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**REMOVAL OF URANIUM FROM URANIUM CONTAMINATED SOILS  
PHASE I: BENCH-SCALE TESTING - (USED AS A REFERENCE IN  
OU2 FS REPORT)**

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ORNL-6762

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**OAK RIDGE  
NATIONAL  
LABORATORY**

**MARTIN MARIETTA**

**Removal of Uranium from Uranium-  
Contaminated Soils  
Phase I: Bench-Scale Testing**

Soil Decon Task Group

Uranium in Soils  
Integrated Demonstration

**MANAGED BY  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY**

000001

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CONTAMINATED SOILS  
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Soil Decon Task Group

Uranium in Soils  
Integrated Demonstration

September 1993

Prepared for the  
Office of Technology Development  
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Prepared by the  
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U.S. Department of Energy  
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## CUMULATIVE ACRONYMS AND INITIALISMS

|         |   |
|---------|---|
| ABS     | aqueous biphasic demonstration                          |
| ACH     | acetohydroxamic acid                                    |
| ACL     | Analytical Chemistry Laboratory of Argonne              |
| AEM     | analytical electron microscopy                          |
| ANL     | Argonne National Laboratory                             |
| CBD     | citrate-bicarbonate-dithionate                          |
| CDTA    | 1,2-diamineocyclohexanetetraacetic acid                 |
| DOE     | U.S. Department of Energy                               |
| DPTA    | diethylenetriaminepentaacetic acid                      |
| ED      | electron-dispersive (X-ray detector)                    |
| EDTA    | ethylenediaminetetraacetic acid                         |
| EELS    | electron energy loss spectrometer                       |
| EPA     | U.S. Environmental Protection Agency                    |
| FEMP    | Fernald Environmental Management Project                |
| FMPC    | Fernald Materials Production Center                     |
| IA      | incinerator area  |
| ICP-AES | inductively coupled plasma-atomic emission spectroscopy |
| ICP-MS  | inductively coupled plasma-mass spectrometry            |
| ID      | inside diameter   |
| LANL    | Los Alamos National Laboratory                          |
| KPA     | kinetic phosphorescence analysis                        |
| NAA     | neutron activation analysis                             |
| NRC     | U.S. Nuclear Regulatory Commission                      |
| ORNL    | Oak Ridge National Laboratory                           |
| PEG     | polyethylene glycol                                     |
| SEM/BSE | scanning electron microscopy/backscatter detector       |
| SITE    | Superfund Innovative Technology Evaluation              |
| SPA     | storage pad area  |
| SRP     | Savannah River Plant                                    |
| TEM     | transmission electron microscopy                        |
| TIMS    | thermal ionization spectrometry                         |
| USID    | Uranium in Soils Integrated Demonstration               |
| WSTC    | Westinghouse Science and Technology Center              |

## FOREWORD

This document presents the initial results of the bench-scale testing of methods to remove uranium from uranium-contaminated soil. The research is sponsored by the U.S. Department of Energy (DOE) Office of Technology Development through the Uranium in Soils Integrated Demonstration program (USED) managed by the Fernald Environmental Management Project (FEMP) at Fernald, Ohio. The USED was established to develop technologies that would enable DOE to remediate uranium-contaminated soils faster, safer, and more economical than traditional landfilling of low-level radioactive wastes. The research in the USID is centered at selectively removing uranium from the contaminated soil using chemical and physical that won't seriously affect the physicochemical characteristics of the soil or produce waste streams that are difficult to manage or dispose of. The intent is to develop soil remediation technologies that can be successfully transferred to other sites that have related contamination problems.

This document was written by investigators funded in FY92 under the Soils Decon Task Group of the USID. The report is composed of four parts. The first part summarizes research conducted at Oak Ridge National Laboratory (ORNL) on effectiveness of carbonate- and citrate-based extraction of uranium from soils at the former DOE Feed Materials Production Center in Fernald, Ohio and the Oak Ridge Y-12 Plant.. The second part presents data from a treatability study conducted by the Westinghouse Science and Technology Center in which ammonium carbonate was used as a chemical extractant and a pilot-scale attrition scrubber and mineral jig were used to remove fine materials and displace the used leachate with rinse water. The third part, by Los Alamos National Laboratory, addresses the use of complex organic chelating agents to remove uranium from soil. The fourth part summarizes the progress made at Argonne National Laboratory in using aqueous biphasic extractions to separate uranium from soil.

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**EXECUTIVE SUMMARY**

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## ACRONYMS AND INITIALISMS

|      |  |
|------|--|
| ANL  | Argonne National Laboratory                |
| CBD  | citrate-bicarbonate-dithionite             |
| CDTA | 1,2-diaminocyclohexanetetraacetic acid     |
| DOE  | U.S. Department of Energy                  |
| DTPA | diethylenetriaminepentaacetic acid         |
| FEMP | Fernald Environmental Management Project   |
| FMPC | Feed Materials Production Center           |
| ID   | integrated demonstration                   |
| LANL | Los Alamos National Laboratory             |
| NRC  | U.S. Nuclear Regulatory Commission         |
| ORNL | Oak Ridge National Laboratory              |
| PEG  | polyethylene glycol                        |
| SRP  | Savannah River Plant                       |
| WSTC | Westinghouse Science and Technology Center |

## EXECUTIVE SUMMARY

### BACKGROUND

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 (FMPC) 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, Ohio. The manufacturing processes were housed in a ~136-acre fenced area and included uranium and thorium metal production and uranium hexafluoride reduction. Production peaked in 1960 (processing of ~10,000 t of uranium) and began to decline in 1964 to a low of about 1230 t in 1975. In the mid-1980s, production increased slightly but was terminated in 1989 because of the decreased demand for uranium products.

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 the 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 yd<sup>3</sup>. To avoid the disposal of these soils in conventional low-level radwaste burial sites, a specific technology is needed to extract/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 are able to (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. This report deals with soil decontamination or removal of uranium from contaminated soils. The report was compiled by the USID task group that addresses soil decontamination; includes data from projects under the management of four DOE facilities [Argonne National Laboratory (ANL), Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), and the Savannah River Plant (SRP)]; and consists of four separate reports written by staff at these facilities.

The fundamental goal of the soil decontamination task group has been the selective extraction/leaching or removal of 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 forms that are difficult to manage and/or dispose of. Emphasis in research was placed more strongly on chemical extraction techniques than physical extraction techniques. This strategy was taken because (1) most of the highly contaminated uranium soils are located in the eastern United States (predominately 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 and (2) research and development of many of the physical separation techniques were being addressed by the Plutonium in Soils Integrated Demonstration program. Chemical extraction techniques being evaluated involved traditional uranium extractions that use carbonate and nontraditional extraction techniques that use citric acid and complex organic chelating agents (for uranium) such as naturally occurring microbial siderophores.

Two organizations (SRP and ORNL) were to address the applicability of carbonate extractions in selective removal of uranium. Carbonate extractions have been used to commercially remove uranium from ore deposits in the uranium mining and milling industry; thus, their effectiveness in the decontamination of uranium from soils was a logical extension. SRP was to manage a contract to conduct bench-scale treatability studies with the Westinghouse Science and Technology Center (WSTC), Pittsburgh, Pennsylvania, an organization that is experienced in bench- and pilot-scale development and testing of carbonate-based extraction to remove uranium from soils at Burni, Texas, and Oak Ridge, Tennessee. ORNL also was to conduct bench-scale testing of carbonate extractions by evaluating the influence of extraction time, temperature, pH, carbonate concentration, and extraction configuration such as attrition scrubbing vs batch-stirred reactors. ORNL also was to investigate the applicability of using citric acid-based extraction procedures (under oxidative and reducing conditions) to remove uranium.

The applicability of using complex organic chelation agents to extract uranium from soils was to be addressed by LANL. This research addresses the utilization of naturally occurring microbial metal chelators (siderophores such as enterobactin and desferrioxamine B) and synthetic analogs to selectively remove uranium from soils. These chelators have very high binding constants for uranium(IV). Because earlier characterization work at LANL (Morris et al. 1992) had indicated that the predominant oxidation state of uranium in Fernald soils was uranium(VI), the LANL soil decontamination group was to investigate the role of redox dissolution chemistry, namely the use of complex organic chelating agents to reductively dissolve and selectively extract uranium(IV).

ANL was to utilize their experience with aqueous biphasic extraction technologies to concentrate high-fired oxides of plutonium from fuel reprocessing residues to investigate uranium removal from contaminated soils. Aqueous biphasic extraction involves the selective partitioning of either solutes or colloid-size particles between two immiscible aqueous phases. Aqueous mixtures of unlike polymers (e.g., a straight-chain polymer such as polyethylene glycol and a highly branched polymer such as dextran) can be used because they are immiscible and form upper and lower phases based on their densities. Mixtures of polyethylene glycol and aqueous solutions of inorganic salts (e.g., sodium carbonate or sulfate) can also be used and are likely candidates for extraction of uranium. Partitioning to selected phases is determined by the surface chemistry of the particles and their preferential wetting by one of the liquid phases.

## STATUS OF RESEARCH

Two years ago, it was unclear whether uranium could be selectively removed from the Fernald soils to levels previously established by regulatory agencies, such as the 35 pCi/g of natural uranium level established by the Nuclear Regulatory Commission (NRC) for uranium mill tailings. Based on the studies recently conducted by the Soils Decon Task Group, it is clear that such removal can be

accomplished. The more important question now is "How can it best be conducted in terms of cost, time, safety, and impact on the environment?" In the Soil Decon Task Group studies, no specific cleanup level of uranium in soil was considered. However, as a guide to assist in the evaluation of removal processes or cleanup technologies, a technology screening level of 35 pCi/g was established (equivalent to a uranium level of 52 mg/kg of soil based on the distribution of uranium isotopes of naturally occurring uranium). This is used as a guide with which to select technologies that should be pursued aggressively. No approved regulatory cleanup level has been established for the Fernald soils.

Most of the research in this report deals with the extraction of uranium from two soils at the Fernald facility. These soils were from an area near the Plant 1 storage pad area and an area adjacent to a waste incinerator located a few hundred yards east of the Fernald production area. Uranium concentrations in the storage pad soil and incinerator soil were ~450 and 540 mg/kg, respectively.

### Carbonate Extractions

Carbonate extraction of soils is an attractive procedure because carbonate and uranium(IV) form a very stable complex [i.e.,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ], and carbonate generates a waste stream with lower concentrations of secondary soil constituents (i.e., iron, aluminum, calcium, and silica) than acid extractions do. ORNL concluded that carbonate extractions probably cannot be used to decontaminate Fernald soils containing uranium at >450 mg/kg level to <50 mg/kg levels. They based their conclusion on extraction data obtained in batch-stirred type reactors that required long residence times (>6 h) and elevated temperatures (40 and 60°C) to lower uranium concentrations of the Fernald storage pad soil to uranium levels <50 mg/kg. Similarly treated soils from the Fernald incinerator site contained uranium at >50 mg/kg. Carbonate extractions in combination with attrition-scrubbing type reactors at residence times of 3 to 15 min were as effective as stirred-batch type reactors at room temperature and 4 h residence times; however, only ~80 and 60% (calculated residual uranium concentrations of 89 and 215 mg/kg of treated soil) of the uranium could be removed from the storage pad and incinerator site soils, respectively. These data imply that carbonate extractions may be only appropriate as a pretreatment or as a method to remove uranium from specific size fractions of soil. Uranium analyses of the five soil size fractions (4.75 to 2.00, 2.00 to 1.18, 1.18 to 0.075, 0.075 to 0.02, and <0.020 mm diam) generated in the ORNL attrition-scrubbing tests have not been completed. Perhaps these data will reveal that attrition scrubbing of the whole soil will result in a specific size fraction or fractions that contain uranium at concentrations <50 mg/kg.

The WSTC study indicated that uranium on the order of 118 and 216 mg/kg remained in the 0.85- to 0.075-mm fraction of the storage pad and incinerator site soils, respectively. Their work involved the use of a mineral jig that used 20 mesh (>0.85 mm) and 200 mesh screens (0.075 mm diam) to make cuts. They found that the >0.85-mm fraction "was relatively clean for both soils." Uranium concentrations in the jig underflow (>0.075 mm) were 72 and 1368 mg/kg, respectively, for the storage pad and incinerator site soils. Most of the soil (85 and 90%, respectively, for the storage pad and incinerator site soils) was in the jig overflow (<0.075 mm). The flocculated solids in the <0.075-mm fractions contained uranium at 257- and 587-mg/kg levels, respectively, for the storage pad soil and incinerator site soils. Scientists at WSTC felt that the "hazy" solution above the settled <0.075-mm fraction contained minute solids containing significant amounts of uranium contamination. They felt that this material was not "soil" even though it could be flocculated from

the suspension. They did not filter or centrifuge this fine particulate from the suspensions to determine if the solid phase was a fine clay particulate containing uranium or a discrete uranium particulate formed as a consequence of the extraction process that could be extracted or removed by other means.

### Citric Acid Extractions

Citric acid extractions were used because initial testing by Lee and Marsh (1992) indicated high removal rates (~75%) of uranium from selected soils sampled at the Fernald site. Citrate is well known for its ability to form strong complexes with uranium (Rajan and Martell 1965) and is also known to effectively remove metals from soils and wastes (WET 1985; Jackson et al. 1986). In 4-h batch-type stirred reactor tests, citric acid was a highly effective extractant of uranium from storage pad soil (i.e., ~95% removal). For incinerator site soil ~60% of the uranium could be extracted, an extraction percentage very similar to that extracted by sodium carbonate and the same method of leaching. The attrition-scrubbing tests with sodium carbonate indicated that similar quantities of uranium could be extracted from either of the two Fernald soils for scrubbing times of 3 to 15 min compared with that extracted for 4 h in batch-type stirred reactors. A similar relationship was not apparent when citric acid was used as an extractant. For example, in the case of the storage pad soil, the leaching of uranium in the attrition-scrubbing tests (3 and 5 min) with citric acid removed ~20% less uranium than was removed in the 4-h batch-type stirred reactor tests. However, for the incinerator soil, citric acid extractions in the attrition scrubber (3 to 15 min) appeared to be similar to the 4-h batch-type stirred reactor tests (i.e., ~60% removal). The extraction of uranium from both soils by citric acid was highly dependent on pH; the most effective extraction occurred at pH values <3.

Citric acid appears to be a good extractant because at low pH values (<3) it promotes dissolution of carbonate minerals and iron and aluminum sesquioxide coatings on soil particles, two mineral phases that may act as contamination sites for uranium in soils. As a consequence, large quantities of calcium and magnesium (from soil carbonates) and iron and aluminum (from sesquioxide coatings) are present in citric acid effluents. The presence of these minerals makes removal of uranium more difficult and disposal of the waste stream more voluminous and complex than extraction with carbonate. Citric acid is not as effective as sulfuric acid in the extraction of uranium (e.g., attrition-scrubber tests revealed ~90% of the uranium could be removed from the incinerator site soil with sulfuric acid compared with ~65% with citric acid under similar leaching conditions). However, citric acid has several advantages over sulfuric acid leaching: (1) it biodegrades rapidly to carbon dioxide and water, making effluent treatment/disposal more environmentally benign; (2) it is inexpensive and may even be obtained as an industrial waste product; and (3) it offers a buffered system in contrast to sulfuric acid in which the pH of the extraction suspension varies widely as carbonates are neutralized. Single additions of sulfuric acid in quantities necessary to reach equilibrium pH values <2 (necessary for effective uranium extraction) often result in much more acidic suspensions. This probably results in significantly more dissolution and degradation of layer silicates (and subsequently higher concentrations of aluminum, silica, and iron in the effluent requiring treatment/disposal) than extractions buffered between pH values of 2 and 3 with citric acid. If the pH of the soil suspension becomes >2 (as a result of dissolution of excess carbonates), the uranium extraction efficiency is greatly reduced. The ability to control the pH of the extraction suspension at values between 2 and 3 by means of a single addition of citric

acid compared with multiple additions of sulfuric acid also has certain advantages in the design costs and operation of a full-scale facility.

A bisequential extraction procedure that uses citric acid in combination with dithionite followed by ammonium carbonate extraction with potassium permanganate removed uranium from both soils to levels <50 mg/kg. The first extraction is based on the citrate-bicarbonate-dithionite (CBD) procedure developed by Jackson et al. (1986) to remove sesquioxides from layer silicates. The basic principle is reduction of the ferric oxides to ferrous forms, which weakens the crystalline characteristics of the mineral phase and results in a phenomenon commonly called reductive dissolution. Citrate is used to chelate the ferrous iron and prevent precipitation. The bicarbonate is used to maintain a pH (7.3) that favors a strong reducing environment created by additions of dithionite, a strong reductant. The higher pH of this extraction environment also extracts significantly less calcium and magnesium from dolomite and calcite (carbonate minerals) than does citric acid or sulfuric acid. The second extraction (that uses ammonium carbonate and potassium permanganate) is intended to oxidize the remaining uranium(IV) to uranium(VI) to form the strong uranyl carbonate complex. Work is under way to modify the procedure to use only CBD and to use citrate to extract the uranium(IV).

### Extractions by Complex Organic Chelating Agents

The strategy in selecting complex organic chelating agents to remove uranium from soil was based on the ability of microbial siderophores to solubilize metals in the environment. Siderophores are low-molecular-weight extracellular chelators produced by microbes that have very high binding constants for metal cations such as iron(III), uranium(IV), and thorium(IV). Enterobactin is a siderophore that can be produced relatively easily in the laboratory. Enterobactin and synthetic chemical analogs such as desferrioxamine B, Tiron (1,2-dihydroxy-3,5-benzenedisulfonic acid), acetyl hydroxamic acid, and catechol were tested as extraction media. Initial experiments with these organic chelating agents revealed that they dissolved uranium from finely ground  $UO_2$  very poorly. Enterobactin at pH 5.1 (1-mM level) extracted <2% of the uranium in 72 h. Desferrioxamine B (0.01 M at pH 6.1) and acetyl hydroxamic acid (0.03 M at pH 6.4) extracted <4% after 144 h. The best synthetic organic chelating agents appeared to be Tiron (0.012 M at pH 7) and catechol (0.012 M at pH 6.8), which removed between 6 and 8% of the uranium after 48 h. Although these chelators did enhance the aqueous dissolution of  $UO_2$  at neutral pH values, the rates were disappointing, and as a consequence, Tiron was the only one of this group used in the soil extraction studies.

Screening tests were used to compare the extraction effectiveness of two amino carboxylate chelators [1,2-diaminocyclohexanetetraacetic acid (CDTA) and diethylenetriaminepentaacetic acid (DTPA)], Tiron, and potassium carbonate. Carbonate and Tiron were the most effective in extracting uranium from the Fernald soils. Fifteen-hour CDTA or DTPA extraction tests revealed very poor extraction of uranium (<1%) from the incinerator soil. On the order of 45% of the uranium was extracted by these two chelators from the storage pad soil. Both Tiron and carbonate extracted ~25% from incinerator soil and ~60% from storage pad soil. Tiron has the same catechol functionality that natural siderophores do and forms highly stable negatively charged complexes with metals. This negative charge should aid in the solubilization and mobility of the uranium from soil matrices containing cation exchange sites. The extraction of uranium from the two Fernald soils varied as a function of Tiron concentration (15 to 20% more uranium was extracted with 0.1 M chelate compared with 0.01 M after 35 to 40 h). Kinetics of uranium removal were in two phases,

an initial rapid dissolution in the first 2 h (~80% of the total extracted) and a slow dissolution rate (~20% of the total extracted) in the remaining 35 to 38 h. The rate of Tiron dissolution and extraction of uranium from the two soils at Fernald is probably too slow to merit further investigation. For example, even after 2 h only 60 and 74% of the uranium, respectively, was removed from the storage pad soil when 0.01 M and 0.1 M Tiron was used (calculated residual uranium concentration of 209 and 135 mg/kg of soil), well above the 35 pCi/g (52 mg/kg) screening level. For the incinerator site soil, 373 and 280 mg/kg (calculated) remained in the soil after 2 h extraction with 0.01 and 0.1 M Tiron, respectively.

Tiron used in combination with 0.1 M dithionite solutions was considerably more effective in removing uranium from both Fernald soils. Dithionite is widely used in soil science to remove sesquioxide coatings from layer silicates (Jackson 1986). It reduces the ferric oxides to ferrous forms, which weakens the crystalline characteristics of the mineral phase, resulting in "reductive dissolution." The reducing properties of dithionite are probably applicable to uranium(VI) forms in soils [i.e., reduction of uranium(VI) to uranium(IV) results in dissolution of the uranium-bearing species]. Tiron extraction with dithionite was quite good in removing uranium from storage pad soil, >95% in 2 h. However, only ~54 and ~72% of uranium (0.01 and 0.1 M Tiron in 0.1 M dithionite, respectively) were removed from the incinerator site soil over the same period. Increasing the extraction time to 37 h did not appear to extract appreciably more uranium (~60 and ~89%, or calculated uranium concentrations of 234 and 66 mg/kg, respectively), indicating that pH adjustment or elevated temperatures may be required to lower the incinerator soil to levels <50 mg/kg by this method. ORNL also used dithionite as the reducing agent in their modified CBD procedure; however, they used heat (60 and 80°C) to activate the reaction and a higher pH (7.3 vs 6.0 to 6.6) to impose a stronger reducing environment. Similar adjustments to the LANL dithionite procedure will probably result in reduction of uranium levels to <50 mg/kg.

Although not thoroughly analyzed at this date, the dithionite extraction data from LANL indicate a linear correlation between the amount of uranium extracted and the quantities of iron and aluminum extracted. This correlation is independent of the Tiron concentration. Dithionite in the CBD procedure is responsible for near-quantitative removal of secondary forms of iron sesquioxide coatings on layer silicates [i.e., predominately goethite (FeOOH) and hematite (Fe<sub>2</sub>O<sub>3</sub>) minerals]. A strong correlation between the levels of iron and uranium extracted indicates that these minerals act as "sinks" or reaction sites for mobilized uranium in soil.

### Aqueous Biphasic Extractions

Aqueous biphasic extraction involves the selective partitioning of either solutes or colloid-size particles between two immiscible aqueous phases. The process is ideally suited for separation of fine-grained particulate from heavy textured soils such as those at Fernald [soils that generally contain >85% silt (<53 to 2 μm diam) and clay (<2 μm diam) size fractions]. Conventional soil-washing (water) processes are not applicable for these soils because of the presence of large amounts of silt and clay. Aqueous biphasic extractions can successfully separate particles ranging from 50 μm to 20 nm.

The ANL group, which used a model system of submicron UO<sub>2</sub> and kaolinite clay, were able to lower uranium concentrations of 200,000 mg/kg to <50 mg/kg by using a polyethylene glycol (PEG) and sodium carbonate extraction media. Work with the two Fernald soils revealed that the efficiency of uranium separation varied significantly between the two samples. For the storage pad soil, there

was little partitioning between the two phases, indicating that a significant portion of the uranium in this soil is sorbed onto soil particles. These data strongly imply that any physical separation technique would probably be ineffective for this soil. With the incinerator soil, uranium was enriched in the carbonate phase and depleted in the PEG phase; however, uranium concentrations in the soil partitioning to the PEG phase ranged from 111 to 137 mg/kg. This is appreciably greater than the 50 mg/kg screening level. Significant quantities of uranium were dissolved from both the Fernald storage pad and incinerator soils into the carbonate phase. To circumvent dissolution of uranium by carbonate, extractions with PEG and either sodium sulfate or sodium hexametaphosphate (rather than carbonate) were conducted; however, this did not have any effect on the extent of uranium dissolution from either soil. In another case, the incinerator soil was previously leached with sodium carbonate and then subjected to a PEG and sodium carbonate biphasic extraction. In this instance, uranium concentration in the soil partitioning to the PEG phase was unchanged but was reduced to 15 mg/kg in the carbonate phase, the reverse of that observed with unleached soil. Mineralogical characterization of the samples separated from the two phases is being conducted.

The effectiveness of aqueous biphasic extraction to separate uranium from contaminated soil is dependent on the degree to which uranium is present as discrete particulates. The principle of partitioning is based on the differences in the interactions of the two aqueous phases and surface chemistry of discrete particles. If uranium is adsorbed on the surfaces of soil particles or if discrete particulates of uranium are bound to larger soil particles, then the separation will be ineffective. To test the possibility that uranium in the incinerator soil sample was composed of small uranium particles aggregated to larger soil particles, a sample of the incinerator soil was ground to  $<5 \mu\text{m}$  diam and dispersed with sodium hexametaphosphate. Partitioning in a PEG/ $\text{Na}_2\text{CO}_3$  extraction showed uranium concentrations in the PEG phase similar to those of unground samples, indicating that size reduction had no effect.

Another interesting observation relating to the form of uranium in Fernald soils was made by the ANL group. Carbonate extraction typically extracts significant quantities of humic acid from soils and is, in fact, the classical procedure for removing humic acids from soils. Humic acids partition into the PEG phase. The ANL group found that partition coefficients of dissolved uranium were unaffected by the presence of humic acid, indicating soil humic acids do not contribute significantly to uranium mobility in these soils, at least under the conditions of the partition experiment.

Aqueous biphasic extraction is a very powerful technique for separating fine particles. Progress is being made in scaling-up the technique by using a countercurrent extraction column in which the soil can be extracted from the carbonate phase into the PEG phase. Its applicability for removing uranium from the Fernald soil is compromised to some extent because of the high dissolution of uranium by sodium carbonate. In a continuous countercurrent extraction process, the carbonate phase would be continuously recycled. Once the extraction system reaches steady state, the uranium concentration would build up to the solubility limit in the carbonate solution (probably about 5 mg/L) and then any further uranium dissolution from the soil would cease. This would then make it possible to recover the uranium from the soil in particulate form. Efforts to partition the residual uranium forms are under way. Aqueous biphasic extractions should also be an excellent method to separate  $\text{PuO}_2$  particulate from soils because  $\text{PuO}_2$  dissolution in carbonate is relatively limited.

## CONCLUSIONS AND FUTURE DIRECTIONS

Significant progress has been made in understanding the factors controlling the removal of uranium from the Fernald soils. This progress has developed quickly considering that many of the research facilities did not actively begin their studies until 6 months to 1 year ago. Research to date has presented a number of options by which the soils may be treated. The most effective leaching procedure involves a reductive dissolution process. Work at LANL and ORNL indicates that these reductive dissolution processes can be used to reduce concentrations of uranium in the Fernald soils from ~500 mg/kg to <50 mg/kg. Uranium can be chemically extracted from the storage pad soil much more easily than from the soil from near the incinerator site. Aqueous biphasic studies indicate that the uranium in the storage pad soil is probably chemically bonded to the layer silicates, whereas discrete particles of uranium are widespread in the soil from the incinerator site. Carbonate and citric acid extractions removed 80 to 90% of the uranium from the storage pad soil but only 60 to 70% from the incinerator site soil. Attrition scrubber tests of 15-min duration that used carbonate and citric acid media resulted in extraction efficiencies similar to those of 2 and 4 h duration in rotary or stirred reactors. These data indicate that, carbonate and citric acid might be applicable as extraction media for the storage pad soil but not for the incinerator soil if a screening level of near 50 mg/kg were adopted. Limited data were generated relating to the effectiveness of mineral acids. Data that are available indicate that sulfuric acid is a good extractant if the pH of the suspension is kept below 2. Both soils contain considerable carbonate minerals; thus, acidification of these soils will generate significant volumes of calcium and magnesium sulfates.

The choice of extraction media is dependent not only on the final concentration of uranium in the cleaned soil but on other factors such as characteristics of the cleaned soil as well as the types and amounts of effluents generated. The treatment methods required for uranium removal or direct disposal also determine the acceptability of an extraction media. The last, but certainly not the least significant determinant of media applicability, is the characteristics and volume of the final waste form requiring disposal.

Future work will center on the development of the most promising extraction processes by manipulating the controlling parameters to make them more efficient in terms of uranium removal and speed. In certain cases, refinements need to be made in terms of quantities and type of reagents required. For all of these processes, detailed information is needed that deals with the characteristics of the waste streams and cleaned soils. Phytotoxicity studies are ongoing at ORNL to determine the suitability of treated surface soils to be returned to place. Evidence indicates that a soils-reconditioning step will be required in conjunction with most uranium-extraction processes. As a final step, baseline equilibrium studies should be initiated to compare the simulated in situ environmental mobility of uranium from leached soils with that of unleached soils. These studies coupled with performance criteria to determine cleanup levels and cost estimates for the various extraction/removal technologies can be used to make a rational selection of the technology most applicable.

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## Part 1

**CARBONATE- AND CITRATE-BASED SELECTIVE LEACHING OF  
URANIUM FROM URANIUM-CONTAMINATED SOILS**

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ACRONYMS AND INITIALISMS

|        |  |
|--------|--|
| CBD    | citrate-bicarbonate-dithionate               |
| DOE    | U.S. Department of Energy                    |
| EPA    | U.S. Environmental Protection Agency         |
| ICP-MS | inductively coupled plasma-mass spectrometry |
| ORNL   | Oak Ridge National Laboratory                |
| SITE   | Superfund Innovative Technology Evaluation   |

## INTRODUCTION

The objective of this research is to use a washing/extraction process to selectively extract uranium from the soil without seriously degrading the soil's physicochemical characteristics or generating a secondary uranium waste form that is difficult to manage and/or dispose of. Several approaches can be taken to achieve this objective. They include (1) the use of conventional soil-washing practices, (2) the deployment of methods used to extract uranium in the mining and milling of uranium, or (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.

### SOIL WASHING

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 extracting solvent (Pollaert 1992)—basically 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 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 the remediation of soils containing highly water soluble constituents or soils containing very low concentrations of silt and/or clay particles (usually <15% smaller than 50  $\mu\text{m}$ ). As a consequence, soil washing that uses water as the only extraction media has very limited application. Such soil-washing systems characteristically are not effective in removing contaminants from heavily textured soils [soils containing high concentrations of clays (<2  $\mu\text{m}$ ) and silts (50 to 2  $\mu\text{m}$ )]. An appreciable proportion of the contaminants of these soils is often contained in the clay and silt fractions. This is generally the case for the Fernald uranium-contaminated soils. For example, initial soil characterization studies of samples collected at Fernald by Lee and Marsh (1992) indicated that the particle-size distribution in three of the six samples contained >66% clay and silt fractions and that these fractions contained ~50% of the uranium. Most important, all of the size fractions contained uranium concentrations >50 mg/kg, the proposed screening level for applicable cleanup technologies. In three of the six samples, the most highly contaminated fraction was the sand fraction (2000 to 53  $\mu\text{m}$  particle-size range), indicating that a simple physical separation processes would not be an effective cleanup technology. Thus, any successful soil-washing approach will probably depend on a chemical extraction process.

