (0.1 and 0.5 M carbonate solutions).

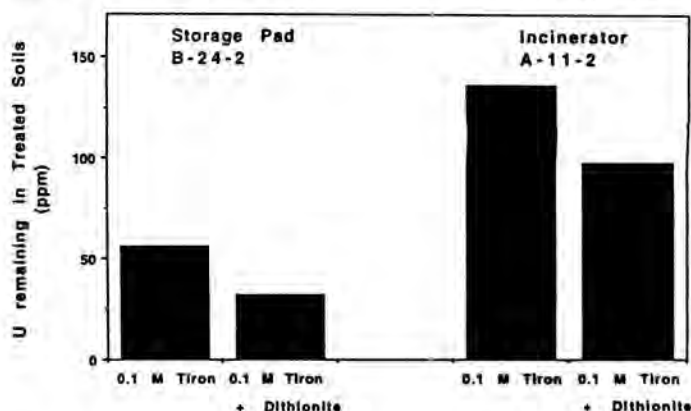


Fig. 2. The influence of dithionite additions on the removal of uranium from Fernald soils using Tiron as an extractant.

addition, this group is investigating further strategies for extracting recalcitrant forms of uranium identified by the characterization team as remaining in treated soils.

BIOEXTRACTION OF URANIUM FROM CONTAMINATED SOILS

Three facets of microbial activity for removal and concentration of uranium are under investigation at Idaho National Engineering Laboratory (INEL): first, the production of oxidizing agents or the ability to oxidize uranium directly; second, the production of organic complexing or chelating agents; and third, the affinity of some cell components for uranium.

Researchers there have investigated the ability of the acid loving iron oxidizing bacterium *Thiobacillus ferrooxidans* to increase oxidation in a soil suspension. Oxidized uranium(VI) is soluble at low pH. Very high levels of uranium were extracted in these experiments, but because most of the uranium in the soil is probably already soluble at low pH, and because of the complex soil chemistry, the contribution of bacteria is unclear. The results suggest that bacteria may be most effective in limited applications, such as low iron soils or soils high in tetravalent uranium.

Recently the researchers using two common molds, *Penicillium simplicissimum* and *Aspergillus niger*, have observed some very encouraging results in the mobilization of uranium. It has been observed that these molds are able to move uranium into solution and that they also accumulate it in their cell mass. Since the mycelial mats that these molds produce are easily collected, the INEL group has been experimenting with using them as biofilters.

The group has developed a twofold strategy in dealing with these fungi. In one set of experiments fungi and soil are placed together in solution. After incubation for a few days, uranium begins to appear in solution and reaches a maximum when the fungi have exhausted their food supply. At the end of this experiment, the mycelial mass is collected and analyzed for uranium. In the other set of experiments, fungi have been grown separately until nutrients are exhausted, then the depleted liquid medium is filtered out and mixed with soil. After incubation of a few days, analysis of solution shows substantial amounts of uranium.

Results from fungal experiments are summarized in Table II. One of the most attractive features of this process is that the pH remains relatively high, so alteration of soil properties likely to be much less than with the low pH bacterial treatment. Since work with fungi has just begun, these results should be considered preliminary. There is good reason to believe that manipulation of culture conditions can increase production of complexing agents and accumulation of uranium in the cells. Experiments are in progress to test this hypothesis.

Results suggest that the processes of uranium solubilization and cell uptake could be combined into a system with potential for high levels of extraction and minimal effect on soil properties.

AQUEOUS BIPHASIC EXTRACTION

The aqueous biphasic separation (ABS) process involves the selective partitioning of ultra fine particles or solutes between two immiscible aqueous phases. Chaiko et al.(6,7) are examining a number of possible applications for this separation technology, including solid waste treatment, soil remediation, high-level liquid waste treatment, and clay beneficiation. The biphasic system is formed from a mixture of aqueous solutions of organic polymers and inorganic salts. Each phase contains at least 70 to 80 wt % water. The inorganic salts used to generate the biphasic become concentrated in the more dense, lower phase, whereas the polymers are concentrated in the less dense, upper phase. When ultra fine particles of different surface characteristics are introduced into the system, the particles partition selectively according to the various physicochemical interactions that occur between the particle surface and the surrounding solvent.

The ABS process is being evaluated for the removal of uranium from contaminated soils. The goal is to selectively remove ultra fine particulate uranium from the soil, leaving residual uranium levels that are below regulatory cleanup limits. The ABS process is a potential alternative to conventional soil-washing techniques that are based on physical separation methods, such as screening, classification, and flotation. Because of its ability to separate ultra fine particles, the ABS process is ideal for remediating high-clay-content

TABLE II
Extraction of Uranium from Fernald Soils by Fungi

Soil	Uranium Extracted (mg/kg of soil)				Control ^a
	by Fungi in Soil		by Depleted Malt Extract		
	<i>P. simp.</i>	<i>A. niger</i>	<i>P. simp.</i>	<i>A. niger</i>	
Storage Pad Soil ^b					
Solution	109	122	233	181	3
Mycelium	18	12			
Total	127	135	233	181	
pH	6.5	7.1	5.6	5.7	
Incinerator Soil ^c					
Solution	43	129	131	249	< 1
Mycelium	93	42			
Total	136	171	131	249	
pH	4.7	4.4	4.5	3.9	

^aControl flasks contained soil and malt extract broth with no fungi.