The U.S. Environmental Protection Agency (EPA) Superfund Innovative Technology Evaluation (SITE) program (EPA 1992) recognizes soil washing as a combination of physical and chemical treatments performed on soil in an aqueous solution. The program now includes soil-washing processes that use extraction media ranging from alkaline mixtures of ionic and nonionic surfactants and bioremediation agents that act as biosurfactants (Armiran and Wilde 1992) to acids that remove heavy metals from contaminated soils and solids (Paff 1992). Both of these processes represent a significant extension of existing soil-washing techniques currently used on a wide scale in Germany and the Netherlands.

## LEACHING PROCESSES USED IN MINING AND MILLING OF URANIUM

Uranium is characteristically leached from uranium ores by acid- and carbonate-based extractants. Alkaline leaching of uranium from various ores has an established history in the uranium industry that extends back to the mid-50s, when uranium milling operations were at peak production. Compared with acid leaching systems, however, only a few mills employed carbonate leaching, primarily because of the slower kinetics associated with the alkaline route. The use of sodium carbonate-sodium bicarbonate as the lixiviant was used in the Grand Junction Pilot Plant, operated by National Lead Company, Inc. (Beverly et al. 1957). The use of carbonate became attractive in cases in which the uranium grade was high or the carbonate or lime content was high. The alkaline leaching 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.

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 ( $<75\mu\text{m}$ ), sulfuric acid can remove 90 to 98% of the uranium. Because of strong acid's destructive action on layer silicates, acid leaching of this type is not appropriate for Fernald soils; however, acid leaching may be useful for removal of uranium from the Oak Ridge Y-12 Plant soils because the final product is a waste form.

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

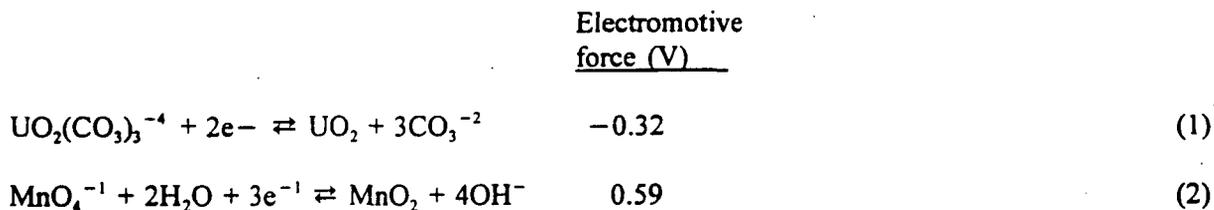
Just as in the uranium industry, when leaching uranium from its numerous mineral forms, a few prerequisites are important to achieve adequate extractions of uranium from either naturally occurring minerals or from contaminated soils. The various prerequisites in the necessary order can be summarized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

1. The uranium must be exposed to the solution so that solubilization can occur. Chemical chelating agents such as citrates can be used to remove oxide coatings, or physical attrition can be used to remove weathering products on soil surfaces.
2. Nonoxidized uranium must be oxidized to the hexavalent state to be effectively removed by either the carbonate or the sulfuric acid leaching process.

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

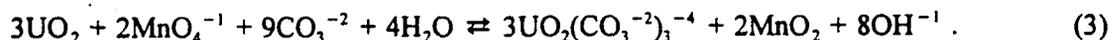
Work performed at Los Alamos (Morris et al. 1992) has shown that most of the uranium in the Fernald soils is present as hexavalent uranium; thus, once dissolution from the solid phase occurs, it is readily complexed by the carbonate anion. However, in cases in which uranium is present in soil as insoluble uranium(IV), it must first be oxidized to uranium(VI). An oxidant such as potassium permanganate will be necessary for this purpose. Only when the uranium is in the hexavalent state can it be complexed by an anion such as carbonate or sulfate and thus stabilized in solution.

Many sufficiently strong oxidants can be used to oxidize the tetravalent uranium in the soil. Permanganate salts are good oxidants in alkaline or acid solutions. Equations (1) and (2) show that the reduction of permanganate to be much more positive than the minimum formal potential necessary to reduce uranium in carbonate solutions.



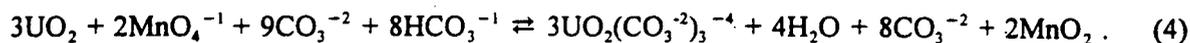
A 0.91-V electrical potential difference exists between the formal reduction potentials of permanganate and uranyl; this large difference again points to the usefulness of permanganate as an oxidant in this case. Additionally, permanganate plus carbonate has been shown to be a better extractor of uranium from some of the Oak Ridge Y-12 soils than are peroxide or hypochlorite plus carbonate (Al Mattus, Chemical Technology Division, Oak Ridge National Laboratory, unpublished data).

Equation (3) is the combination of Eqs. (1) and (2), making the appropriate material balances:



As shown in Eq. (3), hydroxides are produced and if unchecked can react with soluble uranium, resulting in the unwanted precipitation of the uranium from solution. Other sources of hydroxide in solution will function similarly to promote hydrolysis and premature precipitation if the pH is not controlled. The uranium may simply precipitate, as a result of hydrolysis, as  $(\text{UO}_2)_2\text{CO}_3(\text{OH})_2 \cdot \text{XH}_2\text{O}$ . If the pH were to rise as high as 12, uranium might also be precipitated as the diuranate, generally represented as  $\text{Na}_2\text{U}_2\text{O}_7$ . Many polymers of both precipitates also form.

Selected ratios of sodium bicarbonate, which functions as a weak acid, and sodium carbonate are used to stabilize the pH of the reaction and to avoid precipitation of uranium as the reaction becomes more alkaline as a consequence of the oxidation of  $\text{UO}_2$  to the uranyl form by permanganate. The overall equation when both carbonate and bicarbonate are present is as follows:



The general approach will be to emphasize the extraction of uranium from Fernald soils by carbonate-based extractions (because of their less destructive characteristics on the layer silicates of soils vs acid extractions). Also, because the initial citric acid leaching studies conducted by Lee and Marsh (1992) indicated high removal rates of uranium from some of the soils, leaching with citric acid, by itself and in conjunction with carbonate extractions, will also be investigated. General relationships such as the effect of carbonate and citrate concentrations, pH, the presence of oxidants such as  $\text{KMnO}_4$ , temperature, and extraction time will also be investigated.

## SELECTIVE DISSOLUTION TECHNIQUES IN SOIL SCIENCE

Selective dissolution techniques have been used in pedological and mineralogical studies for many years. These methods are necessary for independent determinations of a number of inorganic constituents in soils because it is often difficult to estimate or even recognize noncrystalline and paracrystalline free oxides or aluminosilicates in the presence of crystalline soil components (Jackson et al. 1986). Typical selective dissolution schemes generally employ "specific extractants" to sequentially remove various pedogenic compounds and their associated trace elements. Three to eight extractants are generally used in sequence; the earlier solutions are the least aggressive and the most specific, and subsequent extractants are progressively more destructive and less specific (Beckett 1989). Detailed descriptions of some of these selective dissolution schemes can be found in Jackson (1985), Jackson et al. (1986), and Beckett (1989). The review by Beckett provides detailed descriptions of a number of extractants that have been used in trace metal and soil pollution investigations.

Because most selective dissolution schemes have been proposed by a variety of authors, each scheme removes slightly different groups of compounds at each step in the process. Each scheme is operationally defined by the series of extractants utilized and/or the solid phases that can be dissolved by each extractant. Thus, there are no rigid rules defining the "best" scheme. The use of extractants should be tailored to the individual investigation. The interaction of the sample and extractant may result in changes in the composition of the extractant that in turn may affect the outcome of the extraction (e.g., strong acid-carbonate interactions). Therefore, physical and chemical properties of soil should be considered when choosing an extractant or group of extractants.

A number of solutions have been used to extract the "free oxides" from soils. Free oxides are defined as oxides and oxyhydroxides of iron, manganese, and aluminum and any trace elements associated with these compounds. The most commonly used extraction media for these compounds include sodium dithionite-citrate-bicarbonate (Mehra and Jackson 1960), sodium dithionite-citrate (Holmgren 1967), hydroxylamine-hydrochloride at variable pH (Chao 1972; Chao and Zhou 1983), and acid ammonium oxalate, under different conditions of illumination (Schwertmann 1964). All of these extraction procedures rely on the reduction of iron and/or manganese compounds. The reduced forms of these elements are more soluble than their oxidized species.

Dithionite extraction removes a combination of paracrystalline, crystalline, and organically complexed iron and manganese compounds as well as the trace elements associated with them.

Mehra and Jackson (1960) modified the dithionite-citrate procedure by adding sodium bicarbonate to buffer the solution at pH 7.8. This increased the efficacy of the extractant and prevented (1) the destruction of dithionite and (2) resultant formation of  $H_2S$  and reduced sulfur species. In addition, the extraction was carried out at 80 to 90° C, which increased the reaction kinetics. Holmgren (1967) demonstrated that maintaining a ratio of citrate to dithionite of at least 10:1 could make the bicarbonate buffer unnecessary. He also changed the extraction temperature, reducing it to room temperature and using the heat of reaction to aid the kinetics. This modification required longer extraction times and was slightly less effective than the higher-temperature procedure.

Hydroxylamine hydrochloride solutions extract manganese and iron compounds having both long- and short-range order (Chao 1972; Ross et al. 1985). The solution has a lower reducing potential than dithionite, and by adjusting the pH it can extract both iron and manganese compounds. Chao (1972) demonstrated that a 0.1 M solution at pH 2 selectively removed the manganese compounds from a number of different soils/sediments while removing only a small proportion of the iron species. In a later study, Chao and Zhou (1983) lowered the pH to 1 and adjusted the molarity of the hydroxylamine. These modifications resulted in removal of both manganese and iron species in a manner similar to that of acid ammonium oxalate.

Tamm (1922) was the first to propose the use of acid ammonium oxalate as an extractant for "amorphous" pedogenic compounds. Acid ammonium oxalate, when used in the dark, has been shown to extract iron (principally ferrihydrite) and various manganese compounds (Scwhertmann 1964). Under different lighting conditions (full light or ultraviolet), it will extract more crystalline iron compounds (i.e., goethite and hematite) (Beckett 1989). In addition, the acid ammonium oxalate procedure removes other crystalline iron compounds (magnetite) and affects trioctahedral phyllosilicates (Baril and Bitton 1967; Arshad et al. 1972; Pawluck 1972; Walker 1983). Other investigators (Biermans and Baert 1977; Kodama and Ross 1991) have used Tiron (4,5-dihydroxy-1,3-benzene-disulfonic acid) to selectively remove amorphous sesquioxides, poorly crystalline aluminosilicates, and hydrous oxides of silicon and aluminum from mineral surfaces.

Sequential extraction schemes for other soil components also exist. Chang and Jackson (1957) proposed a technique for partitioning soil phosphorus. Although this scheme was aimed primarily at assessing phosphorus contents in terms of plant nutrient supply, this technique could be utilized to partition other elements associated with the phosphorus compounds extracted. Soil carbonates have been selectively removed by using a variety of solutions (Jackson 1985; Rabenhorst and Wilding 1984). The standard extractant is a sodium acetate solution buffered at varying pH. The most common pH value is 5.0, but Rabenhorst and Wilding (1984) have demonstrated that lowering the pH to as low as 3 will speed the removal of these compounds without damaging the clay minerals in the sample. Sodium acetate buffered at pH 8.2 has also been used to measure exchangeable cations without dissolving carbonates (Bower et al. 1952). In addition to sodium acetate, dithionite has also been shown to be an efficient extractant of soil carbonate (Jackson 1985).

In addition to its use in the uranium industry, sodium carbonate has also been used in soil studies to dissolve gibbsite [ $Al(OH)_3$ ], allophane, and poorly ordered aluminosilicates. Iron compounds and phyllosilicates are not dissolved in this extractant. Sodium citrate solutions extract iron oxides and the trace metals associated with these compounds (Beckett 1989). Citrate solutions have also been used to remove aluminum coatings from soil minerals (Mehra and Jackson 1960).

Various techniques have been used to selectively dissolve silicates and other resistant minerals from soils following the removal of less-resistant species. Bernas (1968) and Nadkarni (1984) used a combination of hydrofluoric acid and aqua regia. The final solution contained boric acid, creating a fluoboric acid solution that stabilized the dissolved silica. Kiely and Jackson (1965) determined levels of quartz, feldspars, and mica in soils by using sodium pyrosulfate fusion. A combination of hydrofluoric and hydrochloric acids (Raman and Jackson 1965) has been used to concentrate rutile and anatase in soils. Various combinations of strong acids (e.g., nitric, sulfuric, and perchloric) have also been used to dissolve the resistant components of soils (Jackson 1985). Because the aim of the research reported herein is to selectively remove uranium from the Fernald soils without effecting the physicochemical properties of the soils appreciably, the use of nonselective, aggressive extractants should be avoided.

## METHODS AND MATERIALS

### SOILS AND SOIL PREPARATION

Three soils and a sediment were used in this study. Two of the soils were obtained from the U.S. Department of Energy (DOE) facility formerly called the Feed Materials Production Center at Fernald, Ohio, through the Uranium in Soils Integrated Demonstration (USID) program. The other soil was obtained from the Oak Ridge Y-12 Plant, which was used to dispose of spent oil in a landfarm operation in the mid 1970s. A sediment sampled from a storm sewer trap at the Y-12 Plant was also used in this study. Detailed descriptions of these soil/sediments and their preparation for leaching studies are presented in Francis et al. (1993).

### SOIL CHARACTERISTICS: CONCENTRATION AND DISTRIBUTION OF URANIUM

The objective of this report is to describe progress in the ongoing leaching studies of the Fernald and Y-12 soils/sediment. The concentrations and distribution of uranium among particle-size fractions of the four soils used in this study are presented in Francis et al. (1993).

The concentration of uranium (538 mg/kg) in the incinerator soil is considerably less than that measured in the top 3 in. of the soil cores (5469 mg/kg) taken from this area by Lee and Marsh (1992), indicating considerable dilution in uranium concentration of the bulk sample on removing soil for treatability studies. However, the whole soil or any of its particle-size fractions were not below the proposed treatability action level (35 pCi/g or 52  $\mu$ g of uranium per gram of soil), indicating that simple physical separation procedures will not generate a clean fraction from this soil.

The treatability sample taken from near the Plant 1 storage pad also contained much less total uranium (446 mg/kg) than that observed (4355 mg/kg) in the top 7 in. of the soil core taken at this site, again indicating considerable dilution in uranium concentration on taking bulk samples of soil. Here, an even greater difference in distribution and concentration of uranium within particle-size fractions of cored samples (Lee and Marsh 1992) and bulk treatability samples was observed than in the soil from the incinerator site. For example, Lee and Marsh (1992) observed that the sand fraction (2 to 0.053 mm) of the cored sample contained the highest uranium concentration

(15,900 mg/kg), constituting ~48% of the uranium in the sample. On the other hand, the clay fraction ( $<2 \mu\text{m}$ ) of the bulk treatability sample contained the highest uranium concentration (983 mg/kg), making up over 56% of the uranium contribution compared with ~15% for the core sample taken at the storage pad site. The difference in total concentration of uranium between the bulk treatability samples and the cored samples is not surprising (i.e., a dilution effect in the treatability samples as a consequence of taking a sample over a larger area and depth); however, the difference in distribution of uranium among particle size fractions is!

The concentrations and distributions of uranium among particle-size fractions of the Y-12 landfarm soil and storm sewer sediment are presented in Francis et al. (1993, Tables 4 and 5). The major difference between the samples from the Y-12 Plant and the Fernald samples is that concentrations of uranium in the Y-12 samples were lower (ranging from 150 to 200 mg/kg compared with 450 to 550 mg/kg in the Fernald samples).

## METHOD OF URANIUM ANALYSES

### Total Uranium in Soils

Neutron activation, wet digestion, and radiocounting procedures were used to analyze the Fernald samples (A-14 and B-16) for total uranium content. The results of these analyses are presented in Francis et al. (1993, Table 6). The neutron activation analyses were conducted by the Neutron Activation Analysis Laboratory at the Oak Ridge National Laboratory (ORNL) High Flux Isotope Reactor (Wade et al. 1992). In this method, count rates determined for the soil samples were compared with count rates for standards that contain known quantities of uranium. The neutron flux was approximately  $5 \times 10^{13}$  neutrons per square centimeter per second. Nuclear Data ACCUSPEC system software and two programs developed at ORNL were used to analyze the gamma spectra of the activated samples.

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

The radiocounting procedure was conducted in the Environmental Sciences Division according to the procedure outlined in Larsen et al. (1984). A conversion factor of 3.03 was used to convert  $^{238}\text{U}$  activity data from picoCuries per gram to milligrams per kilogram. The results from neutron activation and radiocounting are similar. Concentrations of uranium determined by the wet digestion method were ~12% lower than those determined by the neutron activation or radiocounting procedure.

## Uranium in Soil Leachates

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

## LEACHING DESIGNS

Two leaching designs were used: (1) leaching at a low solution-to-soil ratio (~1:1) in which paddle mixers were used for attrition and mixing and (2) leaching at a high solution-to-soil ratio (10:1) in which a rotary extractor was used for mixing. These leaching designs are described in greater detail in Francis et al. (1993).

### Low Solution-to-Soil Ratio Leaching

**Leaching media.** Most of the leaching tests conducted at the low-solution-soil ratio used a sodium carbonate solution (25 g  $\text{NaHCO}_3$  and 25 g  $\text{Na}_2\text{CO}_3$  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 ~10:1 and the carbonate concentration ranged from  $4.5 \times 10^{-2}$  to  $6.8 \times 10^{-2}$  M. Potassium permanganate ( $\text{KMnO}_4$ ) was added (0.02 g/g of soil) to oxidize uranium(IV) to the uranyl(VI) state to form the stable uranyl tricarbonate complex  $\text{Na}_4[\text{UO}_2(\text{CO}_3)_3]$ . Potassium permanganate is a very strong oxidant in this pH range.

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

### High Solution-to-Soil Ratio Leaching

**Leaching equipment and methods.** This leaching design was used to investigate the influence of carbonate and citrate concentrations at varying pH on removal of uranium from the four uranium contaminated soils. A rotary extractor rotating at 50 rpm was used to extract 20 g of soil in 200 mL of extractant. This is the type of extractor used to conduct the extraction procedure and toxicity characteristic leaching procedure tests to comply with Resource Conservation and Recovery (RCRA) regulations (Francis and Maskarenic 1986). After each extraction period, the pH of the soil suspension was recorded and the liquid phase was separated from the solid phase by centrifugation

in a swinging-bucket rotor (Damon/IEC model PR-J centrifuge with a No. 599 rotor) for 45 min at 2400 rpm.

**Carbonate leaching tests.** To test the influence of carbonate and pH on extraction of uranium from the four soils, a factorial-designed experiment that used three levels of total carbonate/bicarbonate (0.10, 0.25, and 0.50 M) at three pH levels (8, 9, and 10) and two replicates was conducted.

**Citric acid/citrate leaching tests.** To test the influence of citrate and pH on uranium extraction from the four soils, a factorial-designed experiment that used 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.

**Bisequential citric acid/carbonate leaching tests.** For the Fernald soils (A-14 and B-16), a bisequential leaching test was conducted by first leaching the soils with 0.1 M citric acid (20 g of soil in 200 mL of water) and then extracting twice with 200 mL of 0.1 M sodium carbonate/bicarbonate at pH 9. The effect of extraction time (0.5, 1, and 2 h) and use of  $\text{KMnO}_4$  (0.02 g/g of soil) in the carbonate extractions were investigated. All treatments were conducted in duplicate.

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

#### **Citrate-Bicarbonate-Dithionite (CBD) Leaching**

Because uranium in soil, regardless of its form, is capable of being coated by weathering products precipitated in the soil, the removal of such products must precede uranium solubilization. Soluble iron, aluminum, silica, and carbonates from atmospheric carbon dioxide may produce an amorphous, gel-like coating that will, with time, crystallize into iron and aluminum oxides and carbonates.

The removal of such coatings to expose uranium to the solution may be accomplished by physical means. In some cases, however, if the particle size of interest is too small, the benefits of attrition may be limited, especially in the presence of clays. If physical attrition alone is not sufficient, a chemical method may be employed alone or in combination with physical attrition to remove the hydrous oxides of iron, aluminum, and manganese, when present, and to dislodge colloidal silica associated with these metals.

The pretreatment method employs three reagents: trisodium citrate as a chelating agent, sodium bicarbonate for pH buffer control, and sodium dithionite as a strong reductant. The CBD method is used at near neutral pH and at an elevated temperature (50 to 80° C). In this method, 0.3 M sodium citrate buffer (1 to 3 mL/g of soil) was added to 200 g of soil. Sodium bicarbonate (20 g) was used to buffer the system. (Citric acid has also been used to adjust the pH downward.) When the mixed

soil slurry is at the required temperature and the pH is  $\sim 7.3$ , sodium dithionite salt is added in increments to reduce Fe(III) to Fe(II), a reaction that is very rapid, only requiring between 15 to 30 min to complete. Sodium dithionite was used in excess in these scoping studies, generally at 150 kg/t, probably far more than is needed. Near-term studies this year will concentrate on the use of a reducing reagent.

The reaction is exothermic and some sulfur dioxide leaves the hot solution, despite the high aqueous solubility of this gas. Once the reaction was complete, the hot slurry was quickly filtered, keeping the solution temperature above 50°C to avoid the loss of iron or uranium from coadsorption or occlusion in various precipitates formed during cooling. The solids were then washed once with a carbonate-based solution. The solids were remixed in a separate vessel at 50° C and then refiltered to remove remaining traces of uranium and iron prior to carbonate leaching of this pretreated material.

### Attrition Scrubbing Tests

The principal interest in the use of attrition scrubbing is to increase the rate of uranium removal from soils. An attrition scrubber, through its bidirectional blending action, forces the soil particles to collide into each other. Thus, abrasion of the soil particles occurs, particularly in slurries having between 50 to 70% solids. In principal, the abrasion causes the removal of weathering products (i.e., Fe and Mn oxides) on soil surfaces that might inhibit contact of the leaching media and uranium. By increasing the degree of reaction (or reactivity) between the contaminated soil particles and the leachant in this manner, the rate of uranium removal should increase.

A Denver bench-top attrition scrubber (Model No. 533000) was used in this investigation. This scrubber is a scaled-down version of the pilot-scale models. The data obtained by the laboratory unit can be directly factored into pilot-scale as well as full-scale attrition units.

For the attrition tests, 500 g of air-dried  $<4.75$ -mm soil and 400 mL of leachant were placed in the mixing chamber. These initial tests were performed at room temperature. Attrition times of 3, 5, and 15 min were used to investigate the dependence of uranium removal on length of attrition at a setting of 2000 rpm. The following four leachants were used in this study: (1) distilled water, (2) 0.50 M total carbonate solution as 0.16 M  $\text{Na}_2\text{CO}_3$ /0.34 M  $\text{NaHCO}_3$ , (3) 3.13 M citric acid solution (equivalent on a gram per gram basis to that used in the 4-h shaking experiment in which 200 mL of 0.25 M of citric acid was used to leach 20 g of soil, 0.48 g of citric acid per gram of soil), and (4) 0.84 M total carbonate solution as 0.52 M  $(\text{NH}_4)_2\text{CO}_3$ /0.32 M  $\text{NH}_4\text{HCO}_3$ . One molar  $\text{H}_2\text{SO}_4$  and 2.5 M  $\text{H}_2\text{SO}_4$  were also used but only at a 15-min attrition time. A combination glass electrode was used to measure the pH of the soil mixture immediately following the attrition episode. A portion of this soil mixture was poured into 250 mL Nalgene bottles and centrifuged at 2000 rpm for 30 min. The supernatant was then collected and acidified with concentrated  $\text{HNO}_3$  to  $\text{pH} \leq 2$ . These acidified supernatants were analyzed for uranium by ICP-MS and for metals by ICP spectrometry.

Particle-size analysis by fractionation techniques (Jackson 1985) was then performed on all soil material that underwent 15-min attrition scrubbing. This analysis was done to document whether the particle-size distribution was affected by the attrition scrubbing and/or leachant for the worst case. The soil material was initially wet-sieved through a nested arrangement of sieves, consisting of 2-,

1.18-, and 0.075-mm sieves. The <0.075-mm fraction was further separated into 0.075- to 0.020-mm and <0.020-mm fractions by elutriation (Follmer and Beavers 1973). Particle-size distribution for the four coarsest fractions was computed on an oven-dry basis. The percentage of the <0.020-mm fraction was calculated by computing the difference.

## RESULTS

### LOW SOLUTION-TO-SOIL RATIO LEACHING

The leaching of uranium from the incinerator soil appears to be more dependent on time and temperature than leaching of uranium from soil near the storage pad area (Table 1.1). For example, increasing the extraction time from 4 to 23 h increased the fraction of uranium leached from the incinerator soil 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 increased uranium removed 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. Pretreatment, by pulverizing and milling the samples, coupled with a long leaching time (23 h) and an elevated temperature (60°C) did not release additional uranium. High leaching efficiencies (>85% removal rates) were observed with all treatments in the case of the storage pad soil.

**Table 1.1. Sodium carbonate leaching of Fernald soils as influenced by temperature and extraction time<sup>a</sup>**

| Treatment           | Waste incinerator soil <sup>b</sup> | Storage pad soil <sup>c</sup> |
|---------------------|-------------------------------------|-------------------------------|
| Temperature, °C     |                                     |                               |
| 22                  | 180                                 | 63                            |
| 40                  | 73                                  | 42                            |
| 60                  | 97                                  | 42                            |
| Extraction times, h |                                     |                               |
| 2                   | 154                                 | 48                            |
| 4                   | 161                                 | 55                            |
| 6                   | 60                                  | 48                            |
| 23                  | 90                                  | 45                            |

<sup>a</sup>Main effects of a three-level temperature and four-level extraction time factorial, no replication (Francis et al. 1993).

<sup>b</sup>Pretreatment level was 470 mg/kg.

<sup>c</sup>Pretreatment level was 387 mg/kg.

## HIGH SOLUTION-TO-SOIL RATIO LEACHING

### Carbonate Leaching Tests

The Fernald storage pad soil showed the highest and the Y-12 storm sewer sediment the lowest removal rates of uranium by carbonate extraction (Fig. 1.1). Removal ranged between 75 and 87% for the Fernald storage pad soil, and there appeared to be little influence with respect to total bicarbonate and carbonate concentrations or pH (see tabular data in Francis et al. 1993). Leaching efficiencies of uranium from the Fernald incinerator soil and the Y-12 landfarm soils were approximately the same (generally from 40 to 75%). However, for these soils, increasing pH and increasing total bicarbonate and carbonate appeared to improve extraction effectiveness. Very small quantities of uranium were extracted from the Y-12 storm sewer sediment by carbonate (generally <5%), indicating the presence of a very-leach-resistant uranium form in this material.

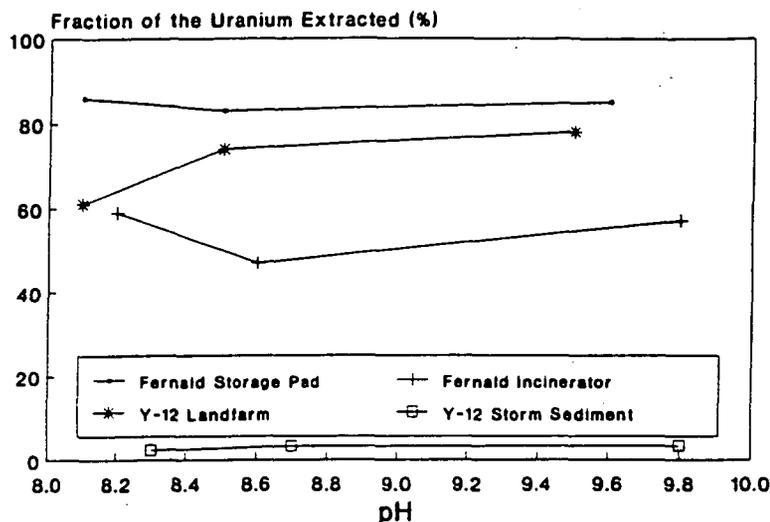


Fig. 1.1. 0.25 M sodium carbonate extraction of uranium.

The basic principle in the use of carbonate leaching to remove uranium from uranium-contaminated soils is the formation of the water-soluble stable uranyl tricarbonate complex  $X_4[UO_2(CO_3)_3]$ , where X is the sodium or ammonium cation. Concentrations of  $CO_3^{2-}$  in the carbonate leaching tests (as determined by the pH of the resulting suspension after the 4-h extraction period) ranged from  $\sim 2.0 \times 10^{-4}$  to 0.1 M but appeared to have little influence in the effectiveness of extracting uranium (Francis et al. 1993, Fig. 12).

### Citric Acid/Citrate Leaching Tests

Leaching with citric acid/citrate was limited to the Fernald soils. Initial leaching studies conducted by Lee and Marsh (1992) revealed that as much as 75% of the uranium in the soil collected near the Plant 1 storage pad could be removed in 2 h by using 0.1 M citric acid at a solution-to-soil ratio of 8. The current study involved a complete factorial design that used three levels of citrate (0.10, 0.25, and 0.5 M) at four pH levels (unadjusted citric acid and pH values of 5, 7, and 9 obtained by neutralizing citric acid with 50% NaOH). These were 4-h tests conducted at liquid-to-soil ratios of 10:1 (200 mL of extractant and 20 g of soil) in a rotary extractor (and duplicate samples for each treatment). Extraction effectiveness was determined by analyzing the quantities of uranium extracted in the supernatants and was expressed as a fraction of that initially

analyzed in the soil. The basic objective was to determine the influence of pH and concentration of citrate on removal of uranium from the two soils.

The extraction of uranium from the two Fernald soils was strongly influenced by the pH of the citrate extractions (Fig. 1.2). Unadjusted citric acid was used to extract an average of ~99 and ~68% of uranium from the storage pad and incinerator soil, respectively. The higher concentration of citrate (0.5 M compared with 0.1 M) significantly increased the extraction of uranium from Fernald storage pad soil ( $P < 0.01$ ) but not from incinerator soil. Extraction pH was the most important of the two variables (pH and concentration of citrate).

The efficiency of uranium extraction is dependent on the stability of the complexes formed between citric acid and the uranyl ion. In the pH range of 2 to 4, the uranyl ion is in equilibrium with mononuclear and binuclear citrate chelates, with a preponderance of

binuclear complexes (Rajan and Martell 1965). Above pH 4, the binuclear chelates tend to react with hydroxide ions and polymerize into larger complex molecules. These larger molecules tend to become less water-soluble, and as the pH of the suspension is increased, the molecules probably bond to the hydroxy groups of clay surfaces and become sorbed on clays. Proposed 1:1 formation constants of uranyl citrate chelates are  $10^{-2.79}$ ,  $10^{-4.30}$ , and  $10^{-5.35}$  for the  $K_1$ ,  $K_2$ , and  $K_3$  dissociation constants, respectively (Rajan and Martell 1965). Analyses of the leaching efficiency for uranium in the pH ranges of  $<2.79$ , 2.79 to 4.30, 4.3 to 5.35, and  $>5.35$  revealed that significantly higher percentages ( $P < 0.01$ ) of uranium were leached from both soils at pH values  $<2.79$  and 2.79 to 4.30 than at pH values  $>5.35$ . Citric acid also forms stable water-soluble complexes with iron and aluminum; thus, the enhanced extraction of uranium at the lower pH values is also likely because of the removal of amorphous iron and aluminum sesquioxides from soil surfaces, thus exposing uranium compounds to citric acid extraction. In this respect, the citric acid extraction is similar to the CBD extraction, which was shown to be very effective in the removal of uranium.

### Bisequential Citric Acid/Carbonate Leaching Tests

The bisequential citric acid/carbonate leaching tests were conducted by first leaching with 0.1 M citric acid (20 g of soil in 200 mL of extractant) followed with two leachings (200 mL each) with 0.1 M sodium carbonate/bicarbonate pH 9 buffer solutions. The effect of extraction time was investigated (i.e., each of the three extractions were carried out at 0.5, 1, and 2 h). The influence of adding  $KMnO_4$  (0.02 g/g of soil) to oxidize uranium(IV) to uranium(VI) in the carbonate extractions was investigated. All treatments were conducted in duplicate at a liquid-to-soil ratio of 10:1 on a rotary extractor rotating at 50 rpm (see Francis et al. 1993).

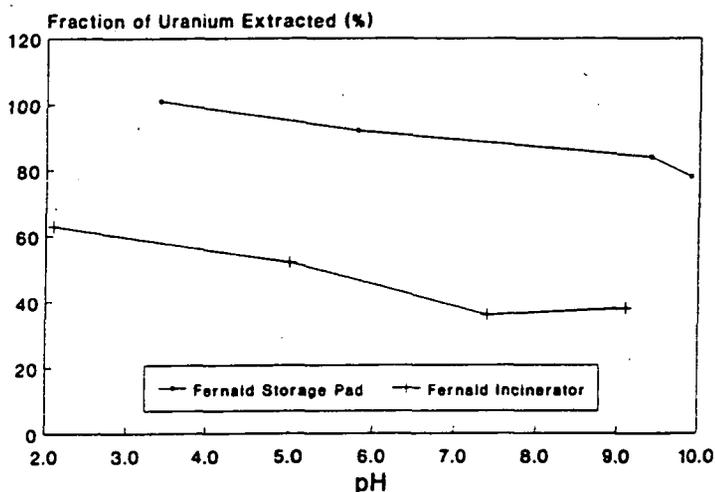


Fig. 1.2. 0.25 M citrate solutions extraction of uranium.

The leached residual from the 2-h extraction of the incinerator soil was analyzed for total uranium by neutron activation procedures (Wade et al. 1992). To determine the effectiveness of extraction with respect to the soil particle size, the leached residual was fractionated into sand, silt, and clay fractions, and the concentration of uranium was determined in each of these size fractions. Uranium appeared to be extracted more effectively from the smaller size fractions of soil. For example, over 80% of the uranium in the clay fraction was removed by this extraction process and only 60 to 70% was leached from the sand size fractions (2-mm to 53- $\mu\text{m}$  fraction). Also, with respect to the use of  $\text{KMnO}_4$  as an oxidant to convert uranium(IV) to (VI), smaller differences in the fraction of uranium leached were noted in the clay fraction compared with the silt and sand fractions, indicating that the  $\text{KMnO}_4$  was more effective in converting uranium(IV) to uranium(VI) in the larger particle ranges. It could also be implied that there were higher levels of uranium(IV) in the larger particle ranges than the smaller particle ranges. Such a relationship is entirely probable because uranium particulate deposited to the soil in particle ranges  $< 2 \mu\text{m}$  would have a significantly larger surface area exposed and be more subject to oxidation reactions than would  $> 53\text{-}\mu\text{m}$  uranium particulate.

### Mineral Acid Leaching Tests

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

In the soil suspensions acidified to pH 2 with ultrapure nitric acid before extraction,  $22.3 \pm 6.1\%$  of the uranium was extracted after 4 h (final pH of 5.6). In the deionized-distilled water extractions (pH  $8.11 \pm 0.01$ ),  $6.29 \pm 2.3\%$  of the uranium was removed after 4 h. In another experiment, quantities of nitric and sulfuric acid were added to the storage pad soil in 15-min increments over a 4-h extraction time in an attempt to keep the pH of the soil suspension below 2. In one case, 4.9 meq of nitric acid per gram of soil was added (final pH was 3.7). In another case, 6.4 meq of nitric acid per gram of soil was added (final pH was 2.4). In both cases, the soil acted as a strong buffer because of the high levels of calcite and dolomite in the soil. Additions of sulfuric acid were more successful in maintaining a low pH. In this case, 7.9 meq of sulfuric acid per gram of soil resulted in a soil pH of 1.7 after a 4-h extraction. In a rough sense, this would be equivalent to 55 gal of concentrated sulfuric acid per ton of soil and represents dissolution of calcite and dolomite with the subsequent production of calcium and magnesium sulfates. Much greater quantities of uranium were extracted as the pH of the suspensions became lower (Fig. 1.3).

In the pH range of 3.0 to 5.0, extractions with citric acid generally removed 80 to 90% of the uranium from this soil under the same extraction conditions, whereas extractions with nitric acid (an acid that does not form strong complexes with uranium) removed significantly less. Thus, these data strongly support the hypotheses that the extraction of uranium from soils by citric acid is not the result of a simple acidification relationship but is probably the result of citric acid's ability to chelate strongly with uranium as well as to remove coatings of amorphous iron and aluminum sesquioxides from solid-phase uranium particulates, thus enhancing the dissolution and extraction of uranium.

## CBD LEACHING

As discussed in the Introduction, the CBD selective extraction procedure is very effective in the selective dissolution of "free oxides" from soils. Dithionite has a very high oxidation potential in alkaline solution; thus, it functions as a very strong chemical reductant. The potential is strongly reducing and has been measured to be  $-0.7$  V vs the hydrogen electrode at pH 7.3 (Jackson 1985). Citrate is used to chelate and remove iron(II) from the suspension. Uranium(IV) may be complexed and removed by citrate in a similar manner. However, information in the literature on uranium(IV) is limited; rather, most studies are based on chelation of uranium(VI) (Rajana and Martell 1965; Adin et al. 1970).

The beneficial effect of CBD pretreatment when used in conjunction with ammonium carbonate leaching was investigated. The effects of CBD pretreatment and ammonium carbonate-permanganate leaching of both soils (storage pad and incinerator) at  $50$  °C for 2 h are shown by stage in Table 1.2. Test 1 involves a 2-h leaching with ammonium carbonate-permanganate alone. Test 2 involves the CBD pretreatment [at which time the residuals are analyzed for uranium (332 mg/kg), a value slightly higher than the residuals after test 1 with ammonium carbonate-permanganate leach].

The residuals from test 2 are then leached (test 3) with the same ammonium carbonate-permanganate leach used in test 1, resulting in a much lower uranium concentration (42 mg/kg). A similar sequence of tests (4, 5, and 6) was used to evaluate the influence of the CBD pretreatment on the extraction of uranium from the storage pad soil. The results presented in Table 2 are typical of the effect that was observed when the CBD pretreatment was used in conjunction with ammonium carbonate leaching. These data strongly support the hypothesis that the CBD pretreatment step removes coatings from soil surfaces that impede uranium removal by carbonate extractions.

These data also indicate that the CBD pretreatment leaching was not as effective as a single leaching with ammonium carbonate (with  $\text{KMnO}_4$ ); however, the same ammonium carbonate leaching following the CBD pretreatment was very effective for both soils. The inability of the CBD pretreatment to extract more uranium may be twofold:

1. Uranium(IV) is very easily hydrolyzed and will precipitate from solution as a hydrated hydroxide if a sufficiently large amount of complexing agent, such as citrate, is not present to stabilize it in solution. Carbonate from the soil is not able to stabilize uranium(IV) as it can for uranium(VI); thus, the solubilization of uranium is primarily dependent on citrate. Citrate's capacity to complex uranium is being compromised by citrate's tendency to form soluble

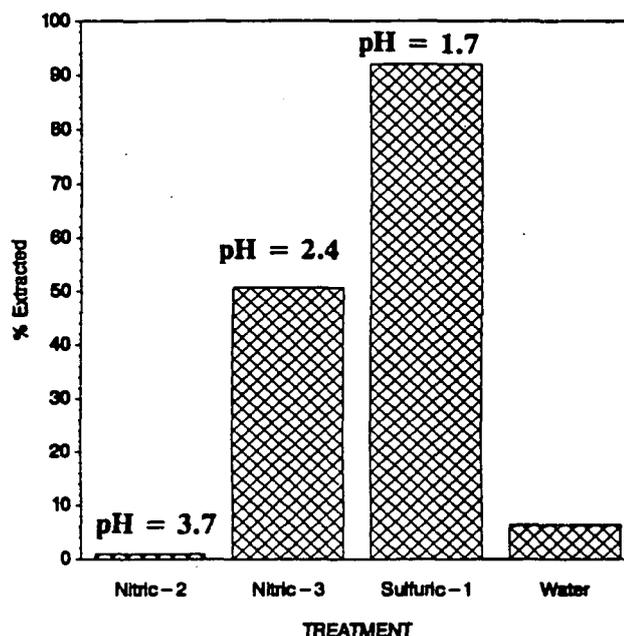


Fig. 1.3. Extraction of uranium from the Fernald storage pad soil by mineral acids.

**Table 1.2. Influence of the citrate-bicarbonate-dithionite pretreatment step on extraction of uranium from Fernald soils with ammonium carbonate**

| Test No. | Fernald soil             | Stage | Operation  | Uranium in residuals |
|----------|--------------------------|-------|--|----------------------|
| 1        | Incinerator <sup>a</sup> | 1     | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> & KMnO <sub>4</sub> only | 277                  |
| 2        |                          | 2     | Citrate-bicarbonate-dithionite   | 332                  |
| 3        |                          | 3     | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> & KMnO <sub>4</sub>      | 42                   |
| 4        | Storage pad <sup>b</sup> | 1     | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> & KMnO <sub>4</sub> only | 100                  |
| 5        |                          | 2     | Citrate-bicarbonate-dithionite   | 123                  |
| 6        |                          | 3     | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> & KMnO <sub>4</sub>      | 34                   |

<sup>a</sup>Pretreatment uranium level was 538 mg/kg.

<sup>b</sup>Pretreatment uranium level was 446 mg/kg.

complexes with other soil components, namely, iron and aluminum from dissolution of sesquioxides and calcium and magnesium from partial dissolution of carbonates. Thus, uranium(IV) probably precipitates as a hydrated hydroxide onto soil surfaces and is not completely extracted.

- Uranium may be removed from the solution phase as a consequence of entrainment processes (adsorption/occlusion) during the possible precipitation of calcium sulfate. Possible precipitation of sulfates results on cooling of the leachate from 80°C to room temperature. Sulfates are generated as a result of the oxidation of the dithionite, and calcium and magnesium may result from partial dissolution of carbonates by the CBD procedure (however, not nearly to the extent as with mineral acid leaching at pH values <2). Concentrations of calcium in the CBD filtrates have ranged from 0.3 to 1.3 g/L. The high levels of calcium in the filtrates may result from carbonate dissolution (principally calcite) as indicated by the fact that the procedure has been used to selectively remove calcite from dolomite in soils (Peterson et al. 1966). However, in this instance the pH of the procedure was modified to 5.85.

In some tests (data not presented), the CBD pretreatment by itself was sufficient to remove uranium concentrations to levels as low as 37 mg/kg from the storage pad soil. Further work is being continued with the CBD procedure: higher liquid-to-solid ratios of citrate are being used to allow for more effective complexing of uranium(IV) with citrate, and the procedure is being combined with attrition scrubbing to increase dissolution rates. The CBD dissolution principle (reducing environment and the presence of a chelator) is similar to the action plan taken by the Los Alamos research group, and the procedure promises to be a very effective extractor of uranium from soils containing residual forms of uranium not effectively removed by carbonate extractions alone.

## ATTRITION SCRUBBING TESTS

The major objective of the attrition scrubbing tests was to investigate the potential of attrition scrubbing in combination with chemical extractants (i.e., sodium and ammonium carbonate and citric and sulfuric acids) to increase the rates of uranium extraction from soils. Previous batch-type extraction tests (in which carbonate and citric acid were the extractants) revealed that residence times on the order to 2 to 4 h would probably be necessary to remove uranium to acceptable technology screening levels (50 mg/kg of soil). The secondary objectives were to determine (1) the influence attrition scrubbing had on particle-size distribution and uranium extraction and (2) the distribution of uranium among particle sizes of soils after different levels of scrubbing (i.e., influence of time and temperature on attrition scrubbing).

The work has been divided into two phases: (1) determining the uranium extraction effectiveness by measuring the uranium concentration in the resulting supernatant after scrubbing and (2) determining the influence of attrition scrubbing on particle-size distribution and uranium concentration in the resulting size fractions. The first phase has been completed. The uranium extraction efficiency was calculated by computing the difference (i.e., that measured in the supernatant after centrifugation subtracted from that measured in the original sample). Consequently, these data should be taken as estimates of extraction. The final effectiveness of extraction will be determined after uranium analyses (by neutron activation) of the soil fractions have been completed. Because of the unusual amount of down time for the Oak Ridge High Flux Isotope Reactor, these analyses have not been completed.

### Influence on Extraction of Uranium

Though no clear trend among the different attrition times was evident, these results showed that attrition scrubbing for 3 to 15 min was equally effective in extracting uranium as the batch-type extractions for 4 h. The one exception may be the extraction of uranium from the storage pad soil. In this case, only 80% of the uranium was leached in 3- and 5-min extraction times with the attrition scrubber compared with quantitative removal (>95%) by 4-h citric acid batch-type extraction.

Results showing the percentage of uranium leached from all the attrition scrubbing tests for both Fernald soils are presented in Table 1.3. Water is not an effective leachant for uranium for either soil, with a maximum extraction of only 6% of the total soil uranium. Citric acid removed ~50 to 60% of the uranium from the incinerator soil and achieved even higher extraction efficiencies (~70 to 80%) with the storage pad soil. Based on the influence of pH on the extraction of uranium by citric acid (see Fig. 1.2), one might have expected greater extraction efficiencies from the incinerator soil than from the storage pad soil because the pH measured immediately after the attrition scrubbing was 1.6 and 2.4, respectively. In this case, the nature of the contamination (physicochemical characteristics of the uranium source term in the soils) appeared to mediate the extraction efficiency of the citric acid (i.e., if the source term for uranium were the same in the two soils, one would have expected similar or better extraction efficiencies at the lower acidity).

Sulfuric acid (at both 1 M and 2.5 M concentrations) was effective in the removal of uranium from the incinerator soil (77 and 89%, respectively); however, sulfuric acid (at the same concentrations) was ineffective in removing uranium from storage pad soil (7 and 18%,

**Table 1.3. Comparison of the uranium leached by attrition scrubbing for 3, 5, and 15 min by various leachants for both Fernald soils**

| Leachant  | Attrition time (min) | Percentage uranium leached    |                               |
|---|----------------------|-------------------------------|-------------------------------|
|   |                      | Incinerator soil <sup>a</sup> | Storage pad soil <sup>b</sup> |
| Water   | 3                    | <1                            | 5                             |
|   | 5                    | <1                            | 6                             |
|   | 15                   | 1                             | 5                             |
| Citric acid                                     | 3                    | 53                            | 81                            |
|   | 5                    | 47                            | 69                            |
|   | 15                   | 65                            | NR <sup>c</sup>               |
| 1 M H <sub>2</sub> SO <sub>4</sub>              | 15                   | 77 <sup>d</sup>               | 7 <sup>d</sup>                |
| 2.5 M H <sub>2</sub> SO <sub>4</sub>            | 15                   | 89 <sup>d</sup>               | 18 <sup>d</sup>               |
| Na <sub>2</sub> CO <sub>3</sub>                 | 3                    | 63                            | 84                            |
|   | 5                    | 37                            | 83                            |
|   | 15                   | 62                            | 81                            |
| (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> | 3                    | 43                            | 64                            |
|   | 5                    | 43                            | NR                            |
|   | 15                   | 40                            | 55                            |

<sup>a</sup>Pretreatment uranium level was 538 mg/kg.

<sup>b</sup>Pretreatment uranium level was 446 mg/kg.

<sup>c</sup>Not reported.

<sup>d</sup>Average of two replicates.

respectively). The disparity between these extraction efficiencies is probably the result of the greater carbonate content of storage pad soil. The higher levels of carbonate would tend to neutralize the acid and buffer the extraction pH above 2, the preferred pH for uranium removal by sulfuric acid. The pH measurements, taken just after the attrition scrubbing, support this belief: pH values were  $\leq 2$  for the incinerator soil and between 2.7 and 4.7 for storage pad soil.

For carbonate extractions, sodium carbonate/bicarbonate extracted greater levels of uranium than did ammonium carbonate/bicarbonate for both Fernald soils. These results are unfortunate because removal of the soluble uranium from the wastewater and recovery of the ammonium carbonate by steam stripping is an effective method of waste minimization. These two carbonate leachants also extracted greater levels of uranium from the storage pad soil than from the incinerator soil. Again, differences in the physicochemical characteristics of the uranium form in the two soils is the probable reason for the difference in extraction efficiency.

Overall, the results of the attrition scrubbing tests showed that the sodium carbonate/bicarbonate leachate was the preferred selective extractant of uranium for the storage pad soil. This leachant extracted the highest levels of uranium without extracting large amounts of additional elements. Sulfuric acid extracted the greatest levels of uranium for the incinerator soil, but it also extracted the greatest levels of Al, Si, Ca, Mg, Fe, Mn, and P. These results indicate that the preferred leachant for the selective extraction of uranium from these two Fernald soils is sodium carbonate/bicarbonate. These extractions probably will not achieve uranium reduction to the proposed screening level of 50 mg/kg of soil by themselves. A postextraction physical separation process (i.e., based on particle-size distribution or particle density) may be necessary to segregate fractions containing unacceptable levels of uranium from those fractions that contain acceptable levels of uranium.

### **Influence on Particle-Size Distribution**

Attrition scrubbing the Fernald incinerator soil did not appear to influence the particle-size distribution (Fig. 1.4). However, a net gain of  $\leq 0.020$ -mm particles at the expense of the 0.075- to 0.020-mm fraction was observed when the Fernald storage pad soil was scrubbed for 15 min (Fig. 1.5). This net gain of  $\leq 0.020$ -mm particles may have resulted from the physical degradation of carbonate minerals, particularly dolomite, in this soil. On a whole-soil basis by weight, both soils have similar calcite contents (20% for incinerator soil and 15% for the storage pad soil); however, the incinerator soil contains only 2% dolomite, whereas the storage pad soil contains 19% dolomite (Lee et al. 1993).

Scrubbing with water or sodium carbonate did not appear to influence particle-size distribution (compared with that without attrition scrubbing). However, there appeared to be a pronounced influence in the distribution of 0.075- to 0.020-mm and  $< 0.020$ -mm size fractions when ammonium carbonate is used. The reason for this apparent change is unknown, and further work is in progress to determine if the change in distribution is real. This anomaly and the influence of using citric and sulfuric acids as extraction media in attrition scrubbing tests on particle-size distributions (and their uranium concentrations) of the Fernald soils are being investigated.

### **SUMMARY AND CONCLUSIONS**

Three soils and a sediment contaminated with uranium were used in this study to determine the effectiveness of carbonate- and citrate-based leaching solutions to decontaminate or remove uranium from contaminated soils.

Carbonate extractions (total carbonate/bicarbonate concentrations ranging from 0.1 to 0.5 M, over pH ranges of  $\sim 8$  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 from the Fernald incinerator and the Y-12 landfarm soils (extraction efficiencies ranged from  $\sim 40$  to  $\sim 75\%$ , respectively). Very small amounts of uranium could be extracted ( $< 8\%$ ) from the storm sewer sediment by means of sodium carbonate extraction. Increasing the extraction temperature from 22 to 40°C for the Fernald waste incinerator soil increased the fraction of uranium leached from  $\sim 40$  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 was as effective as extractions at low solution-to-soil ratios, indicating attrition

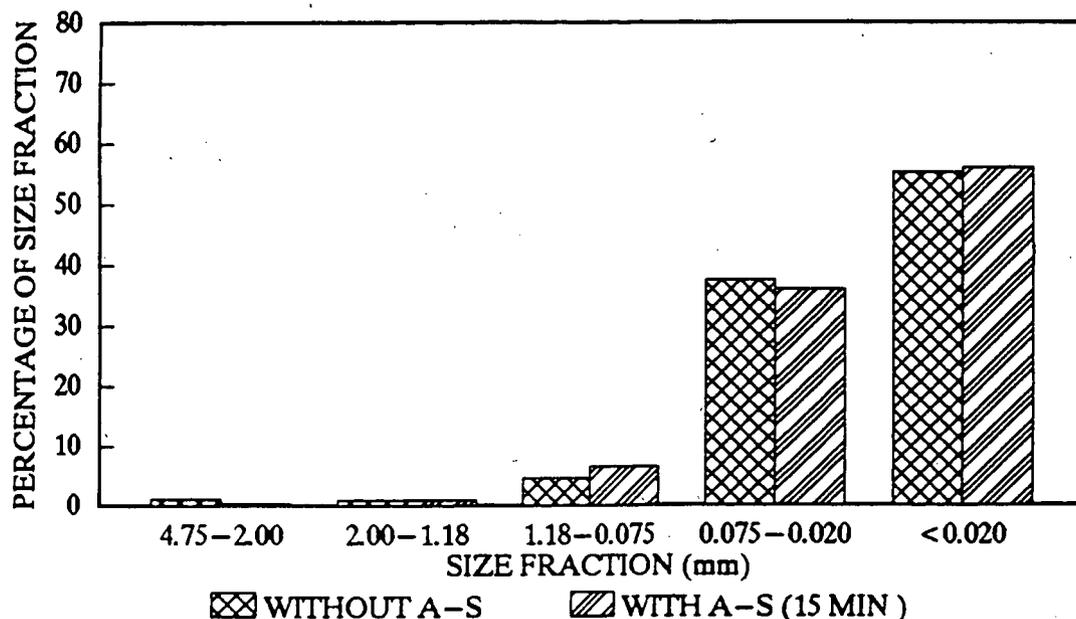


Fig. 1.4. Influence of attrition scrubbing (water) on particle-size distribution of the Fernald incinerator site soil.

by the paddle mixer was not significantly different from that provided in a rotary extractor. Also, pretreatments such as milling or pulverizing did not appear to increase extraction efficiency when carbonate extractions were carried out at elevated temperatures (60°C) or over long extraction times (23 h). Adding  $\text{KMnO}_4$  (to oxidize tetravalent uranium forms to hexavalent forms for extraction as the carbonate complex) appeared to increase extraction efficiency from the Fernald incinerator soil but not the Fernald storage pad soil. Also, additions of  $\text{KMnO}_4$  to the carbonate extractions appeared to be more effective in removing uranium from the silt and sand size fractions ( $>2\mu\text{m}$ ) of soil than from clay size fractions ( $<2\mu\text{m}$ ).

Citric acid also proved to be a very good uranium extractant. 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 by two carbonate extractions containing  $\text{KMnO}_4$  (three sequential 0.5-h extractions) removed  $>80\%$  of the uranium, indicating that a combination of citric acid and carbonate leaching procedures may be a better 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 the result of 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 the result of its ability to chelate strongly with uranium as well as to remove coatings of amorphous iron and aluminum sesquioxides from solid-phase uranium particulates, thus, enhancing the dissolution and extraction of uranium.

The most effective leaching ( $>90\%$  from both Fernald soils) was obtained with CBD extraction, which is designed to remove iron/aluminum sesquioxides from mineral surfaces. This extraction procedure uses sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) with a sodium citrate/carbonate buffer (pH ~7.3) at

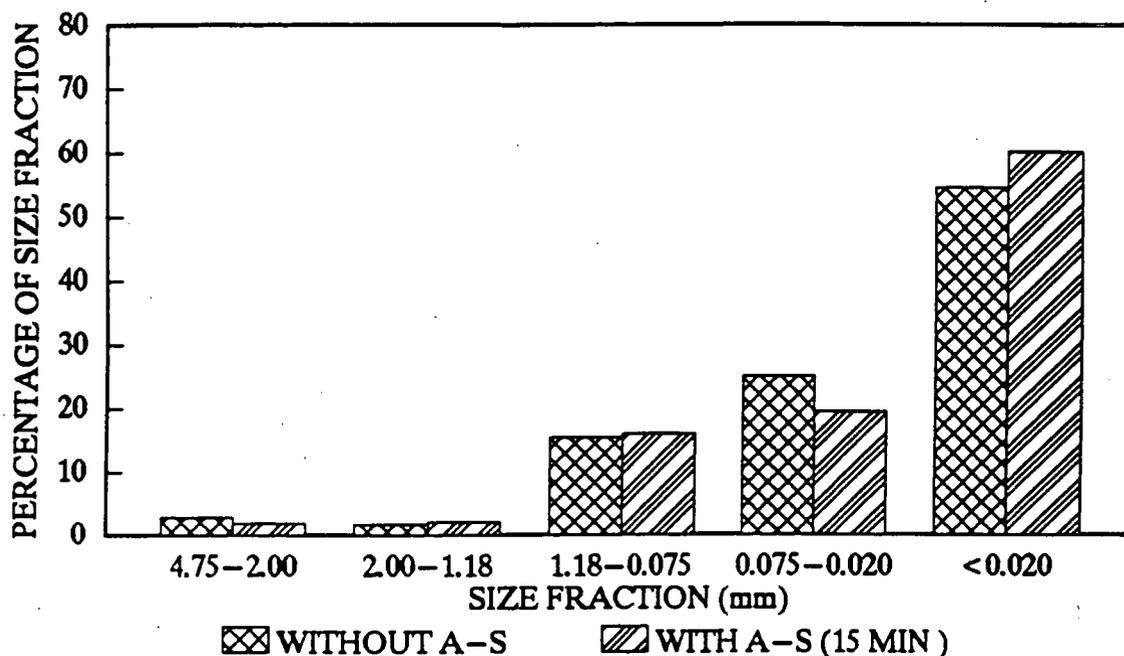


Fig. 1.5. Influence of attrition scrubbing (water) on particle-size distribution of the Fernald storage pad soil.

elevated temperatures (75 to 80°C) to create a potent reducing condition that reduces iron(III) of surface sesquioxides to iron(II), which is readily chelated by the citrate and removed from the soil's surface. This reaction, in the process of removing sesquioxides from the surfaces of soil particles, also releases significant levels of uranium. The mechanism of uranium release is uncertain. It may be simple entrainment of uranium with sesquioxide dissolution, or it may be similar to that of sesquioxide dissolution [i.e., reduction of the uranium(VI) matrix mineral to a uranium(IV) status, which compromises the stability of the matrix mineral, resulting in the dissolution of uranium]. Both mechanisms probably occur. Uranium(IV) is partitioned between a water-soluble citrate complex and a hydrated hydroxide that has a strong tendency to be sorbed onto soil surfaces at a neutral to slightly alkaline pH. Regardless of the mechanism, subsequent leaching with ammonium carbonate [containing  $\text{KMnO}_4$  to oxidize the uranium(IV) to uranium(VI) so that it can be complexed with carbonate] readily removes uranium from both of the Fernald soils to uranium levels well below the 52 mg/kg of soil screening level for applicable cleanup technologies. All extractions were conducted at low liquid-to-solid ratios (1:1 to 2:1). These extractions may not contain sufficient quantities of citrate to adequately complex uranium(IV), considering citrate's tendency to form water-soluble complexes with other soil components, namely, iron and aluminum from dissolution of surface sesquioxides and calcium and magnesium from partial dissolution of carbonates. Other experiments with CBD have been conducted at higher liquid-to-solid ratios and in conjunction with attrition scrubbing to enhance rates of dissolution, but the analytical results (neutron activation) are not available because of reactor down time.

Attrition scrubber studies that use sodium carbonate and citric acid as leaching media revealed that similar fractions of uranium can be extracted (with the same leaching media) from the two

Fernald soils in reaction times of 3 to 15 min compared with 4 h in batch-type stirred reactors. The similarity in extraction efficiency held true more for sodium carbonate extractions than citric acid extractions. For example, the extraction of uranium from the storage pad soil in 4 h batch-type stirred reactors with citric acid appeared to be slightly better (10 to 15%) than attrition scrubbing for 3 to 15 min. Increased attrition time (from 3 to 15 min) did not show any benefit in extraction of uranium. Approximately 5% of the uranium could be extracted from the storage pad soil by using water and attrition scrubbing, whereas <1% could be extracted from the incinerator soil. Attrition scrubbing with sulfuric acid appears to be highly effective if the pH of the final suspension is lowered to values <2.