^bSoil contains 390 mg/kg uranium before treatment.

^cSoil contains 490 mg/kg uranium before treatment.

soils. The upper limit to the size of soil particles that can be accommodated in the biphasic system appears to be about 50 μm .

The majority of the laboratory tests that Argonne National Laboratory (ANL) has conducted to date involve soil collected near the waste incinerator of the Fernald site. The large amount of silt (particle sizes of 2 to 53 μm) and clay (< 2 μm) in the Fernald soils makes treatment by conventional soil-washing techniques difficult. On the other hand, the fact that over 80 wt % of the Fernald soil is < 45 μm makes this soil a good candidate for biphasic extraction.

During 1993 the group conducted test-tube-scale experiments that used up to 1 g of soil per test. All of the biphasic systems used polyethylene glycol (PEG) in combination with an inorganic salt phase (sodium and potassium carbonate, sodium sulfate, and sodium hexametaphosphate).

Initial results show that the ABS process can selectively extract and concentrate uranium from the soil collected near the incinerator at Fernald. Uranium concentrations were reduced from 500 to 600 mg/kg, to about 90 mg/kg, and in certain cases, the uranium concentration was reduced to about 15 mg/kg. The uranium concentrates were recovered in volumes representing only 1 to 2 wt % of the initial soil sample. Less encouraging results, however, were obtained with the soil sample that was collected from the storage pad. With this soil sample, the uranium concentration was reduced to only ~200 mg/kg, and there was no evidence of selective uranium partitioning.

Selective flocculation of the soil particles occurred in all of the biphasic extraction systems studied. Work with model systems suggests that this is not a problem with regard to solid/solid separation, and even aids in solid/liquid separation. The Argonne group has done extraction tests with particles as small as 20 nm and obtained good solid/liquid separation with only mild centrifugation.

In all of the soil extraction tests, significant dissolution of uranium into the salt phase took place. This does not interfere with soil decontamination as the partition coefficient for uranyl species is $\sim 10^{-3}$, whereas the partition coefficient for clean soil particles is $\sim 10^2$.

During 1993, some initial scale-up tests using an uncontaminated clay mineral feed were conducted at the pilot-plant facilities of Otto York in Houston. During these tests, a clay ore containing ~88 wt % kaolinite and 12 wt % cristobalite was fed at a rate of ~70 g/h into a Karr column (2.54 cm ID and 3.6 m high) with countercurrent feed solutions of 30% PEG and 20% Na_2CO_3 . The success of these tests was demonstrated by the ability of the column to handle a feed slurry and produce < 1 vol % of other-phase carryover in the overflow and underflow from the column. At steady-state, the column was producing a clay product stream containing < 0.03 wt % cristobalite. It is anticipated that a full-scale column would achieve solids throughput of ~600 to 1200 kg/h. Initial estimates of operating costs for soil remediation using the ABS process is approximately \$25 to \$50 per ton. A pilot-scale column is being installed at ANL, and researchers there will conduct scale-up tests with Fernald soil during 1994. They will also invest the use of the ABS process as a polishing step for the removal of refractory uranium particulates remaining after conventional carbonate leaching.

SUMMARY AND FUTURE DIRECTIONS

Significant progress has been made in understanding the technical aspects of removing uranium from soils. The most

effective leaching procedures, in terms of total uranium removal, involve a reductive dissolution process or treatment with sulfuric acid. Work at LANL and ORNL indicates that the reductive dissolution processes can be used to lower uranium concentrations in the Fernald soils to concentrations < 50 mg/kg. However, both the reductive dissolution process and treatment with sulfuric acid generate copious quantities of secondary waste (CaSO_4 and iron and aluminum hydroxides). Extraction with carbonate-based media is the most selective in the removal of uranium; the process does not generate significant quantities of secondary waste. However, final uranium concentrations tend to be 50 to 100 mg/kg higher than the aggressive extractants. Future efforts are being directed at coupling the most effective engineering designs (i.e., heap leaching, attrition scrubbing in combination with selected oxidants and heat) with carbonate leaching because of its great selectivity for uranium. Ongoing experiments include the treatment of carbonate-based cleaned soils from the Fernald pilot plant in the countercurrent columnar aqueous biphasic extraction studies at Argonne. This combination of a highly selective chemical extraction technique followed by a physical removal process to partition the recalcitrant particulate uranium may lead to a process in which final soil concentrations meet regulatory levels and excessive quantities of secondary wastes are not generated.

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