Based on these data, the Fernald soils containing uranium at >450 mg/kg levels probably can't be lowered to uranium concentrations of <50 mg/kg by carbonate-based leaching in an acceptable engineering design. For example, the concentration of uranium in the Fernald storage pad soil reached values <50 mg/kg only after 6 and 23 h leaching at 40 or 60°C. The same leaching conditions with the Fernald incinerator soil resulted in residuals containing 60 to 70 mg/kg. Attrition scrubbing (at room temperature) with sodium carbonate yielded extraction efficiencies of ~60 and 80% for the incinerator and storage pad soils, respectively (calculated residual concentrations of ~210 and ~90 mg/kg, respectively). Attrition scrubbing with ammonium carbonate yielded ~20% lower extraction efficiencies than sodium carbonate. However, one should not automatically rule out the use of carbonate-based leaching media to decontaminate the Fernald soils because, of all the leaching media tested, it was the most selective for uranium and generated waste streams with lower concentrations of secondary soil constituents (i.e., iron, aluminum, calcium, and silica). Utilization of carbonate-based leaching media may have merit in a systems engineering approach in which particle-size segregation techniques are used to fractionate soil separates containing acceptable and unacceptable levels of uranium. Soil separates containing unacceptable levels of uranium could be disposed of directly (depending on quantity of materials and disposal options) or subjected to a more aggressive leaching procedure (e.g., the CBD or sulfuric acid extraction).

Citric acid could probably be used to treat the Fernald storage pad soils to levels <50 mg/kg; however, it appears that long reaction times in batch-stirred reactors may be necessary. Preliminary data from extractions that used citric acid in combination with attrition scrubbing indicate that levels <50 mg/kg with the storage pad soil may not be possible. The data on the incinerator site soil indicate only 60 to 70% removal rates, making levels in the residual considerably >50 mg/kg. The limited data for extractions that use sulfuric acid indicate that both Fernald soils could be treated with sulfuric acid (if the final pH of the suspension was lowered to <2) to generate residuals containing <50 mg/kg. The major problems in the utilization of citric and sulfuric acid are the quantities of acid necessary to treat the soil and the resulting characteristics of secondary waste stream resulting from the dissolution of the large quantities of calcite and dolomite carbonate minerals. Both of these leachants will also remove significant quantities of iron and aluminum from the soil layer silicates. Leaching with citric acid has a couple of advantages over leaching with sulfuric acid: (1) because citric acid is not a highly dissociated acid ( $pK_1$  of 3.1), the pH of the suspension will not go much below 2 on excess addition of acid (additions of sulfuric acid will result in significant dissolution of layer silicates and generation of unnecessary quantities of aluminum, iron, and silica) and (2) citric acid readily biodegrades to carbon dioxide and water in the environment.

The data in this report leave little doubt that the CBD procedure can be used to reduce uranium levels in Fernald soils from 450 to 550 mg/kg to <50 mg/kg. Questions remain about optimum

reaction time, quantity of reagents (primarily citrate and dithionite), and engineering design. These are being investigated. Limited data have been compiled, but it appears that CBD will generate considerably less waste than will sulfuric acid. For example, CBD does bring about some dissolution of calcite, however, not nearly as much as sulfuric acid does; the reaction pH for CBD is 7.3 compared with <2 for sulfuric acid. The immediate need is to determine the quantities of these secondary constituents in the effluents from the most promising leaching media so that appropriate decisions can be made with respect to choice of leaching media and engineering configuration. Now that we understand the major dissolution mechanisms and the factors controlling them, the challenge of the future is to develop a leaching media that will be sufficiently aggressive in the dissolution of solid-phase uranium particulate and be truly selective in uranium removal so that waste streams will be minimal.

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**Part 2**

**FERNALD SOIL CHARACTERIZATION AND TREATABILITY STUDY**

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## ACRONYMS AND INITIALISMS

|      |  |
|------|--|
| DOE  | U.S. Department of Energy                  |
| EPA  | U.S. Environmental Protection Agency       |
| FEMP | Fernald Environmental Management Project   |
| FMPC | Feed Materials Production Center           |
| IA   | incinerator area                           |
| SPA  | storage pad area                           |
| WSTC | Westinghouse Science and Technology Center |

**ABSTRACT**

Bench-scale feasibility tests were carried out to determine the applicability of soil washing in treating the storage pad and incinerator areas of the Fernald Environmental Management Project (FEMP) site in Fernald, Ohio. These sites were both contaminated with uranium: the storage pad area (SPA) was contaminated with soluble material through spills and runoff and the incinerator area (IA) was contaminated with particulate material, which was relatively insoluble.

The treatability tests showed that soil washing could be used to remove uranium from both of these sites. The high silt matrix that comprises the surface soils of this site can be effectively leached of uranium. Material balances on uranium were used to estimate uranium levels lower than 20 mg/kg, with soil recoveries of over 80%, may be achievable. Further development of the soil-washing process for this site should be aimed at providing effective separation technologies to remove the contaminated leach solution from the silt fraction of the soil (~5 to 25  $\mu\text{m}$  in size). Because of the ease of treatment and probable low cost for soil washing, further development is recommended.

## INTRODUCTION

### SITE DESCRIPTION

The Feed Materials Production Center (FMPC) in Fernald, Ohio, operated for 38 years between 1950 and 1988. Its mission was to produce uranium metal ingot feed materials for use in reactors at the Savannah River and Hanford sites. During this period, uranium was released on the Fernald site at various locations and in various forms. Because this site sits on a major freshwater aquifer that supplies water to the Cincinnati area, the U.S. Environmental Protection Agency (EPA) placed this site on the National Priorities List as a Superfund site. An environmental restoration program was established in 1986 that resulted in dividing the site into five operable units to facilitate the cleanup process. Operable Unit 5 is responsible for groundwater, surface water, flora, fauna, and the bulk of the site soils.

Operable Unit 5 is scheduled to obtain a Record of Decision from the EPA in August 1995. Operable Unit 5 is currently undertaking a Remedial Investigation and Feasibility Study to fully identify the nature and extent of contamination of the soils and groundwater and to laboratory test the applicability of various proven technologies for remediation (DOE 1992).

Because the Fernald Environmental Management Project (FEMP) is representative of many of the technical challenges that will be faced on numerous DOE sites also contaminated with uranium, it was selected as the host site for demonstrating advanced technologies for removing uranium from soils. The objectives of the Fernald Uranium Soils Integrated Demonstration are to

1. Demonstrate advanced technologies to be used to decontaminate uranium-contaminated soils.
2. Demonstrate advanced technologies for field characterization and precision excavation of soils.
3. Demonstrate a system of advanced technologies that work effectively together to characterize, excavate, decontaminate, and dispose of remaining wastes.
4. Provide a transfer of these technologies to DOE restoration programs and the private sector.

One of the prime technologies under consideration for the Fernald site is soil washing. Therefore, soil-washing studies are being undertaken by multiple vendors to demonstrate the different approaches available.

### WESTINGHOUSE SOIL-WASHING TECHNOLOGY

Westinghouse offers a proven, operating soil-washing process for the remediation of a wide variety of soil types for a wide variety of contaminants. Westinghouse soil-washing technology stands apart from others because:

1. It is an integrated process, designed from the start to use and recycle aqueous-based leachates.
2. It can handle difficult soils such as clays.
3. It is a compact (three-trailer) unit and has a high capacity (20 tons per hour).

4. There is a broad base of experience in handling real, aged, and weathered contaminated soils.
5. The Westinghouse Science and Technology Center (WSTC) has a broad base of experience in site remediation, metals recovery, and process development.
6. Bench- and pilot-scale facilities and procedures are in place to determine the applicability and performance of soil washing to actual contaminated site samples.
7. Aqueous based, biodegradable leachates are used so that soil-washing residuals will not cause contamination problems in the future.
8. Experienced personnel are available to carry out bench-, pilot-, and full-scale work.

The Westinghouse Soil-Washing Process consists of the following operations:

1. Screening with a 6-in. grizzly to remove large items. These items will either be pressure-washed or disposed of as appropriate.
2. Materials less than 6 in. are processed in a rotary screen to be washed with leachate rinse with water and recycled as clean soils greater than 1 in.
3. Materials less than 1 in. are dropped into a screw classifier where soils greater than about 48 mesh are washed with leachate, rinsed with water, and recycled as clean soil.
4. Materials less than 48 mesh are scrubbed in an attrition scrubber and processed in a mineral jig to remove the highly contaminated fine materials and displace the used leachate with rinse water.
5. The jig bottoms are then dewatered and returned to the site.
6. The fines slurry from the jig(s) is then treated to remove organic materials and contaminated suspended fines and leachate from the uncontaminated fine soils. The clean soil fines are then flocced and removed from the process by using a rotary screen and clarifier.
7. The cleaned leachant is refurbished with the active leachates and recycled.

The following are the two key steps in this process:

1. Attrition scrubbing with the leachate solution to remove the highly contaminated fines from the larger soil particles and to remove contaminants from the surfaces of the larger particles. The key variable in this unit operation is the residence time.
2. Jigging to remove the contaminated fines from the larger sand particles and to thoroughly rinse the clean sands.

In addition to our current full-scale (22,000 ton) job completed at Bruni, Texas, Westinghouse has successfully performed numerous bench-scale treatability studies and three pilot studies. The contaminants in these sites included

- uranium and radium in a 40% clay soil
- copper in a coarse soil
- PCBs in a sandy soil, making it an NPL site
- oil landfarm, silty soil contaminated with grease, PCBs, and uranium
- river/sewer sediments contaminated with mercury and uranium
- sandblasting and foundry sands contaminated with lead
- clay contaminated with chromium(VI)
- sludges contaminated with chromium, nickel, and copper
- sandy soil contaminated with lead and petroleum hydrocarbons
- ash contaminated with lead, cadmium, and zinc

Based on such a successful base of soil-washing studies and projects, WSTC proposed that the Fernald soils be evaluated for remediation by soil washing.

## STUDY OBJECTIVES

The objective of this program was to demonstrate the feasibility of using bench-scale equipment to wash uranium out of uranium-contaminated Fernald soils. The objectives of this study were to

1. Characterize soil samples supplied by Fernald by soil-size and contaminant distributions.
2. Perform bench-scale tests to identify potential leachates, unit operations in the soil-washing process, and water treatment options for treating the used leachates from the soil-washing process.
3. Analyze all samples generated by this work for residual uranium levels and, if clean, evaluate their ability to support plant growth.
4. Perform mass balances to determine the percentage of soil recovery and the percentage uranium removal.
5. Evaluate other advanced removal techniques, subject to agreement with a knowledgeable technical representative.

## EXPERIMENTAL

Testing and analysis have been carried out to accomplish the following objectives set forth for this program, including

1. soil-size and contaminant distribution characterizations,
2. identification of potential leachates and unit operations in the soil-washing process,
3. identification of water treatment options,
4. analysis of soil samples for residual uranium levels,
5. performance of mass balances to determine the percentage soil recovery and the percentage uranium removal, and
6. evaluation of an advanced removal technique based on the use of entrained ion-exchange resins in the soil.

A determination of the ability of the cleaned soil to support plant growth was not made because no clean soil samples were produced. The results of the testing aimed at achieving these program objectives is discussed in the following.

## SOIL CHARACTERIZATION

The 5-gal buckets received from the FEMP were labeled as described in Table 2.1.

**Table 2.1. Description of soils received from Fernald**

| Bucket No. | Drum No. | Descriptor | FEMP location | SP No. | Uranium/level (mg/kg) |
|------------|----------|------------|---------------|--------|-----------------------|
| 1          | 8        | 16-B/8     | Plant 1/Pad   | 3,4    | 390                   |
| 2          | 11       | 16-B/11    | Plant 1/Pad   | 3,4    | 410                   |
| 3          | 10       | 10-A/12-14 | Incinerator   | 9,10   | 460                   |
| 4          | 13       | 13-A/14    | Incinerator   | 9,10   | 410                   |

To ensure uniformity of feed, a mixing step was performed on each bucket. The contents of each received bucket was emptied in equal portions alternately into two empty receiver buckets, one pint scoopful at a time. The contents of the receiver buckets was then returned to the received bucket by alternately feeding 1 pint of soil from each of the receiver buckets into the received bucket. The as-received samples were then taken from each of the received buckets.

Characterization tests were then carried out to determine the soil-size and contaminant distributions as a function of soil particle size. In addition, these tests served as an indicator of the solubility of the uranium contaminants in each fraction. The particle-size distribution of each sample was determined by wet sieving. Three hundred grams of SPA No. 1, as-received soil was mixed with 600 mL of water and sieved in a shaker screen through screens of 20, 50, 100, 200, and 325 mesh. The liquid was recirculated. The vibration amplitude was about 6, and the wash time was about 5 min. Because of the large amount of fines in the sample, 3 L of water was then used in a once-through mode to rinse the materials on the screens. The samples from each screen were then dried and their weights determined. These results, reported in Table 2.2, indicated that the soil could be characterized in three fractions: +20, +325, and -325 mesh.

**Table 2.2. Particle-size distribution from wet sieving (SPA No. 1)**

| Mesh size | Size fraction (mm) | Dry weight (g) | Weight fraction (%) | Moisture content (as received) (%) |
|-----------|--------------------|----------------|---------------------|------------------------------------|
| 20        | >0.850             | 29.1           | 12.7                | 18.7                               |
| 50        | 0.850-0.300        | 7.9            | 3.5                 | 16.0                               |
| 100       | 0.300-0.150        | 6.8            | 3.0                 | 23.6                               |
| 200       | 0.150-0.075        | 8.4            | 3.7                 | 23.6                               |
| 325       | 0.075-0.045        | 7.4            | 3.2                 | 27.5                               |
| <325      | <0.045             | <u>168.8</u>   | <u>73.9</u>         | NM <sup>a</sup>                    |
| Total     |                    | 228.4          | 100.0               | 24.3                               |

<sup>a</sup>NM = not measured.

Accordingly, the particle-size distribution of each of the samples was determined by wet sieving by mixing 300 g of as-received soil with 200 mL of water in a blender and sieved in a shaker screen through screens of 20 and 325 mesh. Water was then used in a once-through mode to rinse the materials on the screens. The samples from each screen were then dried and their weights determined. The moisture content for each soil type was determined by drying the as-received material at 80°C for about 60 h. The samples were weighed periodically until the weight of the sample was constant. These results are reported in the Appendix (Table A.1) and summarized in Table 2.3.

Table 2.3. Summary of feed characterization data

| Soil                        | Mesh size | Weight fraction (%) | Moisture content (as received) (%) |
|-----------------------------|-----------|---------------------|------------------------------------|
| Storage pad area (SPA) soil | +20 mesh  | 5                   | 12                                 |
|                             | +325 mesh | 18                  | 20                                 |
|                             | -325 mesh | 73                  | 71                                 |
| Incinerator area (IA) soil  | +20 mesh  | 4                   | 8                                  |
|                             | +325 mesh | 9                   | 28                                 |
|                             | -325 mesh | 85                  | 78                                 |

<sup>a</sup>Pretreatment uranium level was 400 mg/kg.

<sup>b</sup>Pretreatment uranium level was 435 mg/kg.

Analysis of the two liquids used in these tests, water and 0.2 M  $\text{NH}_4\text{HCO}_3$ , was used to determine the relative solubility of the uranium fraction. These tests indicated that the contamination in the samples from the Plant 1/storage pad area (SPA) was concentrated in the finer soil sizes (-325 mesh). This contamination had about the same solubility in water as in the  $\text{NH}_4\text{HCO}_3$ , indicating that the uranium contaminant resulted from spillage of uranium solutions. The characterization tests for the incinerator area (IA) indicated that the uranium was relatively insoluble in water but had the same solubility in  $\text{NH}_4\text{HCO}_3$  as in the SPA. This indicated that it was introduced as a particulate, probably as  $\text{UO}_3$ , which is also relatively soluble in  $\text{NH}_4\text{HCO}_3$ . Unlike that in the SPA, the uranium contamination in the IA was concentrated in the +325 mesh sizes. These results are also presented in the Appendix (Table 2.A.1). Based on these characterization tests, it was decided to utilize the Drum 1 soil as representative of the SPA soils and Drum 3 as representative of the IA soils.

## LEACHING TESTS

The objective of these tests was to develop a leachate suitable for removing the uranium contamination from the soil. Based on the characterization tests described in the preceding,  $\text{NH}_4\text{HCO}_3$  is a suitable leachate. Also based on these tests, it is clear that not all of the uranium was being mobilized. Based on previous experience, this is not an unusual occurrence for uranium species that have been subject to a variety of process and weathering conditions. The usual result of

these time-based processes is that some of the uranium is converted to less-soluble chemical forms in the +6 or +4 valence states. In most of these cases, the use of a pretreatment oxidation step has proved useful. In particular, the use of NaOCl has proved beneficial. To test the preoxidation step, a series of tests were run with

1. a H<sub>2</sub>O wash
2. a 2% NaOCl oxidation + H<sub>2</sub>O wash
3. a 0.2 M NH<sub>4</sub>HCO<sub>3</sub> leach
4. a 2% NaOCl pretreatment +0.2 M NH<sub>4</sub>HCO<sub>3</sub> leach

In addition, ion-exchange resin (Dowex 21K, Cl- form) was added after the +20 mesh material was removed. This was done because it was noted that a large fraction of fines (<325 mesh) was present in the soil. Because this material is too fine to be removed from the bottom of the jig, a method for separating the contaminated leachate from the cleaned soil fines is required. To achieve this separation, it was proposed that ion-exchange resin be added to remove the uranium from the leachate. The resin could then be easily separated from the soil fines by using a 100 mesh screen on the jig overflow after the >200 mesh solids had been removed from the bottom of the jig. The test procedure utilized for these tests is summarized in Table 2.4.

**Table 2.4. Experimental soil extraction steps  
(preoxidation, resin procedure)**

| Step  | Description  | Comments  |
|---|--|---|
| Blend   | 1 min 300 g soil + 200 g NaOCl,<br>45 s + 100 g NH <sub>4</sub> HCO <sub>3</sub> |   |
| Screen  | >20 mesh<br><20 mesh   | Rinse with water and dry<br>Add resin   |
| Jig overflow  | Screen >50 mesh (0.300 mm)<br>Screen <50 mesh (0.300 mm)                         | Resin with adsorbed uranium<br>Fine soil, jig liquid<br>Allow solids to settle<br>Decant liquid |
| Jig underflow   | Screen >200 mesh (0.074 mm)<br>Screen <200 mesh (0.074 mm)                       | Rinsed soil<br>Fine soil to decant  |
| Filter, dry jig overflow  |  |   |
| Precipitate uranium<br>in decanted leachate<br>with ferrous sulfate<br>and floc |  |   |

The results of these tests are summarized in Table 2.5 and presented in full in the Appendix (Table 2.A.2). All tests showed that for the SPA soils, the uranium was highly soluble for any of the leachates. However, the removal efficiency increased in the order of

H<sub>2</sub>O wash < 2% NaOCl + H<sub>2</sub>O < 0.2 M NH<sub>4</sub>HCO<sub>3</sub> < 2% NaOCl + 0.2 M NH<sub>4</sub>HCO<sub>3</sub>

The cleanest soil was produced when the soil was preoxidized and then leached with  $\text{NH}_4\text{HCO}_3$ . For the IA soils, the uranium was much less soluble. The order for leachate effectiveness was



However, the final products had about the same levels of uranium, indicating that the soluble uranium was easily removed and that the insoluble uranium (in the +200 to -20 mesh fraction) remained very insoluble and resisted leaching. In both cases, the combined preoxidation and leaching combination of 2% NaOCl + 0.2 M  $\text{NH}_4\text{HCO}_3$  performed the best.

Table 2.5. Preoxidation test summary

| Soil            | Leachate                                   | Composite clean soil uranium (mg/kg) | Recovered resin + precipitate (% of uranium feed) |
|-----------------|--|--------------------------------------|---|
| SPA soils No. 1 | $\text{H}_2\text{O}$ wash                  | 185                                  | 60  |
|                 | 2% NaOCl + $\text{H}_2\text{O}$            | 152                                  | 82  |
|                 | 0.2 M $\text{NH}_4\text{HCO}_3$            | 141                                  | 111   |
|                 | 2% NaOCl + 0.2 M $\text{NH}_4\text{HCO}_3$ | 118                                  | 86  |
| IA soils No. 3  | $\text{H}_2\text{O}$ wash                  | 224                                  | 27  |
|                 | 2% NaOCl + $\text{H}_2\text{O}$            | 319                                  | 20  |
|                 | 0.2 M $\text{NH}_4\text{HCO}_3$            | 228                                  | 58  |
|                 | 2% NaOCl + 0.2 M $\text{NH}_4\text{HCO}_3$ | 216                                  | 75  |

The +20 mesh fraction was relatively clean for both soils. For the SPA soils, the +200 mesh fraction was clean, whereas for the IA soils, the +200 mesh fraction was contaminated.

Additional tests were then carried out to verify the repeatability of the tests and the effectiveness of the resin. The results of these tests are summarized in Table 2.6. The detailed results are presented in the Appendix (Table 2.A.3). These results indicated that the tests were only moderately repeatable. A firm conclusion on the effectiveness of the resin could not be made because of the variability in the data. However, it appears that the use of ion-exchange resin significantly decreased uranium removal from the washed soils.

Finally, a set of tests was run as outlined in Table 2.7. In these tests, ion-exchange resin was not used and the used leachate and overflow solids from the jig were slurried together and treated by floccing. This varied from the previous treatment approach in which the solids were allowed to settle and the liquid decanted and treated separately. In addition, analytical tests were performed at Oak Ridge National Laboratory (ORNL) facilities to verify the analytical results obtained from the WSTC laboratory services vendor.

Table 2.6. Repeatability and resin test summary

| Soil            | Resin <sup>a</sup> | Composite clean soil uranium (mg/kg) | Recovered resin + precipitate (% of uranium feed) |
|-----------------|--------------------|--------------------------------------|---|
| SPA soils No. 1 | No                 | 128                                  | 38  |
|                 | Yes                | 218                                  | 52  |
|                 | Yes (previous)     | 118                                  | 86  |
| IA soils No. 3  | No                 | 119                                  | 27  |
|                 | Yes                | 195                                  | 35  |
|                 | Yes (previous)     | 216                                  | 75  |

<sup>a</sup>2% NaOCl + 0.2 M NH<sub>4</sub>HCO<sub>3</sub> adjusted to pH = 9 were the oxidizer and extractant.

Table 2.7. Experimental soil extraction steps

| Step   | Description  | Comments   |
|--|--|--|
| Blend  | 1 min 300 g soil + 200 g NaOCl,<br>45 s + 100 g NH <sub>4</sub> HCO <sub>3</sub> |  |
| Screen   | >20 mess   | Rinse with water and dry   |
| Jig overflow   | screen >50 mesh<br>screen <50 mesh   | Resin with adsorbed U<br>Fine soil, jig liquid<br>Floc slurry to settle solids |
| Jig underflow  | screen >200 mesh<br>screen <200 mesh   | Rinsed soil<br>Fine soil to decant   |
| Decant and filter,<br>dry <200 mesh residue          |  |  |
| Precipitate uranium with<br>ferrous sulfate and floc |  |  |

The detailed results are presented in the Appendix (Table 2.A.4). Although the ORNL liquid analyses were not internally consistent with the solid sample analyses (i.e., the after-treatment liquid analysis showed a higher uranium content than the before-treatment analysis, even though the precipitate derived from the treatment was heavily loaded with uranium), these results provided some very valuable insights with regard to the specific separations that have to be performed to produce clean soil from this site. Two points, in particular, are worth noting:

1. The hazy solution above the settled -200 mesh solids resulting from the treatment of the SPA soils contained a large fraction of the uranium found in the flocced solids. This indicates that this contamination was in the form of minute solids that can be flocced from solution. Therefore, although the resin could remove the soluble portion, the insoluble portion would remain with the soils. This conclusion can be arrived at by performing a material balance on the liquid and solids, starting from the final liquids concentration, as shown in Table 2.8. Presuming that the 0.74 ppm measured in the liquid is correct, the uranium that was precipitated from the solution can be added back, giving a total uranium concentration in the liquid of 2.07 ppm. Then, assuming that the initial liquid uranium level was correct (5.74 ppm), the difference that came out of the solution ( $5.74 - 2.07 = 3.67$ ) was added to the soils from the solution. Subtracting this uranium from the solution from the measured soil level after floccing (250 ppm) leaves a level of 4.1 ppm in the soil.
2. The size cut for the contaminated fraction of the incinerator soils extends somewhat below 200 mesh. This was indicated by the fact that the material captured in the 200 mesh screen in the jig overflow had significant levels of uranium contamination. A lower upflow rate for the jig will reduce the entrained contamination. Again, liquid analyses indicated that the hazy solution above the leached solids contains a significant amount of uranium contamination and therefore should not be flocced out with the settled fines.

**Table 2.8. Mass balance analysis for storage pad area data**

|                             | Weight<br>(g) | Uranium<br>measured<br>(ppm) | Uranium<br>calculated<br>(ppm) |
|-----------------------------|---------------|------------------------------|--------------------------------|
| Liquid after solids settled | 12,800        | 5.74                         |                                |
| Flocced and settled solids  | 191           | 257                          | 4.1                            |
| Liquid after 1st floc       | 12,800        | 0.92                         | 2.07                           |
| Liquid after 2d floc        | 12,800        | 0.72                         | 2.07                           |
| Precipitated solids         | 6             | 2,839                        |                                |
| Liquid after precipitation  | 12,800        | 0.74                         | 0.74                           |

These results indicated that an efficient technique to separate contaminated leachates containing very fine suspended uranium contaminant particles from fine soil particles is needed. If one presumes that such a device was identified and used in these tests, then an estimate of the achievable final uranium levels in the soils can be made. The results of these calculations are shown in Table 2.9, where the final composite soil level is constructed based on a weighted average (based on the percentage weight of each soil fraction in the feed soil) of uranium levels in each fraction. The calculated level (16 ppm) indicates that the target level of 30 ppm of uranium is achievable for the SPA soils. Although there is not enough data to calculate the achievable level for the IA soils, if one assumes that a smaller soil size is sent to the jig bottoms (a contaminated stream for this soil sample), then uranium levels of about 6 ppm may be obtained. The calculations for this composite soil are shown in Table 2.10. The results presented in Tables 2.9 and 2.10 are summarized in Table 2.11.

**Table 2.9. Composite FEMP storage pad area soil**

| Soil size fraction | Percentage of soil | Uranium level (ppm) | Weighted uranium level (ppm) |
|--------------------|--------------------|---------------------|------------------------------|
| +20 mesh           | 5                  | 43 <sup>a</sup>     | 2                            |
| +325 mesh          | 18                 | 80 <sup>a</sup>     | 11                           |
| -325 mesh          | 73                 | 4 <sup>b</sup>      | 3                            |
| Composite          | 100                |                     | 16                           |

<sup>a</sup>Average calculated from jig underflow for runs reported in Tables A.2, A.3, and A.4, which used  $\text{NH}_4\text{HCO}_3$  +  $\text{NaOCl}$  as the leachate.

<sup>b</sup>Calculated from Table 2.8.

**Table 2.10. Composite FEMP incinerator area soil**

| Soil size fraction | Percentage of soil | Uranium level (ppm) | Weighted uranium level (ppm) |
|--------------------|--------------------|---------------------|------------------------------|
| +20 mesh           | 4                  | 57 <sup>a</sup>     | 2                            |
| -325 mesh          | 85                 | 4 <sup>b</sup>      | 4                            |
| Composite          | 89                 |                     | 6                            |

<sup>a</sup>Average calculated from jig underflow for runs reported in Tables A.2, A.3, and A.4, which used  $\text{NH}_4\text{HCO}_3$  +  $\text{NaOCl}$  as the leachate.

<sup>b</sup>Calculated from Table 2.8.

**Table 2.11. Summary of treated soil compositions, assuming improved solids/liquids separation**

|             | Soil recovery (%) | Product soil fractions | Final uranium (ppm) <sup>a</sup> |
|-------------|-------------------|------------------------|----------------------------------|
| Plant 1/Pad | About 100         | All except <1 micron   | 16                               |
| Incinerator | >89               | +20 and -325 mesh      | 6 (est)                          |

<sup>a</sup>Assumes improved solids/liquids separation.

## LEACHATE TREATMENT

A key portion of the soil-washing process is the treatment of the contaminated leachate. A process that produces a very concentrated contaminate is preferred because this enhances the possibility for beneficial reuse or, at least, reduces disposal costs if beneficial reuse is not an option.

The process that was developed utilized a combined reduction, precipitation, and flocculation process that produced a high-percentage solids by weight sludge that also had high uranium concentrations. The process first treats the leachate with ferrous sulfate. The  $Fe^{+2}$  reduces any soluble uranium(VI) to insoluble uranium(IV) while providing a very high surface area to act as a "getter" for the suspended uranium particulates present in these leachates. The ferric hydroxide particulates that are loaded with uranium (concentrations as high as 8400 mg/kg obtained in the bench-scale tests) are flocced with a nonionic polymer to produce a readily dewatered sludge with a solids content of between 40 and 50% by weight.

## CONCLUSIONS AND RECOMMENDATIONS

### CONCLUSIONS

Based on the bench-scale treatability tests carried out at WSTC, the following conclusions can be drawn about the treatability of the two Fernald soils by soil washing:

1. Removal of the uranium from both the SPA and IA contaminated soils appears to be technically feasible by utilizing a combination of ammonium carbonate and sodium hypochlorite solutions and physical separation.
2. The contamination in the SPA soils was highly soluble and readily mobilized by the leachate. Additional development is needed identify the equipment required to separate the very fine soil fraction, which makes up the majority of these soils, from the contaminated leachate. Final uranium levels on the order of 16 mg/kg of soil may be achievable.
3. The contamination in the IA soils was divided between a highly soluble fraction and a relatively insoluble fraction in soils from about 200 to 100 mesh in size. Again, additional development is required to identify the equipment necessary to separate the fine soil fraction, which is clean, from the contaminated leachate. The contaminated middle fraction is readily separated by using the available jig technology.

### RECOMMENDATIONS

Based on this study, the following recommendations are made:

1. Because removal of the uranium from both of the contaminated fractions appears to be feasible and the technical screening limits (30 pCi/gm) obtainable, development work aimed

at identifying solids/liquids separation equipment that can cleanly separate contaminated leachates from clean fines in the 5- to 60- $\mu\text{m}$  range should be undertaken.

2. Soil washing will produce the following fractions for the SPA site soils:
  - a. a clean +5- $\mu\text{m}$  soil fraction
  - b. uranium-contaminated precipitates (from the treatment of the contaminated leachate solutions) that can be treated by ion-exchange or precipitation techniques
3. Soil washing will produce the following fractions for the IA site soils:
  - a. a clean +5- $\mu\text{m}$  to -200 mesh soil fraction
  - b. a clean +100 mesh soil fraction
  - c. uranium-contaminated precipitates (from the treatment of the contaminated leachate solutions) that can be treated by ion-exchange or precipitation techniques
  - d. a uranium contaminated fraction between +200 mesh and -100 mesh
4. The leachant of choice appears to be a mixture of ammonium carbonate and sodium hypochlorite solutions.
5. A treatment method developed on smaller samples will probably be applicable to the entire Fernald site because the uranium was effectively removed from two disparate sites that had different types of uranium sources.
6. Because the uranium contamination appears in different size fractions in either insoluble or soluble forms, on-line monitoring of the process streams will probably provide for optimum processing throughput and therefore lowest cost. This is true because soils from various parts of the site are processed, and rework can be minimized by on-line process adjustments.

## REFERENCES

U.S. Department of Energy (DOE). 1992. The Fernald uranium soils integrated demonstration. DOE Publication 1632, Washington, D.C.

**Appendix**

Table 2.A.1. Feed characterization data for 1-min attrition scrubbing

| Leachate                                      | Dry wt (g) | Mesh size (mesh) | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks              | Moisture content (%) |
|---|------------|------------------|---------------------------------|--------------------|-------------------------|----------------------|----------------------|
| <i>Soil No. 1—Storage pad area</i>            |            |                  |                                 |                    |                         |                      |                      |
| Pretreatment                                  | 264        |                  | 390                             |                    |                         | Soil samples = 300 g | 12                   |
| 200 g, H <sub>2</sub> O                       | 12.1       | 20               | 110                             | 94                 | 42                      |                      | 15                   |
|   | 51         | 325              | 140                             |                    |                         |                      | 18                   |
|   | 185        | -325             | 100                             |                    |                         |                      | 69                   |
|   | 1321       | Liquid           | 12                              |                    |                         |                      |                      |
| 200 g, 0.2 M NH <sub>4</sub> HCO <sub>3</sub> | 15         | 20               | 420                             | 101                | 122                     | pH = 8.05            | 11                   |
|   | 49         | 325              | 93                              |                    |                         |                      | 19                   |
|   | 204        | -325             | 280                             |                    |                         |                      | 73                   |
|   | 3972       | Liquid           | 14.5                            |                    |                         |                      |                      |
| <i>Soil No. 2—Storage pad area</i>            |            |                  |                                 |                    |                         |                      |                      |
| Pretreatment                                  | 261        |                  | 410                             |                    |                         |                      | 13                   |
| 200 g, H <sub>2</sub> O                       | 9.5        | 20               | 53                              | 97                 | 104                     |                      | 9                    |
|   | 48         | 325              | 79                              |                    |                         |                      | 21                   |
|   | 196        | -325             | 360                             |                    |                         |                      |                      |
|   | 1191       | Liquid           | 31                              |                    |                         |                      | 14                   |
| 200 g, 0.2 M NH <sub>4</sub> HCO <sub>3</sub> | 18         | 20               | 93                              | 93                 | 81                      | pH = 8.05            | 21                   |
|   | 42         | 325              | 81                              |                    |                         |                      |                      |
|   | 183        | -325             | 240                             |                    |                         |                      |                      |
|   | 3148       | Liquid           | 12.0                            |                    |                         |                      |                      |

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Table 2.A.1 (continued)

| Leachate                                      | Dry wt (g) | Mesh size (mesh) | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks                        | Moisture content (%) |
|---|------------|------------------|---------------------------------|--------------------|-------------------------|--------------------------------|----------------------|
| <i>Soil No. 3—Incinerator area</i>            |            |                  |                                 |                    |                         |                                |                      |
| Pretreatment                                  | 252        |                  | 460                             |                    |                         | pH = 9 with NH <sub>4</sub> OH | 16                   |
| 200 g, H <sub>2</sub> O                       | 18.2       | 20               | 140                             | 94                 | 86                      |                                | 9                    |
|   | 21         | 325              | 810                             |                    |                         |                                | 27                   |
|   | 199        | -325             | 390                             |                    |                         |                                |                      |
| 200 g, 0.2 M NH <sub>4</sub> HCO <sub>3</sub> | 1579       | Liquid           | 2                               |                    |                         |                                |                      |
|   | 6          | 20               | 270                             | 98                 | 98                      |                                | 10                   |
|   | 24         | 325              | 1200                            |                    |                         |                                | 29                   |
|   | 216        | -325             | 230                             |                    |                         |                                |                      |
|   | 3171       | Liquid           | 10.3                            |                    |                         |                                |                      |
| <i>Soil No. 4—Incinerator Area</i>            |            |                  |                                 |                    |                         |                                |                      |
| Pretreatment                                  | 249        |                  | 410                             |                    |                         | pH = 9 with NH <sub>4</sub> OH | 17                   |
| 200 g, H <sub>2</sub> O                       | 3.8        | 20               | 150                             | 99                 | 100                     |                                | 10                   |
|   | 23         | 325              | 830                             |                    |                         |                                | 27                   |
|   | 220        | -325             | 370                             |                    |                         |                                | 78                   |
| 200 g, 0.2 M NH <sub>4</sub> HCO <sub>3</sub> | 1579       | Liquid           | 1                               |                    |                         |                                |                      |
|   | 9          | 20               | 500                             | 99                 | 129                     |                                | 4                    |
|   | 23         | 325              | 1100                            |                    |                         |                                | 29                   |
|   | 215        | -325             | 290                             |                    |                         |                                |                      |
|   | 1743       | Liquid           | 22.8                            |                    |                         |                                |                      |

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Table 2.A.2. Preoxidation and resin tests for storage pad area soils—Drum 1

| Leachate                                      | Attrition scrub time (min) | Dry wt (g) | Mesh size (mesh) | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks                      | Moisture content (%) |
|---|----------------------------|------------|------------------|---------------------------------|--------------------|-------------------------|------------------------------|----------------------|
| <i>Soil No. 1</i>                             |                            |            |                  |                                 |                    |                         |                              |                      |
| Pretreatment                                  |                            | 264        |                  | 390                             |                    |                         | Soil samples = 300 g         | 12                   |
| 300 g, H <sub>2</sub> O                       | 1                          | 9.8        | 20               | 47                              | 100                | 107                     |                              |                      |
|   | 1                          | 19         | 50               | 540                             |                    |                         | Resin stream (15-g original) |                      |
|   | 1                          | 37         | 200              | 78                              |                    |                         | Jig underflow                |                      |
|   | 1                          | 214        | -200             | 210                             |                    |                         | Flocced solids               | 69                   |
|   | 1                          | 13         | Fe-precip        | 4,000                           |                    |                         |                              |                      |
|   | 1                          | 12,500     | Liquid           | 0.02                            |                    |                         |                              |                      |
| Pretreatment                                  |                            | 264        |                  | 390                             |                    |                         | pH = 7                       | 12                   |
| 300 g, 2% NaOCl                               | 1                          | 8.9        | 20               | 70                              | 98                 | 128                     |                              |                      |
|   | 1                          | 14         | 50               | 2,000                           |                    |                         | Resin stream (15-g original) |                      |
|   | 1                          | 39         | 200              | 70                              |                    |                         | Jig underflow                |                      |
|   | 1                          | 212        | -200             | 170                             |                    |                         | Flocced solids               | 70                   |
|   | 1                          | 14         | Fe-precip        | 3,900                           |                    |                         |                              |                      |
|   | 1                          | 12,700     | Liquid           | 0.64                            |                    |                         |                              |                      |
| Pretreatment                                  |                            | 264        |                  | 390                             |                    |                         | pH = 9                       | 12                   |
| 300 g, 0.2 M NH <sub>4</sub> HCO <sub>3</sub> | 1                          | 7          | 20               | 51                              | 95                 | 147                     |                              |                      |

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Table 2.A.2 (continued)

| Leachate   | Attrition scrub time (min) | Dry wt (g) | Mesh size (mesh)  | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks                        | Moisture content (%) |  |
|--|----------------------------|------------|-------------------|---------------------------------|--------------------|-------------------------|--------------------------------|----------------------|--|
|  | 1                          | 18         | 50                | 830                             |                    |                         | Resin stream (15-g original)   |                      |  |
|  | 1                          | 37         | 200               | 56                              |                    |                         | Jig underflow                  |                      |  |
|  | 1                          | 202        | -200              | 160                             |                    |                         | Flocced solids                 | 75                   |  |
|  | 1                          | 15         | Fe-precip         | 6,700                           |                    |                         |                                |                      |  |
|  | 1                          | 12,400     | Liquid            | 0.13                            |                    |                         |                                |                      |  |
| Pretreatment                                       |                            | 264        |                   | 390                             |                    |                         | pH = 9                         | 12                   |  |
| 200 g, 2% NaOCl + 100 g, 0.2 M NH <sub>4</sub> HCO | 1 + 0.75                   | 6.8        | 20                | 45                              | 95                 | 130                     |                                |                      |  |
|  | 1 + 0.75                   | 13         | 50                | 1,400                           |                    |                         | Resin stream (15-g original)   |                      |  |
|  | 1 + 0.75                   | 35         | 200               | 62                              |                    |                         | Jig underflow                  |                      |  |
|  | 1 + 0.75                   | 209        | -200              | 130                             |                    |                         | Flocced solids                 | 74                   |  |
|  | 1 + 0.75                   | 14         | Fe-precip         | 4,900                           |                    |                         |                                |                      |  |
|  | 1 + 0.75                   | 12,700     | Liquid            | 1.20                            |                    |                         |                                |                      |  |
|  |                            |            | <i>Soil No. 3</i> |                                 |                    |                         |                                |                      |  |
| Pretreatment                                       |                            | 252        |                   | 460                             |                    |                         | pH = 9 with NH <sub>4</sub> OH | 16                   |  |
| 200 g, 2% NaOCl + 100 g, 0.2 M NH <sub>4</sub> HCO | 1 + 0.75                   | 4.1        | 20                | 49                              | 94                 | 122                     |                                |                      |  |
|  | 1 + 0.75                   | 13         | 50                | 2,200                           |                    |                         | Resin stream (15-g original)   |                      |  |

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Table 2.A.2 (continued)

| Leachate                | Attrition scrub time (min) | Dry wt (g) | Mesh size (mesh) | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks                      | Moisture content (%) |
|-------------------------|----------------------------|------------|------------------|---------------------------------|--------------------|-------------------------|------------------------------|----------------------|
|                         | 1 + 0.75                   | 12         | 200              | 930                             |                    |                         | Jig underflow                |                      |
|                         | 1 + 0.75                   | 223        | -200             | 220                             |                    |                         | Flocced solids               | 47                   |
|                         | 1 + 0.75                   | 13         | Fe-precip        | 3,600                           |                    |                         |                              |                      |
|                         | 1 + 0.75                   | 10,800     | Liquid           | 0.43                            |                    |                         |                              |                      |
| Pretreatment            |                            | 252        |                  | 460                             |                    |                         |                              | 16                   |
| 300 g, H <sub>2</sub> O | 1                          | 7.4        | 20               | 360                             | 97                 | 72                      |                              |                      |
|                         | 1                          | 12         | 50               | 55                              |                    |                         | Resin stream (15-g original) |                      |
|                         | 1                          | 14         | 200              | 930                             |                    |                         | Jig underflow                |                      |
|                         | 1                          | 226        | -200             | 220                             |                    |                         | Flocced solids               | 11                   |
|                         | 1                          | 14         | Fe-precip        | 1,300                           |                    |                         | Flocced solids               | 11                   |
|                         | 1                          | 13,000     | Liquid           | 0.01                            |                    |                         |                              |                      |
| Pretreatment            |                            | 252        |                  | 460                             |                    |                         | pH = 7                       | 16                   |
| 300 g, 2% NaOCl         | 1                          | 6.5        | 20               | 290                             | 96                 | 84                      |                              |                      |
|                         | 1                          | 11         | 50               | 420                             |                    |                         | Resin stream (15-g original) |                      |
|                         | 1                          | 15         | 200              | 930                             |                    |                         | Jig underflow                |                      |
|                         | 1                          | 223        | -200             | 320                             |                    |                         | Flocced solids               | 26                   |
|                         | 1                          | 15         | Fe-precip        | 340                             |                    |                         |                              |                      |
|                         | 1                          | 13,400     | Liquid           | 0.06                            |                    |                         |                              |                      |

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Table 2.A.2 (continued)

| Leachate                                      | Attrition scrub time (min) | Dry wt (g) | Mesh size (mesh) | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks                        | Moisture content (%) |
|---|----------------------------|------------|------------------|---------------------------------|--------------------|-------------------------|--------------------------------|----------------------|
| Pretreatment                                  |                            | 252        |                  | 460                             |                    |                         | pH = 9 with NH <sub>4</sub> OH | 16                   |
| 300 g, 0.2 M NH <sub>4</sub> HCO <sub>3</sub> | 1                          | 6.3        | 20               | 190                             | 97                 | 104                     |                                |                      |
|   | 1                          | 11         | 50               | 1,300                           |                    |                         | Resin stream (15-g original)   |                      |
|   | 1                          | 14         | 200              | 730                             |                    |                         | Jig underflow                  |                      |
|   | 1                          | 227        | -200             | 230                             |                    |                         | Flocced solids                 | 60                   |
|   | 1                          | 14         | Fe-precip        | 3,000                           |                    |                         |                                |                      |
|   | 1                          | 13,500     | Liquid           |                                 | 0.03               |                         |                                |                      |

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Table 2.A.3. Repeatability and resins for storage pad area soils—Drum 1 for 1.75-min attrition scrubbing and leaching with 200 g, 2% NaOCl and 100 g, 0.4 M NH<sub>4</sub>HCO<sub>3</sub>

| Leachate          | Dry wt (g)       | Mesh size (mesh) | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks                                     | Moisture content (%) |
|-------------------|------------------|------------------|---------------------------------|--------------------|-------------------------|---|----------------------|
| <i>Soil No. 3</i> |                  |                  |                                 |                    |                         |   |                      |
| Pretreatment      | 252 <sup>a</sup> |                  | 460 <sup>a</sup>                |                    |                         | pH = 9 with NH <sub>4</sub> OH <sup>a</sup> | 16 <sup>a</sup>      |
|                   | 2.5              | 20               | 71                              | 83                 | 88                      |   | 60                   |
|                   | 0                | 50               | 0                               |                    |                         | Resin stream (15-g original)                |                      |
|                   | 11               | 200              | 590                             |                    |                         | Jig underflow                               | 48                   |
|                   | 209              | -200             | 120                             |                    |                         | Flocced solids                              | 19                   |
|                   | 6                | Fe-precip        | 4,200                           |                    |                         |   | 6                    |
|                   | 8,900            | Liquid           | 5.09                            |                    |                         |   |                      |
|                   | 6.2              | 20               | 32                              | 97                 | 102                     |   | 21                   |
|                   | 13               | 50               | 1,300                           |                    |                         | Resin stream (15-g original)                |                      |
|                   | 15               | 200              | 540                             |                    |                         | Jig underflow                               | 46                   |
|                   | 226              | -200             | 200                             |                    |                         | Flocced solids                              | 27                   |
|                   | 6                | Fe-precip        | 2,500                           |                    |                         |   | 5                    |
|                   | 13,500           | Liquid           | 2.37                            |                    |                         |   |                      |
| <i>Soil No. 1</i> |                  |                  |                                 |                    |                         |   |                      |
| Pretreatment      | 264 <sup>b</sup> |                  | 390 <sup>b</sup>                |                    |                         | Soil samples = 300 g <sup>b</sup>           | 12 <sup>b</sup>      |
|                   | 3.9              | 20               | 39                              | 89                 | 134                     |   | 61                   |
|                   | 0                | 50               | 0                               |                    |                         | Resin stream (15-g original)                |                      |
|                   | 30               | 200              | 37                              |                    |                         | Jig underflow                               | 37                   |
|                   | 214              | -200             | 140                             |                    |                         | Flocced solids                              | 37                   |

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Table 2.A.3 (continued)

| Leachate | Dry wt (g) | Mesh size (mesh) | Contaminant concentration (ppm) | Solids balance (%) | Contaminant balance (%) | Remarks                      | Moisture content (%) |
|----------|------------|------------------|---------------------------------|--------------------|-------------------------|------------------------------|----------------------|
|          | 5          | Fe-precip        | 7,200                           |                    |                         |                              | 5                    |
|          | 8,300      | Liquid           | 8.13                            |                    |                         |                              |                      |
|          | 7.1        | 20               | 36                              | 100                | 132                     |                              | 41                   |
|          | 15         | 50               | 2,400                           |                    |                         | Resin stream (15-g original) |                      |
|          | 37         | 200              | 64                              |                    |                         | Jig underflow                | 30                   |
|          | 221        | -200             | 250                             |                    |                         | Flocced solids               | 7                    |
|          | 6          | Fe-precip        | 2,700                           |                    |                         |                              | 7                    |
|          | 8,400      | Liquid           | 2.87                            |                    |                         |                              |                      |

<sup>a</sup>Pretreatment—Soil No. 3.

<sup>b</sup>Pretreatment—Soil No. 1.

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Table 2.A.4. Repeatability and resin tests for 1.75-min attrition scrubbing and leaching with 300 g, 2% NaOCl and 100 g, 0.2 M NH<sub>4</sub>HCO

| Leachate          | Dry wt (g)       | Mesh size (mesh) | Contaminant concentration (ppm) | Solid balance (%)                  | Contaminant balance (%) | Remarks                           | Moisture content (%) |
|-------------------|------------------|------------------|---------------------------------|------------------------------------|-------------------------|-----------------------------------|----------------------|
| <i>Soil No. 1</i> |                  |                  |                                 |                                    |                         |                                   |                      |
| Pretreatment      | 264 <sup>a</sup> |                  | 442 <sup>a</sup>                | (370 ppm ORNL, by GS) <sup>a</sup> |                         | Soil samples = 300 g <sup>a</sup> | 12 <sup>a</sup>      |
|                   | 4.7              | 20               | 51                              | 89                                 | 76                      | Screened                          | 53                   |
|                   | 36               | 200              | 72                              | (WSTC feed analysis)               |                         | Jig underflow                     | 30                   |
|                   | 3                | 200              | 152                             | 89                                 | 67                      | Jig overflow                      | 85                   |
|                   | 191              | -200 (floc)      | 257                             | (ORNL feed analysis)               |                         | Flocced solids                    |                      |
|                   | 6                | -200 (Fe-precip) | 2,839                           |                                    |                         | Fe precip solids                  |                      |
|                   | 12,800           | Liquid           | 0.74                            |                                    |                         |                                   |                      |
| <i>Soil No. 3</i> |                  |                  |                                 |                                    |                         |                                   |                      |
| Pretreatment      | 252 <sup>b</sup> |                  | 634 <sup>b</sup>                | (420 ppm ORNL, by GS) <sup>b</sup> |                         | Soil samples = 300 g <sup>b</sup> | 16 <sup>b</sup>      |
|                   | 10.1             | 20               | 76                              | 71                                 | 142                     | Screened                          | 39                   |
|                   | 13               | 200              | 1,368                           | (WSTC feed analysis)               |                         | Jig underflow                     | 37                   |
|                   | 1                | 200              | 2,635                           | 71                                 | 103                     | Jig overflow                      | 98                   |
|                   | 162              | -200 (floc)      | 587                             | (ORNL feed analysis)               |                         | Flocced solids                    |                      |
|                   | 6                | -200 (Fe-precip) | 8,452                           |                                    |                         | Fe precip solids                  |                      |
|                   | 11,000           | Liquid           | 0.23                            |                                    |                         |                                   |                      |

<sup>a</sup>Pretreatment—Soil No. 1.

<sup>b</sup>Pretreatment—Soil No. 2.

2-23

000081

6656

**Table 2.A.5. Measured and calculated uranium levels after 1.75-min attrition scrubbing and leaching with 300 g, 2% NaOCl and 100 g, 0.2 M NH<sub>4</sub>HCO**

|   | Weight<br>(g) | Measured<br>(ppm) | Calculated<br>(ppm) |
|---|---------------|-------------------|---------------------|
| <i>Soil No. 1</i>                       |               |                   |                     |
| Liquid after solids settled             | 12,800        | 5.74              |                     |
| Uranium added to soil                   | 191           | 250.00            | 323.08              |
| Liquid after 1st flocculation           | 12,800        | 0.92              |                     |
| Liquid after 2d flocculation            | 12,800        | 0.72              |                     |
| U added to flocced material             | 6             | 2,839             | -42.67              |
| Liquid after Fe precip and flocculation | 12,800        | 0.74              |                     |
| <i>Soil No. 3</i>                       |               |                   |                     |
| Liquid after solids settled             | 11,000        |                   | 1.61                |
| Uranium added to soil                   | 162           | 587.00            | 92.35               |
| Liquid after 1st flocculation           | 11,000        |                   | 0.25                |
| Liquid after 2d flocculation            | 11,000        |                   | 0.17                |
| U added to flocced material             | 6             | 8,452             | -111.83             |
| Liquid after Fe precip and flocculation | 11,000        |                   | 0.23                |

**Part 3****SELECTIVE EXTRACTION/LEACHING-CHELATION APPROACHES TO  
URANIUM DECONTAMINATION IN SOILS: PROGRESS REPORT**

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Prepared for the Office of Technology Development  
Uranium in Soils Integrated Demonstration

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## ACRONYMS AND INITIALISMS

|         |   |
|---------|---|
| ACH     | aceto hydroxamic acid                                   |
| CBD     | citrate-bicarbonate-dithionate                          |
| CDTA    | 1,2-diamineocyclohexanetetraacetic acid                 |
| DPTA    | diethylenetriaminepentaacetic acid                      |
| EDTA    | ethylenediaminetetraacetic acid                         |
| FEMP    | Fernald Environmental Management Project                |
| ICP-AES | inductively coupled plasma-atomic emission spectroscopy |
| NAA     | neutron activation analysis                             |
| ORNL    | Oak Ridge National Laboratory                           |
| USID    | Uranium in Soils Integrated Demonstration               |

## INTRODUCTION

The objective of this project is to develop and test chelator-based extraction processes for the near quantitative removal of uranium from contaminated soils. Requirements for the process are that it should not destroy the soil or generate secondary waste streams that are difficult to treat. The project is directed specifically at remediation of the uranium-contaminated soils at the Fernald Environmental Management Project (FEMP). However, we expect that the results of this decontamination project will have potential applicability to other sites and other contaminants.

The FEMP site was originally a uranium production complex established by the Atomic Energy Commission in 1951. This facility, which was previously called the Feed Materials Production Center, purified and processed uranium and thorium metals used in the U.S. weapons complex from 1953 to 1989. These activities resulted in significant uranium contamination of the soils near Fernald. The precise extent of the contamination is unknown, but estimates suggest that 2,000,000 to 4,000,000 m<sup>3</sup> of soil may have unacceptable levels of uranium contamination (Francis et al. 1993).

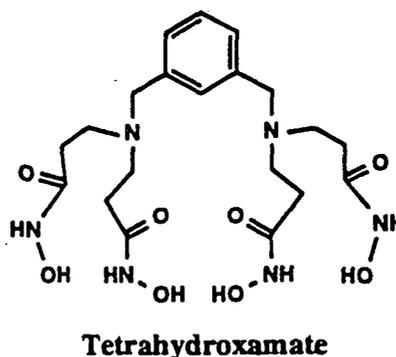
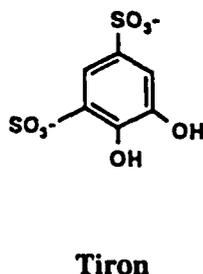
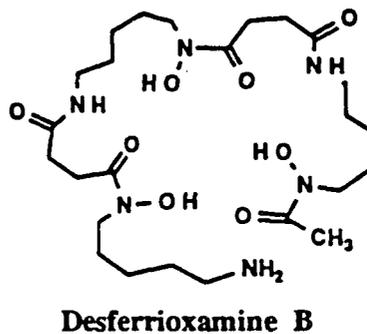
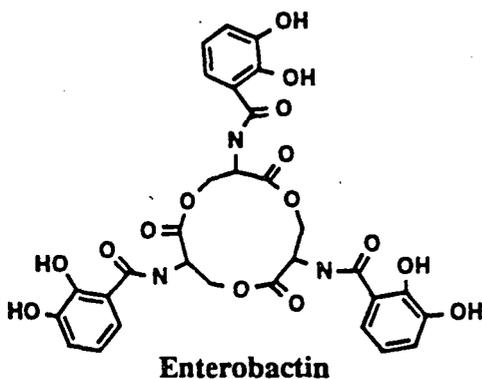
Current technologies for remediation of radioactivity contaminated soils involve excavation of the site and transport of the contaminated soil to a secure repository, immobilization of the radioactive metals in place, or separation (usually by density or size) of the more highly contaminated soil fractions. Transport and storage of the entire volume of contaminated soil at Fernald would be exceedingly expensive. Immobilization approaches suffer from poor public acceptance and from costly ongoing monitoring. The most cost-effective, permanent, and publicly acceptable treatment option is likely to be separation of the contaminant from the soil and return of the decontaminated soil to the site. Physical separation methods for soil decontamination can be effective for soils in which a large fraction of the contamination is concentrated in a small volume of soil that can be separated from noncontaminated soil by particle size or density. However, initial characterization of the uranium contamination at Fernald demonstrated that significant contamination is associated with all size and density fractions of the soil (Lee and Marsh 1992). Consequently, it appears that traditional physical separation methods based on size or density fractionation alone will not be feasible for Fernald soils and that effective soil decontamination approaches for Fernald soils will probably include a chemical extraction process.

One promising approach for the extraction of toxic or radioactive metals from contaminated soils involves the use of chelators to complex and thus solubilize the target metals. This approach would involve solubilization of the metals into a leaching solution by the chelator and separation of the leaching solution from the decontaminated soil. The pregnant leach solution is recycled to leach more contaminant. The metals are separated from the leachate for permanent storage or reuse, and the decontaminated soil is returned to the site. Such a process can be implemented in a vat (Rubin et al. 1990; Richardson et al. 1989) or in a heap configuration (Samani et al. 1991). For metals that are readily hydrolyzed and/or are strongly sorbed to soil surfaces, quantitative solubilization of the metal contaminant under mild conditions can be challenging.

Leaching solutions for the decontamination of soils have characteristically employed water, acids, carbonates, or chelators, most notably carboxylates (citric acid) and amino carboxylates [ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA)]. The dissolution of solid metal phases (particularly iron and manganese oxyhydroxides) by various

chelators has been studied extensively (Lin and Benjamin 1990; Schindler and Stumm 1987; Stumm and Furrer 1987; Eisenlauer and Matijevic 1980). Although the chemical speciation of uranium in Fernald soils is still under investigation, it appears that hydroxide and oxide and, perhaps, carbonate and phosphate phases are prime candidates. We expect the approaches used for the dissolution of sparingly soluble metal oxyhydroxides to be generally applicable to uranium in soils. These studies have shown that the rate and extent of dissolution of metal oxyhydroxide phases are increased by chelators that have high binding constants for the metal or that have structural features related to a high binding constant (i.e., are bidentate or multidentate and/or are capable of forming five-membered rings during coordination with the metal).

A particularly interesting class of chelators with extraordinarily high affinity for metal ions are the microbial siderophores (Neilands 1984; Raymond et al. 1984) and synthetic analogs of the siderophores (Durbin et al. 1980; Raymond and Smith 1981). Siderophores are low-molecular-weight extracellular metal chelators produced by microbes in response to low availability of soluble iron in the environment. Approximately 300 natural siderophores have been isolated and characterized; almost all of the siderophores characterized to date employ either the catecholate or the hydroxamate functionality for metal binding. The structures of two siderophores and two synthetic analogs are shown here.



These chelators have some of the highest known binding constants for hard Lewis acid metal cations, such as iron(III), uranium(IV), and thorium(IV). The potential application of siderophores and synthetic analogs to actinide decontamination has been recognized by Raymond and colleagues (Durbin et al. 1980; Raymond and Smith 1981). The use of siderophores or siderophore analogs for soil decontamination is especially attractive because siderophores function in soil environments to do exactly what soil decontamination requires: to solubilize metals from sparingly soluble phases.

## MATERIALS AND METHODS

### SOIL SAMPLES

Uranium-contaminated soil samples used in this study were obtained at FEMP, mixed, and shipped to Los Alamos by FEMP personnel. One of the treatability samples (B-12, Drum 8) was obtained from the Plant 1 storage pad area; this sampling site is designated sp4 in the Uranium in Soils Integrated Demonstration (USID) Soil Characterization Report (Tidwell et al. 1992). The other samples (A-12, Drums 6 and 9, and A-14, Drums 11 and 14) were obtained near the waste incinerator site, which is outside of the Fernald production area; this site is designated sp9 in the USID Soil Characterization Report. The treatability samples from the incinerator site were nonuniform in gross appearance; one sample was fairly dry and crumbly, and another had water standing on portions of the soil surface. The moisture contents of "nonsaturated" cores taken from the A-12 and A-14 samples varied between 17.0 and 19.1% on an oven-dried basis. Initial analysis of the uranium content of 2.5-g samples taken from the same and from different A-12 and A-14 drums indicated that the uranium concentration in the treatability samples varied significantly.

To improve the homogeneity of samples used for leach testing, we took random cores from A-14, Drum 11, and air-dried them in a laboratory hood. The dried soils were mixed and sieved through a 1.7-mm sieve, and the material >1.7 mm was discarded. Soil <1.7 mm was further mixed in a paint shaker containing steel ball bearings for 45 s. Soil from B-12, Drum 8, was likewise dried and mixed.

### CHEMICALS

Desferrioxamine B was purchased from Ciba-Giegy as the mesylate salt and used as received. Enterobactin was prepared and purified as previously described (Brainard et al. 1992). Tiron (1,2-dihydroxy-3,5-benzenedisulfonic acid) was purchased from Sigma. All other chemicals were reagent grade or better and used as received.

### URANIUM ANALYSIS

#### Solids

Treated and untreated soil samples were analyzed for uranium by neutron activation analysis (NAA) by the Medical Radioisotopes and Reactor Application group at Los Alamos National

Laboratory (Garcia et al. 1982). Uranium concentrations reported here are based on the  $^{238}\text{Np}$  daughter resulting from activation of  $^{238}\text{U}$  and were calculated assuming the natural abundance of  $^{238}\text{U}$ . A limited number of soil samples were analyzed by acid digestion and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Soil digestion was performed in concentrated nitric acid for 120 to 144 h (1 g of soil in 25 mL of acid), and dilutions were prepared for ICP-AES analysis in 1%  $\text{HNO}_3$ . The results of the acid digestion, ICP-AES uranium analysis were generally 8 to 20% lower than the NAA analysis.

### Liquids

Leachates were analyzed for uranium and other metals of interest by ICP-AES on a Varian Model Liberty 200 spectrometer. Samples were run in 1%  $\text{HNO}_3$  with scandium correction. Some of the samples were spiked with known quantities of the metal of interest to ensure that matrix interferences were insignificant for the emission lines used for analysis. The lines used for analysis were 263 nm for uranium, 396 nm for aluminum, and 259 nm for iron. Other metals were analyzed by using the Rapid Quant software supplied by the manufacturer.

In some early experiments involving dissolution of solid uranium phases, dissolved uranium was determined by using the arsenazo dye method (Savin 1961).

### SOIL EXTRACTIONS

A 20:1 liquid-to-solid ratio was used in laboratory-scale batch extraction of soils. For the majority of the experiments presented in this report, 50 mL of extractant solution was added to 2.5 g of soil in a 50 mL centrifuge tube. Initial screening tests used a 6:1 liquid-to-solid ratio in a 50 mL centrifuge tube. The centrifuge tubes were placed on laboratory rotators and rotated at 15 rpm at room temperature for 0.5 to 120 h, depending on the experiment. Periodically, the centrifuge tubes were removed from the rotator and centrifuged at  $1500\times g$  for 10 min and 5 mL samples of the supernatant were removed for ICP-AES. The pH of the supernatant samples were measured after each centrifugation and acidified with nitric acid to  $\text{pH} < 2$ . All treatments were carried out in duplicate or triplicate, and the efficiencies of uranium removal were determined by calculating the fraction of uranium in the supernatant as a percentage of the total uranium. In experiments in which mass balance was not determined, the total uranium in the sample was estimated based on NAA of blended homogenized soil samples.

### MASS BALANCES

In some experiments, mass balances were determined at the end of the extraction. In these experiments, the treated soils were washed once with 50 mL of 0.001 M  $\text{Ca}(\text{NO})_2$  to more fully recover extractant solution remaining with the solids; washing the treated soil with distilled water resulted in dispersion of fine silt particles that remained suspended in the supernatant after centrifugation.

## RESULTS AND DISCUSSION

DISSOLUTION OF SOLID  $UO_2$  BY SIDEROPHORES

Before receiving the soil treatability samples from FEMP, we investigated the dissolution of  $UO_2$  by enterobactin, desferrioximine B, and monofunctional analogs of these siderophores. In part, the rationale for these experiments was based on the suitability of these chelators to bind uranium(IV) and the assumptions that (1)  $UO_2$  and related uranium(IV) minerals would be most difficult to dissolve, (2) the uranium in soils at some of the sites at Fernald would be uranium(IV), and (3) other systems under investigation by USID would be more suitable for dissolving uranium(VI) minerals and phases. The dissolution of  $UO_2$  by desferrioxamine B, acetyl hydroxamic acid, Tiron, catechol, and enterobactin are compared in Figs. 3.1 and 3.2.

The data in Fig. 3.1 show that hydroxamate chelators aid in the dissolution of  $UO_2$ , but the rate of dissolution under these conditions is very slow. By way of comparison, the addition of iron(III) as an oxidant at pH 2 resulted in quantitative dissolution of  $UO_2$  within 30 min in the presence of 0.01 M desferrioxamine B. In addition, these data show that 0.03 M acetyl hydroxamic acid is about

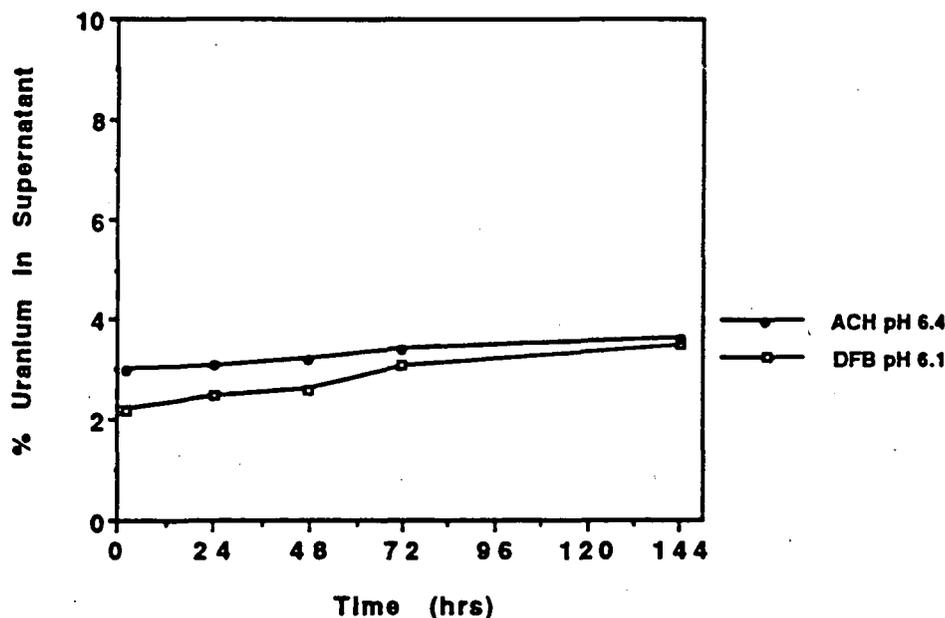


Fig. 3.1. Dissolution of  $UO_2$  by 0.01 M desferrioxamine B and 0.03 M acetyl hydroxamic acid.

equivalent to 0.01 M desferrioxamine B, suggesting that for dissolution of  $UO_2$  at pH ~6 the preorganization of the siderophore chelator does not enhance the rate of dissolution.

Figure 2 shows that chelators containing catechol functionalities are also effective in dissolving  $UO_2$ . Tiron and catechol are slightly more effective in dissolving  $UO_2$  than the hydroxamate chelators acetohydroxamic acid (ACH) and desferrioxamine B. However, the siderophore enterobactin was not particularly effective in dissolving  $UO_2$ . Unfortunately, the pH in the enterobactin sample dropped to <5 during the experiment, which makes the enterobactin result somewhat equivocal. This negative result for enterobactin may be related to the low pH in this experiment and the high basicity of the enterobactin hydroxyl groups, rather than a lack of competence of enterobactin.

These results confirm the difficulty in dissolving refractory mineral phases of uranium. Although these chelators do enhance the aqueous dissolution of  $UO_2$  at neutral pHs, the rates are disappointing.

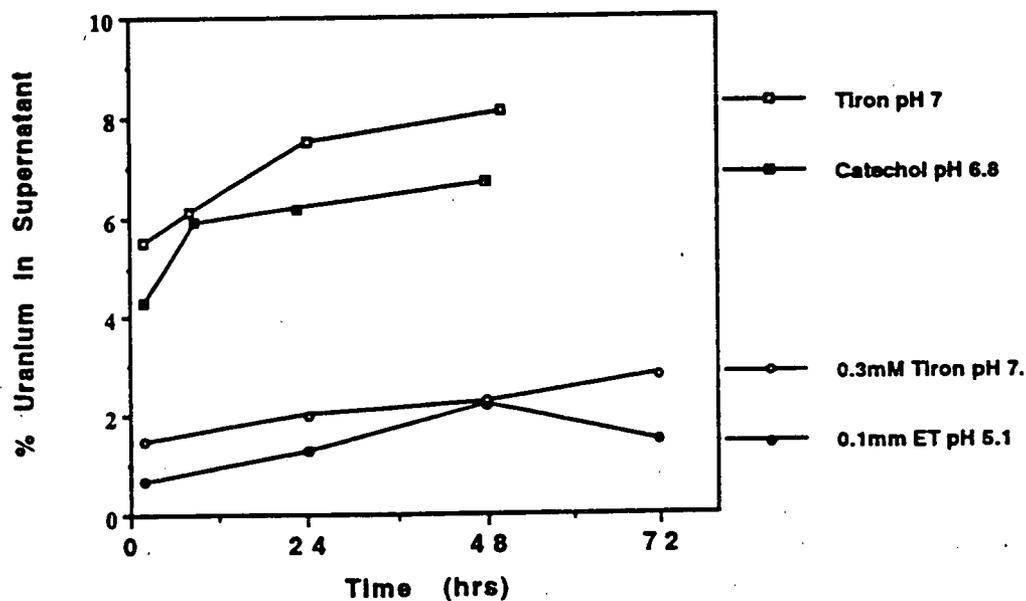


Fig. 3.2. Dissolution of  $UO_2$  by 0.012 M Tiron, 0.012 M catechol, 0.003 M Tiron, and 0.001 M enterobactin.

## SCREENING OF SYNTHETIC CHELATORS

The extraction of uranium from the Fernald treatability samples by three synthetic Chelators selected for their high affinity for uranium(VI) and uranium(IV) is compared in Tables 3.1 through 3.6. As a benchmark, the extraction of uranium by carbonate is given in Tables 3.7 and 3.8. These screening tests were performed to assess the importance of pH and concentration on the extraction efficiencies and to screen for promising synthetic chelators for further study. All extractions were performed for 15 h at a 1:6 solid-to-liquid ratio.

Table 3.1. Screening test: Extraction of uranium from incinerator site soil by CDTA<sup>a</sup>

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.007                | 6.5         | 0.2                        |
| 0.007                | 7.0         | 0.2                        |
| 0.007                | 7.1         | 0.3                        |
| 0.015                | 6.3         | 1.2                        |
| 0.015                | 6.9         | 0.2                        |
| 0.015                | 7.1         | 0.3                        |
| 0.031                | 5.7         | 0.8                        |
| 0.031                | 6.9         | 0.7                        |
| 0.031                | 7.0         | 0.3                        |

<sup>a</sup>CDTA = 1,2 diaminocyclohexanetraacetic acid.

\*Hydroxamate chelators were not included in the screening because speciation diagrams [based on thorium(IV) data] and sorption isotherms of uranium(VI) hydroxamate complex on clays suggested that the cationic character of hydroxamate complexes resulted in sorption of the complex to clay surfaces. Consequently, hydroxamate chelators are unlikely to be effective extractants in soils.

**Table 3.2. Screening test: Extraction of uranium from storage pad soil by CDTA<sup>a</sup>**

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.016                | 7.0         | 20.7                       |
| 0.016                | 7.2         | 28.5                       |
| 0.016                | 7.6         | 21.5                       |
| 0.032                | 6.8         | 35.7                       |
| 0.032                | 6.5         | 35.1                       |
| 0.032                | 7.4         | 45.0                       |
| 0.064                | 6.6         | 43.7                       |
| 0.064                | 7.1         | 44.3                       |
| 0.064                | 7.6         | 39.9                       |

<sup>a</sup>CDTA = 1,2-diaminocyclohexanetetraacetic acid.

**Table 3.3. Screening test: Extraction of uranium from incinerator site soil by DTPA**

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.007                | 6.7         | 0.4                        |
| 0.007                | 7.1         | 0.6                        |
| 0.007                | 7.6         | 1.2                        |
| 0.015                | 6.2         | 0.4                        |
| 0.015                | 6.8         | 0.4                        |
| 0.015                | 7.5         | 0.9                        |
| 0.031                | 5.4         | 0.8                        |
| 0.031                | 6.4         | 0.7                        |
| 0.031                | 7.5         | 1.2                        |

**Table 3.4. Screening test: Extraction of uranium from storage pad soil by DTPA**

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.016                | 7.15        | 39.0                       |
| 0.016                | 7.48        | 42.6                       |
| 0.016                | 7.88        | 44.0                       |
| 0.032                | 7.07        | 41.3                       |
| 0.032                | 7.37        | 50.9                       |
| 0.032                | 8.27        | 51.6                       |
| 0.064                | 6.78        | 41.5                       |
| 0.064                | 7.02        | 47.7                       |
| 0.064                | 7.92        | 63.6                       |

**Table 3.5. Screening test: Extraction of incinerator site soil by Tiron**

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.007                | 7.0         | 5.2                        |
| 0.007                | 7.5         | 13.7                       |
| 0.007                | 7.8         | 4.1                        |
| 0.015                | 7.1         | 15.6                       |
| 0.015                | 7.1         | 19.4                       |
| 0.015                | 8.1         | 28.3                       |
| 0.031                | 6.8         | 20.6                       |
| 0.031                | 7.0         | 21.3                       |
| 0.031                | 8.3         | 33.3                       |

**Table 3.6. Screening test: Extraction of uranium from storage pad soil by Tiron**

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.008                | 7.9         | 32.5                       |
| 0.008                | 8.2         | 28.5                       |
| 0.008                | 8.5         | 39.7                       |
| 0.016                | 7.1         | 70.6                       |
| 0.016                | 7.1         | 69.6                       |
| 0.016                | 8.1         | 70.9                       |
| 0.032                | 6.8         | 72.1                       |
| 0.032                | 7.0         | 55.8                       |
| 0.032                | 8.3         | 66.1                       |
| 0.064                | 7.1         | 60.3                       |
| 0.064                | 7.4         | 62.6                       |
| 0.064                | 8.5         | 61.5                       |

**Table 3.7. Screening test: Extraction of uranium from incinerator site soil by  $K_2CO_3$**

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.007                | 8.0         | 9.6                        |
| 0.007                | 8.7         | 25.4                       |
| 0.015                | 8.1         | 19.5                       |
| 0.015                | 8.7         | 31.1                       |
| 0.031                | 8.6         | 29.5                       |
| 0.031                | 9.2         | 41.2                       |

**Table 3.8. Screening test: Extraction of uranium from storage pad soil by  $K_2CO_3$**

| Concentration<br>(M) | Final<br>pH | Amount<br>extracted<br>(%) |
|----------------------|-------------|----------------------------|
| 0.016                | 7.5         | 35.8                       |
| 0.016                | 8.1         | 33.7                       |
| 0.032                | 7.6         | 51.9                       |
| 0.032                | 8.5         | 59.7                       |
| 0.064                | 7.6         | 46.8                       |
| 0.064                | 9.6         | 63.7                       |

A 6:1 liquid-to-solid ratio was used in these initial screening experiments, which were performed overnight (~15 h). The concentrations used in these initial tests were selected to give uranium ligand ratios of 1:5, 1:10, and 1:20, based on the uranium concentrations reported by Lee and Marsh (1992). The concentrations of uranium in the treatability samples received by Los Alamos were much lower. Consequently, the uranium ligand ratios are ~1:20, 1:40, and 1:80 for the incinerator soil and ~1:40, 1:80, and 1:160 for the storage pad soil. The pH of the leachate solutions at each chelator concentration was adjusted to 4, 7, or 10 prior to the experiment. However, the soil buffered these batch tests rather significantly, so that the pH range examined in these tests is narrow. The rationale for the relatively long leaching times employed was based on the belief that soil decontamination at Fernald would probably be implemented by heap leaching rather than vat leaching because of the predicted lower cost and larger throughput.

Comparison of these data indicates that the amino carboxylate chelators 1,2-diaminocyclohexanetetraacetic acid (CDTA) and DTPA are least effective and the carbonate and Tiron were most effective in extracting uranium from the Fernald soils. In agreement with results obtained by Lee and Marsh (1992), the uranium in the storage pad soil is more readily leached than in the incinerator soil.

The effectiveness of all of the chelators studied showed a modest dependence on concentration over the range of concentrations (0.007 to 0.064 M) used in these tests; higher concentrations of chelator and of carbonate yielded better extractions. All of the chelators also showed relatively small pH dependences over the limited range of pHs examined.

## SOIL EXTRACTIONS WITH TIRON

Results from dissolution experiments on solid  $UO_2$  and initial batch tests on Fernald soils suggested that Tiron was the most effective chelator of those initially examined. This synthetic

chelator has the same catechol functionality as natural siderophores and forms highly stable negatively charged complexes with metals. The negative charge of the uranium-Tiron complex is expected to aid in the solubility and mobility of the dissolved metal in a soil matrix containing cation exchange sites. These properties make Tiron particularly attractive as a potential extractant for uranium. It is very likely that the understanding gained with Tiron will have applicability to other catecholate-based extractants (e.g., siderophores).

The extraction of uranium from Fernald soils by 0.01 and 0.1 *M* Tiron is shown in Tables 3.9 and 3.10. These data further confirm that Tiron is an effective extractant for uranium in Fernald soils. At room temperature, with 0.1 *M* Tiron, the storage pad soil could be decontaminated to calculated levels (46.5 mg/kg) below the initial target level of 50 mg/kg, although a leaching time of 41 h was required. However, the incinerator site soil was only decontaminated to a calculated level of 194 mg/kg, well above the initial target level. The dependence on concentration observed in the initial screening was confirmed.

The kinetics of uranium extraction are strongly biphasic; ~80% of the total uranium removed over a 37- to 41-h leaching time is removed within the first 2 h. The biphasic nature of the extraction kinetics can be visualized in Figs. 3.3 and 3.4. These data suggest that, although the second phase of extraction is relatively slow, the leaching of the uranium from the soil in a batch test is not complete after 40 h. Consequently, higher extraction efficiencies may be expected for longer extraction times.

**Table 3.9. Tiron extraction of uranium from incinerator site soil<sup>a</sup>**

| Extractant                         | Time (h) | Amount extracted (%) |
|------------------------------------|----------|----------------------|
| Deionized water,<br>pH 7.7-8.3     | 2        | < 1.                 |
|                                    | 16       | 5                    |
|                                    | 37       | < 1.                 |
|                                    |          | 5                    |
|                                    |          | < 1.                 |
|                                    |          | 5                    |
| 0.01 <i>M</i> Tiron,<br>pH 7.4-7.9 | 2        | 35.2 ± 0.7           |
|                                    | 16       | 38.0 ± 1.4           |
|                                    | 37       | 41.5 ± 1.6           |
| 0.1 <i>M</i> Tiron,<br>pH 7.3-7.4  | 2        | 51.7 ± 0.2           |
|                                    | 16       | 58.6 ± 4.0           |
|                                    | 37       | 66.3 ± 1.8           |

<sup>a</sup>Initial concentration 577 mg/kg.

Table 3.10. Tiron extraction of uranium from storage pad site soil<sup>a</sup>

| Extractant                  | Time (h) | Amount extracted (%) |      |
|-----------------------------|----------|----------------------|------|
| Deionized water, pH 8.3-9.6 | 2        | 8.9                  | ±0.5 |
|                             | 20       | 12.0                 | ±0.6 |
|                             | 41       | 14.8                 | ±1.4 |
| 0.01 M Tiron, pH 7.8-8.2    | 2        | 60.1                 | ±0.6 |
|                             | 20       | 74.1                 | ±2.8 |
|                             | 41       | 72.0                 | ±2.5 |
| 0.1 M Tiron, pH 7.3-7.6     | 2        | 74.0                 | ±3.2 |
|                             | 20       | 83.6                 | ±1.0 |
|                             | 41       | 91.1                 | ±0.5 |

<sup>a</sup>Initial concentration 523 mg/kg.

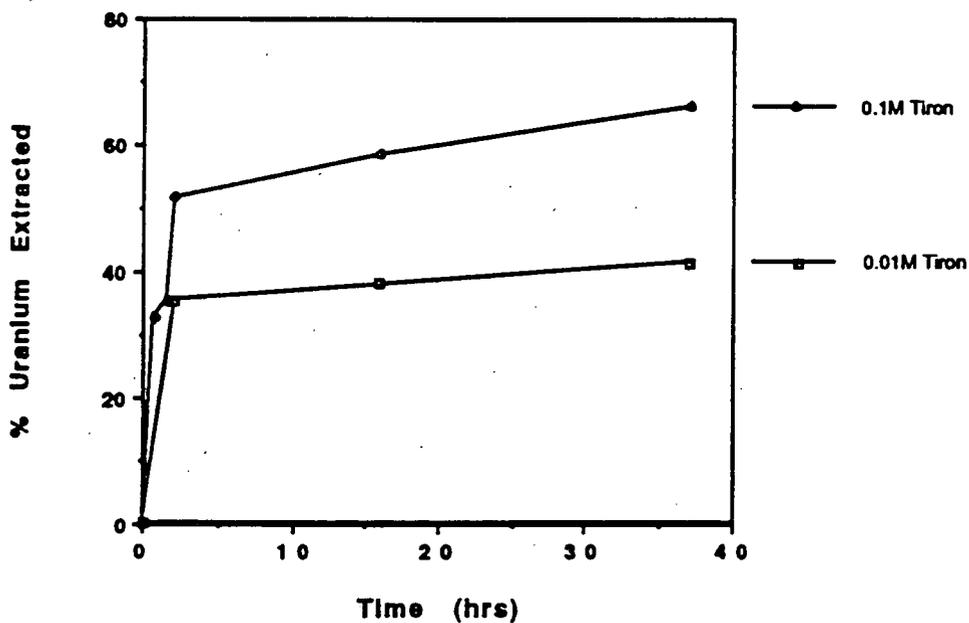


Fig. 3.3. Kinetics of uranium extraction from incinerator site soil.

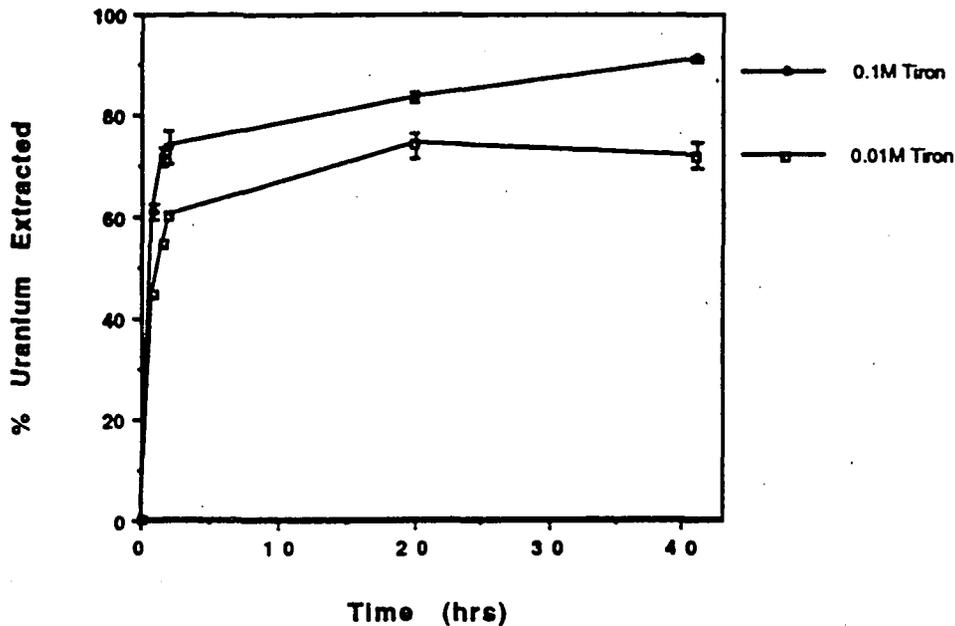


Fig. 3.4. Kinetics of uranium extraction from storage pad site soil.

#### SOIL EXTRACTIONS WITH TIRON-DITHIONITE

X-ray absorption spectroscopy of soil samples from Fernald have shown that most of the uranium is present as uranium(VI) (Morris et al. 1992). This finding is important in developing an optimal remediation strategy that uses siderophores or synthetic analogs because, although oxygen donor ligands (such as Tiron) bind uranium(VI) strongly, they are better suited to binding uranium(IV). Consequently, we have suggested that reduction of insoluble uranium(VI) phases in the presence of a strong chelator for uranium(IV) to prevent hydrolysis of and precipitation of uranium(IV) might enhance uranium extraction from soils. This suggestion is based on the coordination preferences of oxygen-donor ligands and on the effects that changes in oxidation state can have on the stability and solubility of metals in solid phases. Reductive dissolution mechanisms are known to enhance dissolution of sparingly soluble metal oxyhydroxide phases by weakening interactions between the reduced metal center and the solid lattice (Stone and Morgan 1987). This is believed to lower the kinetic barrier to metal dissolution. The extraction of uranium from Fernald soils by Tiron in the presence of a strong reductant (dithionite) is shown in Tables 3.11 and 3.12.

**Table 3.11. Tiron-dithionite extraction of uranium from incinerator site soil<sup>a</sup>**

| Extractant                                       | Time (h) | Amount extracted (%) |      |
|--|----------|----------------------|------|
| 0.1 M Dithionite,<br>pH 5.1-6.4                  | 2        | 3.9                  | ±2.1 |
|  | 16       | 5.6                  | ±0.7 |
|  | 37       | 5.3                  | ±1.1 |
| 0.01 M Tiron,<br>0.1 M Dithionite,<br>pH 5.3-6.3 | 2        | 53.6                 | ±3.4 |
|  | 16       | 59.8                 | ±3.7 |
|  | 37       | 59.5                 | ±3.9 |
| 0.1 M Tiron,<br>0.1 M Dithionite,<br>pH 6.0-6.6  | 2        | 71.6                 | ±3.0 |
|  | 16       | 83.1                 | ±0.7 |
|  | 37       | 88.6                 | ±2.2 |

<sup>a</sup>Initial concentration 577 mg/kg.

**Table 3.12. Tiron-dithionite extraction of uranium from storage pad site soil<sup>a</sup>**

| Extractant                                       | Time (h) | Amount extracted (%) |      |
|--|----------|----------------------|------|
| 0.1 M Dithionite,<br>pH 5.8-6.3                  | 2        | 12.7                 | ±0.5 |
|  | 20       | 9.5                  | ±0.6 |
|  | 41       | 7.8                  | ±0.1 |
| 0.01 M Tiron,<br>0.1 M Dithionite,<br>pH 6.1-6.4 | 2        | 96.7                 | ±2.7 |
|  | 20       | 97.9                 | ±2.1 |
|  | 41       | 99.9                 | ±2.3 |
| 0.1 M Tiron,<br>0.1 M Dithionite,<br>pH 6.0-6.6  | 2        | 101.2                | ±2.0 |
|  | 20       | 97.0                 | ±3.1 |
|  | 41       | 104.3                | ±5.2 |

<sup>a</sup>Initial concentration 523 mg/kg.

Notably, dithionite enhances the extraction of uranium by Tiron by about 30% in the incinerator site soil and from 10 to 25% in the storage pad soil. Extraction of the incinerator site soil with 0.1 M dithionite and 0.1 M Tiron removes 88% of the uranium, leaving a residual uranium concentration of 66 mg/kg. Although this level is still above the initial target value, we emphasize that the extractions to date have been performed at room temperature. Higher temperatures are very likely to improve the extraction efficiency, and further work is planned to investigate the effect of

temperature on leaching efficiency. In addition, the pH of these extractions is probably not optimal; these experiments were performed in unbuffered media, and the pH is probably a full pH unit too low, decreasing the reductive strength of the dithionite. In some experiments (not presented here), we have observed that the extraction efficiency is markedly decreased at lower pH values and enhanced at higher pH; batch tests with better pH control are in progress.

Extraction of the storage pad soil with 0.1 M dithionite and 0.1 M Tiron removes between 97 and 99% of the uranium, leaving a residual uranium concentration of <16 mg/kg.

### SELECTIVITY OF TIRON-DITHIONITE FOR URANIUM

A desirable characteristic of an efficient soil-extraction process is selectivity for the metal of concern so that soil properties are minimally altered and generation of secondary waste is minimized. The uranium, iron, and aluminum composition of the incinerator site leachates from batch tests with Tiron and Tiron-dithionite are shown in Table 3.13.

**Table 3.13. Uranium-iron-aluminum compositions of 2-h leachates from incinerator site soil**

| Extractant                        | Uranium<br>(mg/L) | Aluminum<br>(mg/L) | Iron<br>(mg/L) |
|-----------------------------------|-------------------|--------------------|----------------|
| 0.01 M Tiron                      | 10.5              | 31.8               | 32.0           |
| 0.1 M Tiron                       | 15.3              | 23.9               | 36.0           |
| 0.01 M Tiron,<br>0.1 M dithionite | 15.5              | 69.1               | 507            |
| 0.1 M Tiron,<br>0.1 M dithionite  | 22.1              | 86.5               | 679            |

This table demonstrates that the presence of dithionite in the extraction solution results in a large increase in the amount of iron and a modest but significant increase in the amount of aluminum in the leachate. It is clear from these results (and from reduction potentials) that dithionite is a nonselective reductant. The use of reducing agents to remove and characterize crystalline and amorphous iron and aluminum oxyhydroxides and aluminosilicates is well known in soil science (Jackson et al. 1986). Citrate/bicarbonate/dithionite (CBD) extraction has been employed to selectively dissolve oxides and hydroxides of iron, manganese, and aluminum in soils.

Although the concentrations of aluminum and iron exceed the concentration of uranium in the leachates, the fractions of iron and aluminum removed from the soil are modest. Based on the iron and aluminum contents of the incinerator site soil (56,000 and 32,000 mg/kg, respectively), the fractions of iron and aluminum leached by Tiron-dithionite extraction are 28 and 18%, respectively. However, these metals do contribute quite significantly to the complexity of waste stream treatment.

In addition, the presence of these metals in the leachate and the use of complexants and reducing agents to dissolve iron oxyhydroxides raises questions concerning the mechanism by which reductants act to enhance the extraction of uranium from the Fernald soils. Although our strategy in using reductants was derived from considerations of the coordination preferences of our chelators and the effectiveness of reductive dissolution mechanisms, it is likely that additional mechanisms may be important. As the Oak Ridge National Laboratory (ORNL) research group has pointed out, the amorphous iron and aluminum phases in soil are surface active and it is not unreasonable that the uranium contamination in soils is mostly associated with iron and aluminum oxyhydroxide phases. The dissolution of these phases by CDB or by Tiron-dithionite would be expected to liberate any associated trace metals. The CBD strategy developed and demonstrated by the ORNL group is probably quite similar in mechanism to that of Tiron-dithionite. It would appear that both groups have arrived at the same approach through different pathways.

It is instructive to compare the uranium, aluminum, and iron compositions of the leachates obtained under various conditions. Although indirect, potential evidence for the association of uranium contamination with iron oxyhydroxides could be obtained by correlation of the iron and aluminum dissolved with the uranium removed from the soils. Figures 3.5 through 3.8 show the relationships between iron and aluminum and uranium concentrations in the supernatants obtained from Tiron and Tiron-dithionite extractions.

Although there is some correlation between the levels of iron, aluminum, and uranium dissolved, the correlation is weak. Notably, the proportions of iron, aluminum, and uranium in the leachates

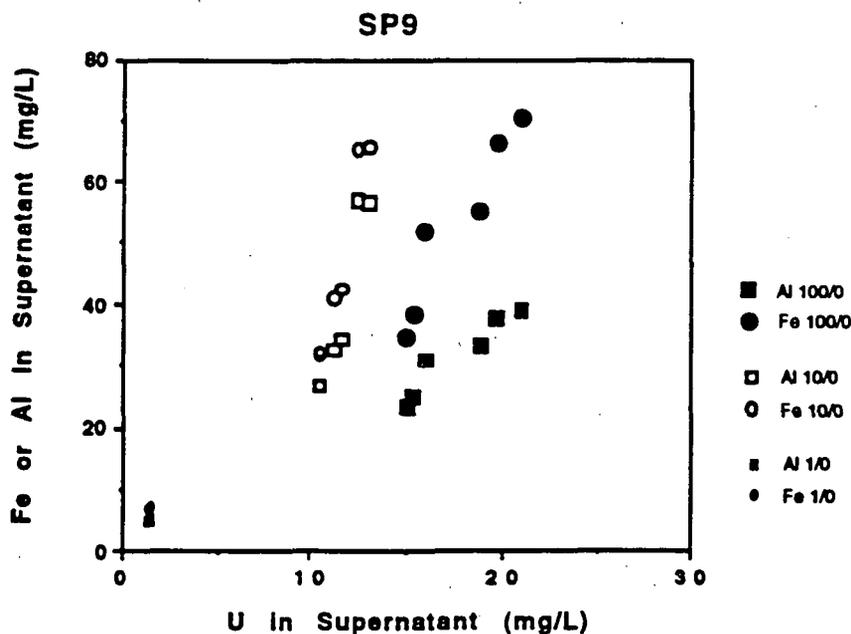
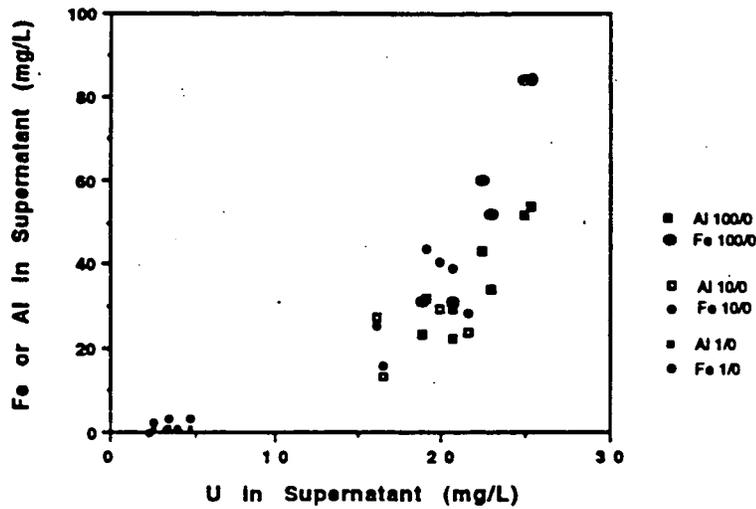


Fig. 3.5. Incinerator site leachates in the absence of dithionite. The legends refer to the metal (aluminum or iron) and concentrations of Tiron and dithionite (e.g., Al 1/0 refers to data obtained from aluminum at 1 mM dithionite).

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3.6. Storage pad site leachates in the absence of dithionite.

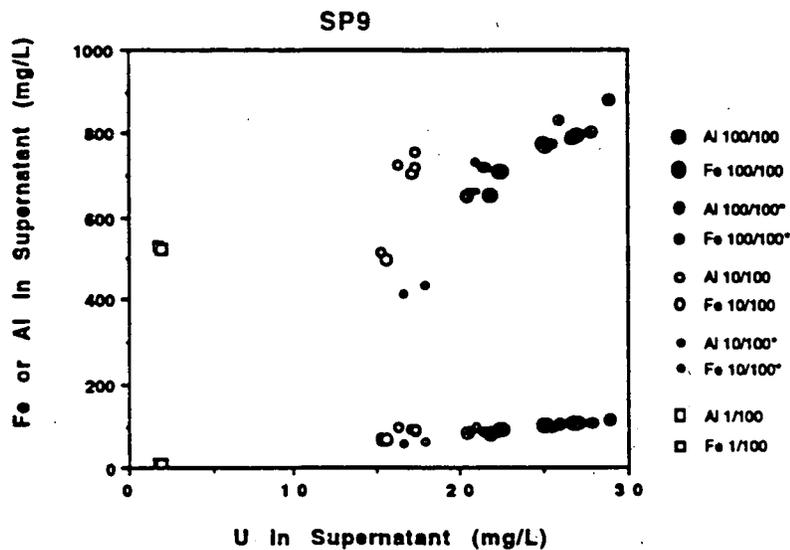


Fig. 3.7. Incinerator site leachates in the presence of dithionite.

vary significantly with chelator concentration. Consequently, it appears that the extraction of uranium into the leaching solution is not strictly correlated with the extraction of iron. Paradoxically, at lower chelator concentrations in the presence of dithionite, the extraction of iron appears to be favored over uranium. Coordination preferences predict that thermodynamically, Tiron should favor uranium(IV) over iron(II) and the extraction should be more selective at lower chelator concentrations. The reason for this behavior is unknown, but possible explanations include kinetic effects or hydrolysis of uranium(IV) at low chelator concentrations. Further work in this area is in progress.

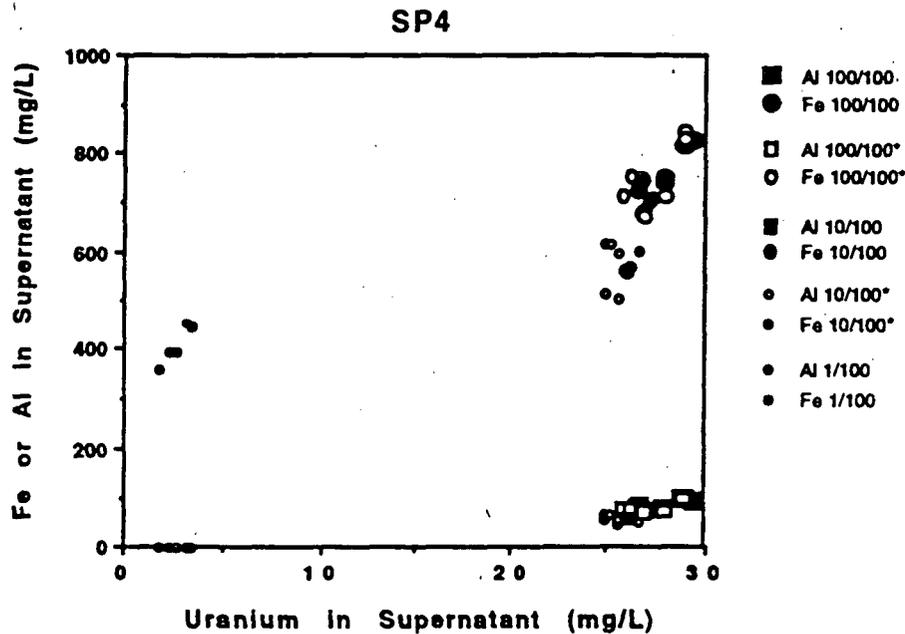


Fig. 3.8. Storage pad leachates in the presence of dithionite.

### SUMMARY AND CONCLUSIONS

The data in this progress report demonstrate that substantial fractions of the uranium in contaminated soils from Fernald can be removed by Tiron or Tiron-dithionite extraction.

Tiron extractions at room temperature removed from 60 to 90% of the uranium in the storage pad soil and from 35 to 65% of the uranium in the incinerator site soil, depending on the concentration of chelators (ranging from 0.01 to 0.1 M) and the duration of the extraction (2 to 40 h).

More effective leaching was obtained by combining Tiron with a reductant for uranium and iron. It is likely that this approach works by reducing uranium and iron phases in the soils and by enhancing the affinity of Tiron for uranium. Tiron-dithionite extractions removed 97 to 99% of the uranium in the storage pad soil and 50 to 88% of the uranium in the incinerator site soil.

The kinetics of uranium extraction by Tiron and Tiron-dithionite are biphasic: a substantial fraction of the uranium is removed in the first 2 h, and additional uranium is removed more slowly over the next 40 h.

These data suggest that Fernald soils similar to the storage pad soil can be decontaminated to levels exceeding the initial target level of 50 mg/kg, if sufficient throughput in an engineering design can be accommodated with residence times of 2 h or longer. The slow kinetics of dissolution makes heap leaching very attractive because longer residence times can be accommodated easily by increasing the size of the heap. Fernald soils characteristic of the incinerator site will be difficult to decontaminate to levels below 50 mg/kg by Tiron or Tiron-dithionite extraction under conditions examined thus far. However, it is probably premature to rule out use of chelator-based chemical decontamination methods for the incinerator soil because none of the tests reported to date have examined the effects of higher concentrations of chelator, higher temperatures, or better pH control. These strategies will probably improve the efficiency of extraction such that the target goal of 50 mg/kg may be attainable.

In closing, we emphasize the differences between batch leaching and column leaching. It is important to recognize that extraction efficiencies in a batch test are frequently exceeded in a column test. In tests involving the removal of lead from soil, Hanson and colleagues (Samani et al. 1991) have demonstrated that chelators that yielded only 30 to 60% removal in batch tests yielded 90 to 95% removal in column tests. One should recognize that removal efficiencies of 70 to 80% in batch tests are really quite adequate to justify optimism for effective column tests.

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## Part 4

**SOIL DECONTAMINATION BY AQUEOUS BIPHASIC EXTRACTION\***

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## ACRONYMS AND INITIALISMS

|         |   |
|---------|---|
| ABS     | aqueous biphasic separation                       |
| ACL     | Analytical Chemistry Laboratory of Argonne        |
| AEM     | analytical electron microscopy                    |
| ED      | electron-dispersive (X-ray detector)              |
| EELS    | electron energy loss spectrometer                 |
| KPA     | kinetic phosphorescence analysis                  |
| PEG     | polyethylene glycol                               |
| SEM/BSE | scanning electron microscope/backscatter detector |
| TEM     | transmission electron microscopy                  |
| TIMS    | thermal ionization mass spectrometry              |

## INTRODUCTION

The Aqueous Biphasic Separation (ABS) process is a new soil-washing technique that is being evaluated for the removal of uranium from contaminated soils. The process goal is to selectively separate and recover ultrafine particulate uranium from the soil without altering the physicochemical properties of the soil particles. The biphasic extraction process is a potential alternative to conventional soil-washing techniques that are based on physical separation methods, such as screening, classification, and flotation. Conventional methods of soil washing operate on the assumption that the contaminants are associated with fine soil particles. Because of their large specific surface area, separation of these fine soil particles can often be used as a means of concentrating soil contaminants. We hope to produce high levels of concentrated contaminant by selectively separating contaminant particulates from the ultrafine soil particles. The ABS process makes this separation feasible by taking advantage of the differences in the surface chemical properties of the contaminants and the soil particles.

The ABS process involves the selective partitioning of ultrafine particles between two immiscible aqueous phases (Chaiko et al. 1992, 1993). 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 system become concentrated in the more dense, lower phase, whereas the polymers are concentrated in the less dense, upper phase. When ultrafine particles of different surface characteristics are introduced into the system, they partition selectively according to the various physicochemical interactions that occur between the particle surface and the surrounding solvent.

The ABS process is capable of separating metal oxides, including  $UO_2$ , from clay and quartz. Preliminary experiments in which we have used model systems consisting of  $UO_2$ /clay mixtures have shown that the ABS technique is capable of selectively partitioning submicron-size  $UO_2$  particles from clay (D. J. Chaiko, Argonne National Laboratory, Argonne, Ill., unpublished data, 1993). In a polyethylene glycol (PEG)/ $Na_2CO_3$  biphasic system, the clay partitions into the top, PEG layer, with a partition coefficient of about 34. The submicron-size  $UO_2$  particles partition preferentially into the carbonate phase, with a partition coefficient of about 0.001. Thus, in a completely liberated clay/ $UO_2$  mixture, we would expect to achieve single-stage separation factors above 10,000.

The great advantage of the biphasic extraction process for remediating high-clay-content soils is its ability to separate submicron-size particles. In fact, there is no lower limit on particle size that can be treated in the ABS process. We have successfully separated particles as small as 20 nm and have selectively partitioned polymeric metal oxides as small as 2 nm (D. J. Chaiko, Argonne National Laboratory, Argonne, Ill., unpublished data, 1993). The upper limit on the size of soil particles that can be accommodated in a biphasic system appears to be about 40 to 50  $\mu m$ . In principle, particle size is limited by the settling rate because partitioning should depend on surface chemistry and not on bulk phase properties such as density.

The major objective of this work is to develop biphasic extraction technology for removing particulate uranium from soil to below regulatory cleanup limits. Our approach is to selectively partition particulate uranium into the lower, salt phase of the biphasic system and simultaneously partition the decontaminated soil into the upper, PEG layer. Our goal is to achieve a high

concentration of uranium partitioning into the lower, salt phase within a solids volume of less than 2% of the soil feed.

This report summarizes the results of batch partition studies that were designed to evaluate the effect of aqueous biphasic composition on uranium recovery from soil samples provided by the U.S. Department of Energy's (DOE's) Fernald Environmental Management Project (FEMP). The effect of grinding on the liberation of uranium and its subsequent recovery from the soil was also evaluated. The data that we collected include distribution coefficients, hydrodynamic properties of the biphasic systems, and phase diagrams. This information will be used in process design and scaleup.

Initial results from this work show that biphasic extraction is capable of selectively extracting and concentrating uranium from the soil samples collected near the waste incinerator at Fernald. Uranium concentrations were easily reduced from 500 to 600 mg/kg, to ~90 mg/kg, and in certain cases, the uranium concentration was reduced to ~15 mg/kg. However, the soil sample that was collected from around the Plant 1 storage pad did not respond as well to biphasic extraction. With this sample, the uranium concentration was reduced to only ~200 mg/kg and there was no evidence of selective uranium partitioning. Unfortunately, significant dissolution of the uranium took place during the biphasic separation of both soil samples. Methods to deal with this dissolution problem are discussed in this report. Our ongoing efforts to scale up the biphasic extraction process are also discussed.

## MATERIALS AND METHODS

### SOIL SAMPLES

Two soil samples contaminated with uranium were provided by FEMP and used in this study. One of the soil samples, designated 3810 and B-14, was taken from near the Plant 1 storage pad area. The second soil sample, designated 3812 and A-14, was collected near the waste incinerator. On receipt, the soil samples were dried at 110°C to a constant weight to determine moisture content. Sample A-14 contained 17.9 wt % moisture, and sample B-14 contained 12.7 wt % moisture. After drying, the soil samples were blended in a ceramic ball mill to break the clay lumps. Particle-size distributions were determined by wet sieving through 20.3-cm (8-in.) Tyler screens. The screen mesh size ranged from 2000  $\mu\text{m}$  (8 mesh) down to 44  $\mu\text{m}$  (325 mesh) in a geometric progression. Particles less than 44  $\mu\text{m}$  were further fractionated with an Andreasen pipette method according to the methods described by Loomis (1938). All of the screened size fractions were oven-dried at 100°C and then pulverized with a ceramic mortar and pestle before aliquots were removed for uranium analysis.

### REAGENTS

PEG, with an average molecular weight of 3350, was purchased from Fisher Scientific Company. PEG, with average molecular weights of 1500 and 1000, together with sodium sulfate, were purchased from Aldrich Chemical Company. Sodium hexametaphosphate and anhydrous

sodium carbonate were purchased from Mallinckrodt. All reagents were reagent grade or better and were used as received.

## URANIUM ANALYSIS

The screened fractions from the bulk Fernald soil samples were analyzed for total uranium content by the Analytical Division of Hazen Research, Inc. (Golden, Colo.) by means of wet digestion and fluorescence measurement. Hazen Research reported the uranium concentration as percentage  $U_3O_8$ , which we converted to elemental uranium concentration in units of milligrams per kilogram. All other samples were analyzed by wet digestion/phosphorescence, delayed neutron counting, or neutron activation. The wet digestion method was performed by the Analytical Chemistry Laboratory (ACL) of Argonne, while the delayed neutron counting and neutron activation analyses were performed by Activation Laboratories Ltd. (Ancaster, Ontario, Canada). All uranium concentrations are reported on a dry-weight basis.

### Wet Digestion Method

Samples analyzed by wet digestion included dry soil samples and solutions and slurries generated by biphasic extraction studies. Uranium in each type of sample was determined by kinetic phosphorescence analysis (KPA) after chemical treatment to dissolve solids, destroy organics (e.g., PEG), and remove interfering ions such as chloride. Dry solids were dissolved with a mixture of water, nitric acid, and hydrofluoric acid in a closed-vessel acid decomposition system (Parr bomb) heated overnight at 140 to 150°C. Slurries and solutions containing PEG (up to 30% in water) were either wet ashed with nitric acid and hydrogen peroxide or decomposed with nitric acid at elevated temperature and pressure in a microwave-heated digestion system. Solutions were freed of potential KPA interferences by taking them to dryness in the presence of nitric acid two or more times. Residues from this nitric acid treatment were brought to known volume with ~5% nitric acid for the laser KPA uranium measurements. A Model KPA-10 Kinetic Phosphorescence Analyzer (Chem Chek Instruments, Richland, Wash.) equipped with an autosampler and a flow-through cell was used to determine total uranium content.

### Isotopic Analysis

The isotopic distribution of uranium in some of the soil samples was determined by ACL. The procedure involves thermal ionization mass spectrometry (TIMS) after decomposition of the soil with nitric acid and hydrofluoric acid and isolation of the uranium by column-extraction chromatography (Horwitz et al. 1992). Details of the analytical procedure are presented in the Appendix.

### Analytical Electron Microscopy

Soil particles were mounted in epoxy, and polished cross sections were examined with a scanning electron microscope that uses a backscatter detector (SEM/BSE). After the uranium-containing regions of the soil were identified by SEM/BSE, they were isolated and remounted in nanoplast resin. The samples were then thin-sectioned and analyzed by analytical electron microscopy (AEM) by using a JEOL 2000FXII transmission electron microscope (TEM) fitted with

energy dispersive (ED) X-ray detectors and a Gatan parallel electron energy loss spectrometer (EELS).

This work was performed as part of the soils characterization subtask, and detailed results will be published separately by the soils characterization group.

## **BIPHASIC EXTRACTION TESTS**

Test-tube-scale batch extractions were performed by adding a weighed amount of soil to the salt solution in a 50-mL centrifuge tube. Each test used 0.2 to 1.0 g of soil to give a solids concentration of 0.5 to 2.5 wt %. This solids concentration is based on the total weight of the biphasic system. The solids were dispersed by thoroughly mixing the suspension with a high-speed mixer (Bio-vortexer, Biospec Products, Bartlesville, Okla.) for 90 s before adding the polymer solution. In some extraction tests, the order of adding the liquid phase was reversed (i.e., the solids were dispersed in the polymer solution). The biphasic system, with the suspended solids, was then mixed on a laboratory vortex mixer (American Scientific Products, McGaw Park, Ill.). The liquid phases were allowed to separate by gravity into two distinct layers that contained the partitioned solids.

The liquid phase ratios were varied, but rapid phase separation times depend on the PEG phase being the dispersed phase. After the phases were separated, the top PEG layer was scrubbed one or two times with fresh salt solution. Solid-liquid separation was performed by centrifuging the slurry in a laboratory centrifuge (Clinical Centrifuge, IEC, Needham, Mass.). The clear supernatant was decanted, and the solids were washed at least once with distilled water to remove any remaining polymer or salt. The solids were oven-dried at 90 to 100°C overnight, pulverized, and sent for uranium analysis. In instances in which we attempted to obtain a complete mass balance of uranium, the liquid phases were first filtered through 0.02- $\mu\text{m}$  syringe filters (Whatman Anotop).

## **RESULTS AND DISCUSSION**

### **SOIL CHARACTERIZATION**

#### **Particle-Size Distribution**

The soil samples were fractionated according to size so that we could determine the distribution of uranium as a function of particle size and prepare samples for the biphasic extraction tests. The size distribution data are given in Table 4.1. It should be noted that the silt fraction was screened at 44  $\mu\text{m}$  instead of the conventional 53  $\mu\text{m}$ . In future work we will use soil that is fractionated at 53  $\mu\text{m}$ .

The large amount of silt (53 to 2  $\mu\text{m}$ ) and clay (<2  $\mu\text{m}$ ) in the soil would make treatment by conventional soil-washing techniques difficult. On the other hand, the fact that over 80 wt % of the soil particles are <45  $\mu\text{m}$  makes this soil a good candidate for biphasic extraction. During screening, we did not observe the presence of organic material, such as leaves or roots in the soil.

#### **Uranium Distribution**

**Table 4.1. Size distribution of Fernald soil samples**

| Particle size<br>( $\mu\text{m}$ ) | Cumulative amount passing <sup>a</sup><br>(%) |        |
|------------------------------------|---|--------|
|                                    | A-14  | B-14   |
| 2000                               | 95.2  | 99.4   |
| 1000                               | 93.5  | 99.2   |
| 500                                | 90.8  | 98.0   |
| 250                                | 88.6  | 97.6   |
| 125                                | 86.9  | 96.4   |
| 75                                 | 85.4  | 91.5   |
| 45                                 | 83.6  | 85.5   |
| 5                                  | (27.2)  | (49.2) |
| 4                                  | (23.2)  | (36.8) |
| 3                                  | (18.7)  | (30.0) |
| 2                                  | (13.5)  | (23.2) |
| 1.3                                | (10.3)  | (17.6) |
| 0.6                                | (4.6)   | (8.6)  |

<sup>a</sup>The values in parentheses were determined with an Andreason pipette.

Two analytical methods, neutron activation and wet digestion, were used for determining the uranium concentrations in the fractionated soil samples. The results for both soil samples are given in Tables 4.2 and 4.3. Although the uranium concentrations are lower in the gravel-sized fractions of both soil samples, none of the fractions meets the proposed cleanup limit of 35 pCi/g (50 mg/kg). The majority of the uranium is distributed in the silt and clay fractions. As a result, conventional soil-washing techniques, such as size fractionation alone, would not be able to concentrate the uranium sufficiently to make that approach feasible. Although biphasic extraction is able to treat only the silt and clay, this approach can be justified by the large amount of the soil that is contained in these size fractions.

The uranium is not distributed homogeneously in the soil as a whole or within the individual size fractions listed in Tables 4.2 and 4.3. For example, microscopic examination of the silt and clay portion of A-14 soil was able to identify two major uranium phases appearing as discrete particles: uranium oxide and uranium phosphate. Some minor amounts of uranium were also associated with unidentified iron and calcium phosphate phases. Figure 4.1 shows a typical TEM

**Table 4.2. Concentration and distribution of uranium in sample A-14**

| Size fraction<br>( $\mu\text{m}$ ) | Particle-size<br>distribution<br>(wt %) | Uranium<br>(mg/kg) | Uranium<br>distribution<br>(wt %) |
|------------------------------------|---|--------------------|-----------------------------------|
| Whole soil                         |   | 505                | 100                               |
| >2000 (gravel)                     | 4.8                                     | 59.4               | 0.6                               |
| 2000-44 (sand)                     | 11.6                                    | 1151               | 26.5                              |
| <44 (silt & clay)                  | 83.8                                    | 441                | 72.9                              |

image of several thin-sectioned uranium particles from A-14. The uranium oxide phase was crystalline, as evidenced by electron diffraction patterns. The uranium phosphate phase appears to be an outgrowth from the uranium oxide and is probably a result of weathering of the oxide phase. It should be noted that the detection limit for uranium analysis by the ED detectors is about 1000 mg/kg. Although no uranium was found to be associated with the clay particles, it could have been present at concentrations below the ED detection limit.

The presence of particulate uranium in the soil is encouraging from the standpoint of using aqueous biphasic extraction to clean the soil. The ABS process is able to separate fine particles, but as in other physical separation techniques, it cannot remove uranium that is homogeneously distributed on all soil particles.

The heterogeneous nature of the uranium contamination has made it difficult to obtain reproducible uranium analyses. This, in turn, has made it difficult to derive accurate mass balances on uranium in the biphasic extraction tests. To quantify the reproducibility of the uranium analysis, four or five aliquots of soil sample A-14 were analyzed by wet digestion and neutron activation. The results, presented in Table 4.4, indicate the difficulty that was encountered in obtaining representative soil samples for analysis. The uranium concentrations ranged from 468 to 577 mg/kg, with wet digestion results being the most variable. The uranium concentrations determined by neutron activation were almost always lower than those obtained from wet digestion. This was surprising because one would expect less than 100% dissolution of the uranium during the wet digestion process. This would lead to underreporting of the uranium concentration. However, neutron activation and delayed neutron counting do not require dissolution of the sample to determine the uranium concentration. Therefore, one would not expect the uranium concentrations from neutron activation or delayed neutron counting to be less than those determined by wet digestion.

Uranium analysis, based on measurement of the  $^{235}\text{U}$  concentration by delayed neutron counting, has a better sensitivity than analysis based on measurement of  $^{238}\text{U}$  concentration by neutron activation. For this reason, our samples are now analyzed exclusively by delayed neutron counting.

Neutron activation and delayed neutron counting require knowledge of the isotopic composition of the sample to accurately calculate its total uranium concentration. Therefore, we analyzed several

**Table 4.3. Concentration and distribution of uranium in sample B-14**

| Size fraction, (μm) | Particle size distribution (wt %) | Uranium (mg/kg) | Uranium distribution (wt %) |
|---------------------|-----------------------------------|-----------------|-----------------------------|
| Whole Soil          |                                   | 455             | 100                         |
| >2000 (gravel)      | 0.6                               | 76.3            | 0.1                         |
| 2000-44 (sand)      | 13.9                              | 146.3           | 4.5                         |
| <44 (silt & clay)   | 85.5                              | 509             | 95.4                        |

soil aliquots of A-14 and B-14 to determine the isotopic distribution of uranium. The various source terms for the uranium contamination were slightly depleted in  $^{235}\text{U}$ , and we were interested in finding out if the isotopic distribution was the same for both A-14 and B-14. We were also interested in finding out if the isotopic distribution changed as a result of soil treatment by biphasic extraction or carbonate leaching.

The isotopic data are listed in Table 4.5. We were somewhat surprised to find detectable amounts of  $^{236}\text{U}$  in the soil. This is not a natural isotope and is found only in irradiated fuel. Its half-life is quite long because of the low disintegration rate, and therefore, this isotope does not significantly contribute to the radioactivity of the soil.

For natural uranium the abundance of  $^{234}\text{U}$  and  $^{235}\text{U}$  is 0.0054 and 0.7110 wt %, respectively. Clearly, the uranium in the untreated aliquot of A-14 is very close to its natural isotopic distribution. Leaching of A-14 and B-14 aliquots with sodium carbonate had no significant effect on the isotopic distribution. However, the uranium in the leached and unleached aliquots of B-14 were slightly depleted in  $^{235}\text{U}$ , and the activation analysis data were corrected accordingly.

## BIPHASIC EXTRACTION

The biphasic extraction studies conducted to date have been carried out at the test-tube scale. These were batch studies designed to evaluate the effects of (1) biphasic composition, (2) temperature, and (3) soil pretreatment on the recovery of uranium from Fernald soil samples. Partitioning data for several model systems were also determined to aid in process design and scaleup. All of the biphasic systems studied used PEG in combination with an inorganic salt phase. The three salts that we used were sodium carbonate, sodium sulfate, and sodium hexametaphosphate.

In each of the biphasic systems that we examined, optimum performance was obtained under conditions in which the more-viscous PEG phase was the dispersed phase. When the biphasic system was set up with the PEG phase as the continuous phase, the phase separation times became impractically long.



Fig. 4.1. TEM photomicrograph of thin-sectioned uranium particles found in the silt and clay portion of sample A-14.

**Table 4.4. Multiple analyses of uranium in the silt and clay portion of sample A-14**

|                   | Method of analysis |                    |                          |
|-------------------|--------------------|--------------------|--------------------------|
|                   | Wet digestion      | Neutron activation | Delayed neutron counting |
| Av uranium, mg/kg | 530.2 ± 40.7       | 494 ± 16           | 500                      |
| Range, mg/kg      | 468-577            | 474-510            |                          |
| No. of samples    | 5                  | 4                  | 1                        |

It should be emphasized that the purpose of the biphasic extraction is to separate and recover particulate uranium from the silt and clay portions of the soil. We are not interested in leaching the uranium from the soil. One of the advantages to not relying on dissolution processes is that the biphasic separation technology could then be applied to the removal of extremely refractory contaminants, such as high-fired  $\text{PuO}_2$ , from soils and wastes. In fact, the salt phases that we chose to investigate were not the kinds of solvents with which one would expect to obtain significant dissolution of either uranium(IV) or uranium(VI). For example, we did not add any oxidizing agents to convert insoluble uranium(IV) to the soluble uranium(VI) species.

Even with our choice of solvents, we still observed significant dissolution of uranium from samples A-14 and B-14 during all of our biphasic extraction tests. Fluorescence measurements have confirmed that the uranium species appearing in the salt solutions is  $\text{UO}_2^{2+}$  and not colloidal uranium(IV).

Uranium dissolution could have seriously degraded our separation efficiency if the partition coefficient of  $\text{UO}_2^{2+}$  had been approximately equal to that typically found for other dissolved salts. For example, sodium carbonate has a partition coefficient of 0.15 in the 15% PEG-3400/10%  $\text{Na}_2\text{CO}_3$  system. Fortunately, in this biphasic system the partition coefficients for  $\text{UO}_2^{2+}$  and submicron  $\text{UO}_2$  are 0.004 and 0.001, respectively.

When working in a high pH system such as PEG/ $\text{Na}_2\text{CO}_3$ , significant amounts of humic acids are leached from the soil. The partition coefficients of humic acid are ~2 or greater. We have found that the partition coefficients of dissolved uranium are unaffected by the presence of humic acids. This suggests that humic acids do not contribute significantly to uranium mobility in soil and groundwater.

Early in our experimental program, we carried out separations of submicron  $\text{UO}_2$  from clay. This model system was used to test the ability of the biphasic extraction process to decontaminate clay to below the proposed cleanup limit of ~50 mg/kg. During one of these tests, we combined ground  $\text{UO}_2$  with clean kaolinite, giving a feed that contained ~20 wt % of uranium on a dry-weight

**Table 4.5. Isotopic distribution of uranium in Fernald soil samples A-14 and B-14**

| Sample <sup>a</sup> | Abundance<br>(wt %) |                  |                  |                  |
|---------------------|---------------------|------------------|------------------|------------------|
|                     | <sup>234</sup> U    | <sup>235</sup> U | <sup>236</sup> U | <sup>238</sup> U |
| A-14                | 0.0055              | 0.7105           | 0.0054           | 99.2876          |
| Leached A-14        | 0.0062              | 0.7080           | 0.0070           | 99.2788          |
| B-14                | 0.0055              | 0.6598           | 0.0078           | 99.3269          |
| Leached B-14        | 0.0064              | 0.6586           | 0.0088           | 99.3262          |
| Error               | ±0.0015             | ±0.0025          | ±0.0015          | ±0.0033          |

<sup>a</sup>All samples were from the combined silt and clay portions of the soil.

basis. During extraction on the solids in a 15% PEG-3400/10% Na<sub>2</sub>CO<sub>3</sub> biphasic system, the clay partitioned to the PEG phase (top) and was then scrubbed several times with fresh sodium carbonate solution. This produced a bright white clay product that had a uranium concentration of <45 mg/kg. The extraction was carried out at a PEG-to-salt phase ratio of 1 to 4.

During the test, it became apparent that the upper, PEG phase was being recontaminated with UO<sub>2</sub> particles each time that the lower carbonate phase was withdrawn from the test tube. This is because some of the UO<sub>2</sub> particles became attached to the test tube walls and were swept into the PEG phase as the liquid level in the test tube was lowered. We tried to avoid this problem by removing the top phase between successive scrubs. However, because of the low phase ratio, we were not able to pipette the PEG phase without contaminating it with some of the bottom phase. We are confident that this difficulty will only be problematic in the test-tube-scale experiments. When the process is scaled up by using continuous, countercurrent contactors, recontamination of the PEG phase should no longer be as serious a problem.

Typical results for biphasic extraction tests with soil samples A-14 and B-14 are presented in Tables 4.6 and 4.7, respectively. The partitioning data for sample B-14 were disappointing (Table 4.7). Although there was an unequal distribution of soil within the liquid phases, no selectivity with regard to uranium partitioning was found. This suggests that a significant portion of the uranium is adsorbed onto the soil particles, in which case any physical separation technique would be ineffective.

**Table 4.6. Effect of biphasic composition on uranium recovery from silt and clay of sample A-14<sup>a</sup>**

| System composition  | Top phase               |                 |                      | Bottom phase            |                 |                      | Uranium dissolved (%) | Uranium loss or (gain) (%) | Weight loss (%) |
|---|-------------------------|-----------------|----------------------|-------------------------|-----------------|----------------------|-----------------------|----------------------------|-----------------|
|   | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) |                       |                            |                 |
| 15% PEG-3400<br>10% Na <sub>2</sub> CO <sub>3</sub>                     | 65.0                    | 138.0           | 16.4                 | 1.1                     | 904             | 1.8                  | 6.0                   | 75.8 <sup>b</sup>          | 33.9            |
| 15.0% PEG-3400<br>10.0% (NaPO <sub>3</sub> ) <sub>6</sub>               | 14.0                    | 84.2            | 2.2                  | 58.0                    | 148.0           | 15.7                 | 46.0                  | 36.1                       | 28.0            |
| 11.0% PEG-3400<br>11.0% Na <sub>2</sub> CO <sub>3</sub><br>2.2% Dextran | 68.0                    | 140.0           | 17.5                 | 4.9                     | 616.0           | 5.5                  | N/A                   | 77.0 <sup>b</sup>          | 27.1            |
| 15.0% PEG-3400<br>7.5% Na <sub>2</sub> SO <sub>4</sub>                  | 5.1                     | 268.0           | 2.5                  | 76.0                    | 203.0           | 28.3                 | 98.9                  | (29.7) <sup>b</sup>        | 18.9            |

<sup>a</sup>Pretreatment uranium level was 545 mg/kg.

<sup>b</sup>Incomplete uranium balance because some of the aqueous streams were not analyzed for uranium content.

**Table 4.7. Effect of biphasic composition on uranium recovery from silt and clay of sample B-14<sup>a</sup>**

| Biphasic composition   | Top phase               |                 |                      | Bottom phase            |                 |                      | Uranium solubilized (%) | Uranium loss (%) | Weight loss (%) |
|--|-------------------------|-----------------|----------------------|-------------------------|-----------------|----------------------|-------------------------|------------------|-----------------|
|  | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) |                         |                  |                 |
| 15% PEG-3400<br>10% Na <sub>2</sub> CO <sub>3</sub>                  | 62.0                    | 245.8           | 27.4                 | 14.0                    | 233.0           | 5.9                  | 21.0                    | 45.8             | 24.0            |
| 13% PEG-3400<br>8.7% Na <sub>2</sub> CO <sub>3</sub><br>2.2% Dextran | 64.0                    | 193.0           | 22.2                 | 17.0                    | 191.0           | 5.8                  | N/A <sup>b</sup>        | 72.0             | 19.0            |

<sup>a</sup>Pretreatment uranium level was 557 mg/kg.

<sup>b</sup>N/A = not available.

The partition experiments with sample A-14 showed definite evidence of uranium concentration taking place in the PEG/ $\text{Na}_2\text{CO}_3$  systems (see Table 6). We have, therefore, chosen to work almost exclusively with the soil obtained near the incinerator (A-14). In the phosphate and sulfate systems, the extent of uranium concentration with sample A-14 was small or nonexistent.

In all of the biphasic extraction tests, we were unable to obtain a complete mass balance of uranium and suspended solids. Considerable uranium dissolution occurred in all of the tests; once we realized that this was occurring, we began to filter and analyze the aqueous phases for uranium. The later experiments showed that considerable amounts of uranium were dissolving in the salt phases, but the amount of uranium found in the PEG phases was always just at the detection limit of the analytical techniques (0.1 mg/kg).

Loss of submicron-size particles to the aqueous phases during solid/liquid separation probably contributed, at least in part, to the poor mass balances. However, we have noticed that the high ionic strength and the presence of PEG causes significant flocculation to occur during biphasic extraction. This would have aided the solid/liquid separation considerably. We are interested in the fact that the flocculation appears to be quite selective. When the solids are centrifuged from the biphasic solutions, the appearance of alternating bands of color become clearly evident at the bottom of the test tube. This phenomenon was most dramatic in the model tests with ground  $\text{UO}_2$  and kaolinite; alternating bands of black and white were produced when the solids were centrifuged from the biphasic system.

The effect of the solids concentration in the biphasic system on uranium extraction was examined. Test results for the PEG-3400/ $\text{Na}_2\text{CO}_3$  and PEG-1500/ $\text{Na}_2\text{CO}_3$  systems are reported in Tables 4.8 and 4.9, respectively. All of these tests were performed with a liquid/liquid phase ratio of 1/4. The solids content, listed in the first columns of Tables 4.8 and 4.9, refers to the final solids concentration in the top, PEG phase. A clay concentration of about 10 wt % in the PEG phase is about as high as the biphasic system can tolerate. Higher concentrations lead to excessively long phase separation times and increased entrainment of the carbonate phase in the PEG phase.

Obviously, we would like to operate a biphasic system with as high a solids concentration as possible to maximize throughput in a full-scale process. However, the balance between solids concentration, suspension viscosity, and phase separation time needs to be optimized. Fortunately, uranium partitioning does not appear to depend on the suspended solids concentration.

In each of the partitioning tests, significant amounts of uranium dissolved into the salt phases. The concentration of uranium in the aqueous streams ranged from 1.0 to 3.0  $\mu\text{g}/\text{mL}$ . In some of the tests, over 70% of the uranium in the soil dissolved into the salt phase during the 1 to 2 min it took to do the extraction. This is undoubtedly because a significant portion of the uranium in the soil was in the form of soluble uranyl species. Uranium dissolution has the unfortunate effect of reducing the concentration of uranium recovered in the bottom phase solids and increasing the burden on any secondary processes for aqueous waste treatment.

To test the ability of the ABS process to recover refractory, particulate uranium without any interference from uranium dissolution, we pretreated the soil (A-14) by leaching with 5 wt %  $\text{Na}_2\text{CO}_3$  for 4 h at 25°C. This pretreatment reduced the soluble uranium concentration in the soil, giving a residual uranium concentration of ~142 mg/kg. The results of the biphasic extraction tests

**Table 4.8. Effect of solids concentration on uranium recovery from Fernald soil A-14  
with 6% PEG-3400/16% Na<sub>2</sub>CO<sub>3</sub> system at 25°C.  
Liquid/liquid phase ratio = 0.25**

| Solids in PEG phase (wt %) | Phase separation time (min) | Top phase               |                 |                      | Bottom phase            |                 |                      |                 |                         |                  |
|----------------------------|-----------------------------|-------------------------|-----------------|----------------------|-------------------------|-----------------|----------------------|-----------------|-------------------------|------------------|
|                            |                             | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Weight loss (%) | Uranium solubilized (%) | Uranium loss (%) |
| 2.5                        | 4                           | 80.3                    | 126.0           | 18.5                 | 6.1                     | 389.0           | 4.4                  | 13.6            | 76.1                    | 1.0              |
| 5.0                        | 1 <sup>a</sup>              | 88.4                    | 111.0           | 17.9                 | 2.4                     | 354.0           | 1.6                  | 9.2             | 69.7                    | 10.8             |
| 10.0                       | 1 <sup>a</sup>              | 85.2                    | 137.0           | 21.4                 | 1.8                     | 441.0           | 1.4                  | 13.0            | 68.9                    | 8.2              |

<sup>a</sup>Liquid phases separated by mild centrifugation.

**Table 4.9. Effect of solids concentration on uranium recovery from Fernald soil A-14 with 6% PEG-1500/16% Na<sub>2</sub>CO<sub>3</sub> system at 25°C. Liquid/liquid phase ratio = 0.25**

| Solids in PEG phase (wt %) | Phase separation time (min) | Top phase               |                 |                      | Bottom phase            |                 |                      |                 |                         |                  |
|----------------------------|-----------------------------|-------------------------|-----------------|----------------------|-------------------------|-----------------|----------------------|-----------------|-------------------------|------------------|
|                            |                             | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Weight loss (%) | Uranium solubilized (%) | Uranium loss (%) |
| 2.5                        | 4                           | 74.1                    | 124             | 16.8                 | 3.6                     | 236             | 1.6                  | 22.3            | 64.3                    | 17.4             |
| 5.0                        | 1                           | 53.3                    | 111             | 10.8                 | 4.1                     | 465             | 2.0                  | 42.6            | 71.4                    | 15.8             |
| 10.0                       | 1 <sup>a</sup>              | 91.0                    | 118             | 19.6                 | 2.5                     | 434             | 2.0                  | 6.5             | 71.4                    | 7.0              |

<sup>a</sup>Liquid phases separated by mild centrifugation.

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that used pretreated soil are presented in Table 4.10. In these tests, we used two different biphasic systems: 6% PEG-3400/16%  $\text{Na}_2\text{CO}_3$  at pH 12, and 6% PEG-3400/12%  $\text{Na}_2\text{SO}_4$  at pH 3.

The reason for operating at two different pHs was to examine the effect of selective quartz partitioning on uranium recovery. This series of tests was designed to determine if selective partitioning of quartz to the top, PEG phase would lead to a higher uranium concentration in the bottom-phase solids.

We have found that the partitioning of clay to the PEG phase is independent of pH but the partitioning behavior of quartz is pH dependent (D. J. Chaiko, Argonne National Laboratory, Argonne, Ill., unpublished data, 1993). At pHs near 2 to 3, quartz partitions to the PEG phase, whereas at pHs above ~5 to 6, quartz partitions to the lower, salt phase. The reason for using a sulfate system at pH 3 instead of a carbonate system is that we have not been able to form a biphasic system with PEG and carbonate at pHs below about 10.

The results in Table 4.10 show that ~85 to 90 wt % of the leached soil partitions to the PEG phase, with a uranium concentration of ~85 to 90 mg/kg. The uranium concentration in the pretreated feed was thus reduced by 60% during the biphasic extraction. Some of this reduction can be attributed to additional dissolution of uranium into the salt phase. For example, 25 wt % of the uranium dissolved into the carbonate phase, whereas 8.6 wt % dissolved into the sulfate phase.

The lowest uranium concentration, after biphasic extraction, was in the solids that partitioned to the bottom phase of the carbonate system. There, the uranium concentration was reduced to about 15 mg/kg, which is the natural background concentration of uranium in the soil surrounding the Fernald facility (Lee and Marsh 1992). Coincidentally, the percentage of the feed solids partitioning to the carbonate phase, 10.7 wt %, is very close to the amount of quartz present in the Fernald soil, 15 wt % (Lee and Marsh 1992). It is not clear why the same amount of quartz is not extracted into the carbonate phase when unleached soil was treated. We are attempting to characterize the mineralogical phases present in the top- and bottom-phase solids from the PEG/carbonate extractions.

## URANIUM LIBERATION STUDIES

The effectiveness of the ABS process for the removal of uranium depends on the degree to which the uranium is present as discrete particles. If discrete uranium phases are strongly attached to larger soil particles, or if the uranium is adsorbed on the surfaces of soil particles, physical separation will be ineffective. We carried out a grinding/extraction test to evaluate the effect of grinding on the liberation of uranium from the soil and its subsequent concentration and recovery during biphasic extraction.

A portion of the silt and clay fraction from sample A-14 was ground wet in a ball mill for 17 h with 0.1 wt % sodium hexametaphosphate as a dispersant. Table 4.11 compares the size distribution data of the ground sample with that of the unground soil. The soil sample for the liberation test was purposely ground to an extremely fine size to more easily identify any potential liberation problems. It should be understood that, except for attrition scrubbing, we do not propose that grinding of the Fernald soil be included in any full-scale decontamination process.

Table 4.10. Biphasic extraction of Na<sub>2</sub>CO<sub>3</sub> leached soil (A-14) at 25°C

| Biphasic composition                               | Top phase               |                 |                      | Bottom phase            |                 |                      |                         |                  |                 |
|--|-------------------------|-----------------|----------------------|-------------------------|-----------------|----------------------|-------------------------|------------------|-----------------|
|  | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Weight distribution (%) | Uranium (mg/kg) | Uranium recovery (%) | Uranium solubilized (%) | Uranium loss (%) | Weight loss (%) |
| 6% PEG 3400<br>12% Na <sub>2</sub> SO <sub>4</sub> | 89.4                    | 91.6            | 57.8                 | 1.6                     | 107.7           | 1.2                  | 8.6                     | 32.4             | 9.0             |
| 6% PEG 3400<br>16% Na <sub>2</sub> CO <sub>3</sub> | 84.4                    | 85.9            | 51.2                 | 10.7                    | 15.5            | 1.2                  | 25.0                    | 22.6             | 4.9             |

**Table 4.11. Size distribution of sample A-14 used in uranium liberation studies**

| Size<br>( $\mu\text{m}$ ) | Cumulative wt % passing |          |
|---------------------------|-------------------------|----------|
|                           | Ground                  | Unground |
| 5                         | 100                     | 27.2     |
| 4                         | 99.6                    | 23.2     |
| 3                         | 98.0                    | 18.7     |
| 2                         | 92.3                    | 13.5     |
| 1.3                       | 86.1                    | 10.3     |
| 0.6                       | 30.9                    | 4.6      |

Biphasic extraction of the ground soil in the 6% PEG-3400/16%  $\text{Na}_2\text{CO}_3$  system resulted in 81 wt % of the soil partitioning to the PEG phase, with a uranium concentration of 126 mg/kg. Compared with a uranium concentration of 138 mg/kg obtained for the unground sample, it is obvious that size reduction had no effect on uranium liberation/recovery. About 20 to 25 wt % of the uranium in sample A-14 appears to be intimately associated with the soil particles and not accessible to physical separation or leaching by the biphasic system. This second form of uranium in the soil may be encapsulated in amorphous iron and aluminum sesquioxides on the particle surfaces. Attrition scrubbing would not have any effect on the recovery of this form of uranium in the soil.

It is interesting that the grinding increased the amount of soil partitioning to the PEG phase. In the liberation test, 81 wt % of the soil partitioned to the PEG phase, whereas in the test with unground soil (see Table 4.6), 65 wt % partitioned to the PEG phase. Although the liberation tests suggest that attrition scrubbing won't lead to better particulate uranium recovery during biphasic extraction, it probably won't decrease it either. However, increased soil recovery might be one benefit of attrition scrubbing.

## PROCESS SCALEUP

To date, all of the biphasic extraction tests have been conducted in test tubes and used a maximum of 1 g of soil per extraction test. The scale of these tests has made it difficult to obtain complete mass balances for uranium on the extraction system. During FY 1994, we plan to scale up the biphasic extraction tests to accommodate several hundred grams of feed. We estimate the throughput of a medium sized commercial column, with an inner diameter of 152.4 cm (5 ft), to be in the range of 600 to 1200 kg/h.

We have already used noncontaminated clay feeds at the pilot-plant facilities of Otto York in Houston, Texas, to conduct two tests. In each test, we fed ~70 g of clay per hour into a Karr column (2.54 cm ID  $\times$  3.6 m high) with countercurrent feed solutions of 30% PEG-3400 and 20%  $\text{Na}_2\text{CO}_3$ . During the tests, the clay/carbonate slurry was fed to the middle of the column, and the

PEG solution was fed at the bottom. Fresh carbonate solution was fed at the top of the column. The clay was extracted from the carbonate solution into the PEG solution and exited at the top of the column.

The clay feed was a raw ore sample that was pretreated by screening at 53  $\mu\text{m}$ . Thus, the particle sizes of the feeds ranged from 53  $\mu\text{m}$  to submicron. Even with this broad size distribution, we encountered no problems with mass transport through the column and detected no holdup of solids at the overflow and underflow ports or on the mixing plates. Given the success of the tests at Otto York, we will be purchasing a 2.54-cm-diam column to conduct extraction tests with Fernald soil.

In addition to the column tests, we have derived some phase diagrams and will continue this work in FY 1993. The phase diagrams are required for flowsheet development and process scaleup. The phase diagrams provide valuable information regarding the operating conditions under which a biphasic system can be maintained. In addition, the measurement of tie lines on the phase diagram enables us to predict liquid/liquid volume ratios at equilibrium.

Phase diagrams for the PEG/ $\text{Na}_2\text{CO}_3$  system are shown in Figs. 4.2 and 4.3. The binodal curve of the phase diagrams separates the two-phase region located above the curve from the single-phase region below and to the left of the curve. The position of the binodal curve depends on the concentrations of polymer and salt and on the molecular weight of the polymer (see Fig. 4.2). It also depends on the temperature of the system (see Fig. 4.3).

The higher the PEG molecular weight, the lower the PEG concentration required to form a biphasic system. However, higher molecular weight PEGs increase the viscosity of the solution, which adversely affects the mass transfer rates and increases phase separation times. These problems can be mitigated to some extent by operating at elevated temperatures. For example, in the pilot tests that we conducted, we operated the Karr column at 40°C. We are planning to switch to the less viscous PEG-1500 in future treatability studies.

## CONCLUSIONS

Our studies with completely liberated clay/ $\text{UO}_2$  mixtures show that aqueous biphasic extraction can be used to separate and recover uranium from clay. In the model systems, the uranium concentration was reduced from 200,000 mg/kg (20 wt %) to less than 50 mg/kg. The system works well when the contaminants are refractory and well liberated from the soil particles. The individual partition coefficients of clay and  $\text{UO}_2$ , in the PEG/ $\text{Na}_2\text{CO}_3$  system, are 34 and 0.001, respectively. This gives a theoretical, single-stage separation factor of 34,000. Of course, the actual separation

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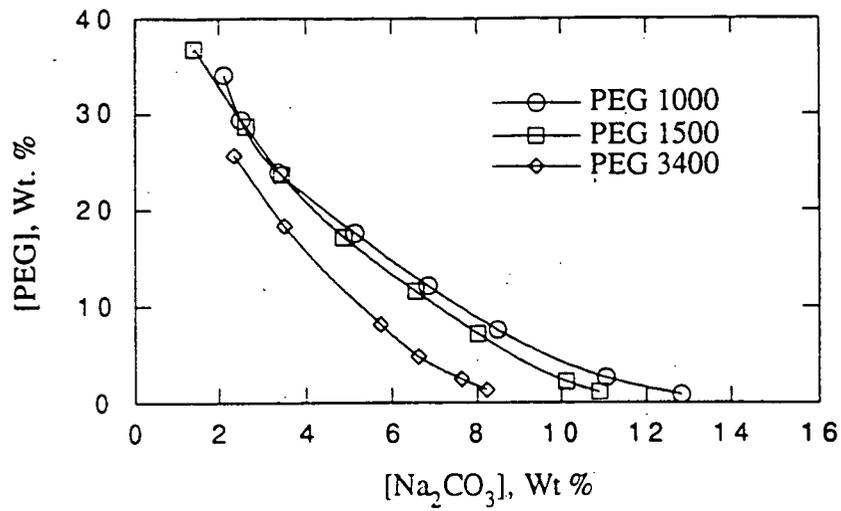


Fig. 4.2. Phase diagrams for the PEG/Na<sub>2</sub>CO<sub>3</sub> system at 25°C.

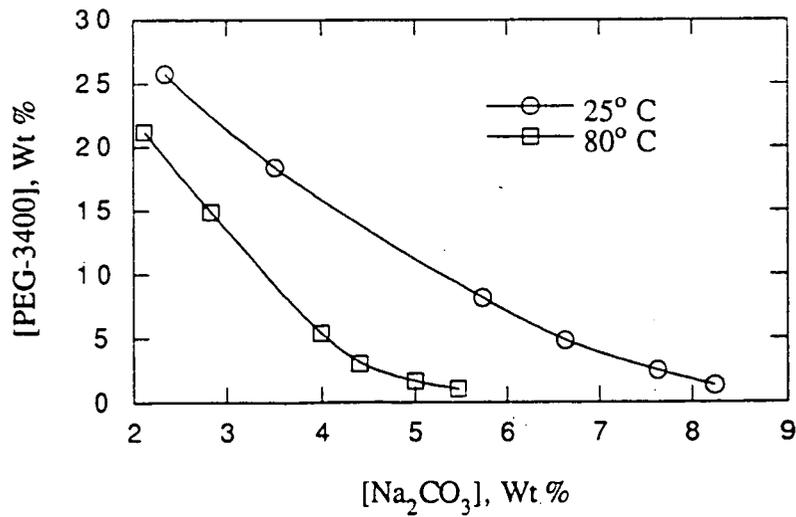


Fig. 4.3. Effect of temperature on the PEG/Na<sub>2</sub>CO<sub>3</sub> system.

factor observed with contaminated soil in a full-scale process would depend on the degree of contaminant liberation and the efficiency of the contactor equipment.

Test results with the Fernald soil showed that the uranium could be extracted and concentrated in particulate form, but the presence of uranyl species in the soil led to significant dissolution of uranium during the biphasic partitioning tests. This reduces the amount of uranium recovered in the solid concentrate stream and increases the burden on secondary liquid waste treatment. We will attempt to improve particulate uranium recovery by reducing uranium(VI) to uranium(IV) with reducing agents (e.g., sodium dithionite). The concentration of the reducing agent will be kept low to reduce only the top surface layers of the uranium(VI) particulates.

Selective flocculation of the soil particles occurred in all of the biphasic extraction systems that we studied. The work with the model systems suggests that this is not a problem with regard to solid/solid separation, but it does aid in solid/liquid separation. We have done extraction tests with particles as small as 20 nm and obtained good solid/liquid separation with only mild centrifugation.

Our initial scaleup tests with a 2.54-cm-(1-in.-)ID Karr column were very successful. The biphasic extraction system is able to handle a very broad distribution of particle sizes—from 53  $\mu\text{m}$  to well below 1  $\mu\text{m}$ . The degree of other-phase carryover in the overflow and underflow from the column was <1 vol %. The column tests were run with a 1 wt % feed slurry, but we feel that the solids concentration in the feed could be increased to 2.5 to 5 wt % without any detrimental effects on column performance. With a 2.54-cm column and a feed concentration of 2.5 wt % solids, the solids throughput would be at least 175 g/h. A full-scale column of 152 cm (5 ft) would give a solids throughput of ~630 to 1260 kg/h. We will be conducting scaleup studies with a 2.54-cm Karr column during FY 1993.

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## APPENDIX

## ISOTOPIC DISTRIBUTION OF URANIUM

The isotopic distribution of uranium in soil samples A-14 and B-14 was determined by TIMS (thermal ionization mass spectrometry) after decomposition of the soil matrix and isolation of the uranium by column-extraction chromatography. Details of the procedure are as follows:

**Reagents**

Nitric Acid: Baker Instra-Analyzed Reagent (J. T. Baker Chemical, Phillipsburg, N.J.)

Hydrofluoric Acid: Fisher ACS Reagent Chemical (Fisher Scientific, Fair Lawn, N.J.)

Water: Laboratory deionized water that was further purified with a Millipore Super-Q water purification system (Millipore, Bedford, Mass.) to a specific resistivity >17.0 megohm-cm.

Sulfuric Acid: S/P Mallinckrodt Analytical Reagent (Mallinckrodt, Inc., Paris, Ky.).

Chromatographic Columns: Prepacked columns (4.0 mL resin, 1.3-mL free column volume) containing 80 to 100 mesh U/TEVA•Spec resin (EI Chrom Industries, Inc., Darien, Ill.) were washed with 2 *N* nitric acid and 0.015 *N* nitric acid, and then equilibrated with 2 *N* nitric acid prior to use.

**Procedure**

A portion of the soil was weighed into a Teflon cup of a Parr acid-digestion Bomb (Model 4745 General Purpose Bomb, 23-mL capacity, Parr Instrument Co., Moline, Ill.), and water, nitric acid, and hydrofluoric acid were added to the cup. Nominal sample weights of 50 to 250 mg were used with 2 mL water, 4 mL HNO<sub>3</sub>, and 1 mL HF. The Teflon cup was encased in the Parr bomb metal jacket, and the closed vessels were heated in an oven overnight at 140 to 150°C to effect dissolution of the soil. After cooling, the solution in the cup was transferred to a Teflon beaker and heated to dryness. The residue was treated twice to remove fluorides by adding 1 to 2 mL nitric acid and 5 mL of 1 *M* sulfuric acid and taking the mixture to dryness again. The sulfuric acid was added to promote decomposition of AlF<sub>3</sub>, which can form when Al is a major component (>5 wt %) of the soil matrix and follows uranium in the separation scheme with the U/TEVA•Spec chromatographic columns. The fluoride removal step also removes Si as SiF<sub>4</sub> from the sample solution (thereby reducing dissolved solids in the sample solution) and eliminates chloride that might be present from the sample matrix.

To isolate uranium from the soil matrix components for isotopic analysis by TIMS, the residue from the acid treatment was first dissolved in 1 to 2 mL of 2 *M* HNO<sub>3</sub> and loaded on a previously equilibrated U/TEVA•Spec column. Uranium is selectively retained by the column, whereas virtually all other cations show no affinity for the column material. These unwanted cations were washed from the column with 2 *M* HNO<sub>3</sub> totaling 18 to 20 mL, which was added to the column in 1- to

3-mL increments. Uranium was then eluted with 9 mL of 0.015 M HNO<sub>3</sub> added to the column in increments of 3 mL or less. The uranium eluate was heated to dryness, 0.25 mL HNO<sub>3</sub> was added to the residue, and this solution was heated to dryness again to ensure the absence of organic material from the column. The resulting dry uranyl nitrate salt was submitted to the TIMS laboratory for isotopic analysis.

#### Mass Spectrometric Analysis

Uranium isotopic analyses were performed with a VG Isomass Model 54R thermal ionization mass spectrometer (VG Instruments, Inc., Danvers, Mass.) equipped with Faraday-cup and Daly-scintillation detector systems. Fractionation corrections to the measured ion-current ratios were determined relative to <sup>235</sup>U/<sup>238</sup>U atom ratio in Standard Reference Material U-500, certified by the National Bureau of Standards.

The samples were analyzed in the triple-filament configuration with rhenium-ionizing filament and tantalum side (sample) filaments. The sample was loaded on one side of the filament only. Loading was accomplished by dissolving the dried uranyl nitrate salt product from sample preparation in 5% NIST-distilled HNO<sub>3</sub> (National Institute of Standards and Technology, Gaithersburg, Md.) and drying the appropriate volume of this solution on the sample filament. Some of the samples were analyzed with the Daly-scintillation detector and utilized a sample load of 50 mg uranium, and other samples were analyzed with the Faraday-cup collector and a sample load of 1.0 μg uranium.

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