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Contaminant Uranium Phases and Leaching at the Fernald Site in Ohio

EDGAR C. BUCK,*
NEIL R. BROWN, AND NANCY L. DIETZ
*Chemical Technology Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439*

Electron beam techniques were used to characterize uranium-contaminated soils at the Fernald site in Ohio. Uranium particulates had been deposited on the soil through chemical spills and from the operation of an incinerator plant on the site. The major uranium phases were identified using analytical electron microscopy (AEM) combined with electron diffraction as uranyl phosphate (meta-autunite), uranium oxide (uraninite), and uranium metaphosphate [$\text{U}(\text{PO}_3)_4$]. The $\text{U}(\text{PO}_3)_4$ was found predominantly at an incinerator site at Fernald. Carbonate leaching in an oxygen environment has removed some of the U(IV) phases; however, $\text{U}(\text{PO}_3)_4$ has not been removed by any of the chemical remediation technologies tried to date. These observations suggest that an additional physical extraction procedure is needed to remove this phase. Some evidence suggests that the uranium has undergone weathering, resulting in its redistribution within the soil.

Introduction

The uranium processing plant at Fernald, run by the National Lead Company of Ohio, was the starting point for weapons manufacture in the United States during the Cold War years. Uranium ore was brought from mines both in North America and from the Belgian Congo for processing at Fernald (1). The soils around the Fernald processing plant became contaminated with uranium after decades of uranium extraction and purification to the tetrafluoride-using processes involving organophosphorus ion exchangers (2). Efforts are now being made to remediate the site. Detailed characterization protocol was developed to help the remediation groups optimize their treatment methods (3). The uranium-bearing solid phases that control the solubility of uranium in the soil must be identified both for carrying out remediation efforts and determining the long-term behavior of the uranium.

The Fernald plant is located 20 mi northwest of Cincinnati, by the Great Miami River. Radiological surveys of the site, conducted using a portable γ -spectrometer, located the regions of high uranium contamination. A number of highly contaminated regions were found with uranium

contents up to 5000 ppm (4). Characterization efforts have been concentrated at two regions at Fernald, the incinerator site and two storage pad (SP) site soils, where the soil was ~500 ppm uranium (labeled SP2 and SP4). These areas were considered representative of the types of contaminated soils to be found at the site. SP2 was the site of decontamination operations, and SP4 was contaminated through product spills (4).

Lee and Marsh (4) used X-ray diffraction (XRD) of the Fernald soils to determine the distribution of the major non-uranium-bearing phases as quartz, clays, calcite, and dolomite. Local soils contain low levels of carbonate-bearing rocks; however, road construction at the Fernald site introduced these minerals. Bertsch et al. (5) and Allen et al. (6) used X-ray absorption spectroscopy (XAS) to determine the uranium oxidation state of bulk soil samples from Fernald. The shift to higher energies of the uranium L_{III} X-ray absorption edge indicated that 80% of the uranium was in the VI oxidation state. Furthermore, Bertsch et al. (5), using a micro-beam XAS technique, suggested that the distribution of uranium was in-homogeneous in incinerator soil samples because the signal varied as the focused beam was moved across the sample. In contrast, the uranium appeared to be uniformly distributed through the SP4 soil samples. This observation was in agreement with radiochemical analysis and particle sizing performed by Lee and Marsh (4), who reached the same conclusion on the distribution of uranium in the soils.

Electron beam methods of analysis have also been used to investigate the nature of the uranium in contaminated soils from the Fernald site. The technique of analytical transmission electron microscopy (AEM) combined with electron diffraction, other microscopic techniques, and XAS can provide important representative information, allowing remediation efforts to be directed on a sound scientific basis (7, 8). In this paper, a description is given of types of uranium-bearing phases found in Fernald soils and how this information has been used in assisting remediation.

Experimental Procedures

Untreated soil samples from the Fernald site were obtained from the incinerator site and storage pad area, as were soil samples on which bench-scale chemical leaching experiments had been performed. These samples were size and density fractionated and sent to a number of laboratories for determination of the uranium-bearing phases. At Argonne, Fernald soil samples were placed into polyethylene capsules and infiltrated with a few milliliters of a water-soluble resin. The details of the sample preparation are described elsewhere (7). The sample block was polished and examined in a scanning electron microscope (SEM) with back-scattered electron (BSE) imaging as well as an X-ray energy dispersive spectrometer (EDS). Uranium-rich particles were located using atomic density contrast through BSE imaging. The uranium-bearing particles were isolated and, using ultramicrotomy, made into thin sections suitable for observation in the transmission electron microscope (TEM) (7). This method of sample preparation allowed direct comparison between BSE and TEM images. The TEM analysis provided the resolution required to probe the composition and structure of the small uranium phases

* Corresponding author telephone: 708-252-7093; fax: 708-252-4771.

TABLE 1

Distribution of Particulate Uranium Phases in Incinerator Soil Samples Determined Using SEM/AEM^a

	meta-autunite [U(VI)]	uranium meta-phosphate [U(VI)]	uraninite [U(IV)]	uranium calcium oxide [U(VI)]	uranium silicate [U(VI)]
heavy sand	45	10	10	35	
medium sand	3	37	1	59	1
heavy silt	24	33	14	17	13
medium silt	47	47		6	
total area (μm^2) of U phases	27675	17700	6010	16905	19930
total	31	20	7	20	22

^a Data calculated from determining the area of each uranium phase found in polished SEM samples of the soil.

that are within a matrix of other soil components. A much larger volume of soil can be examined in detail using this SEM/TEM combination than solely using TEM.

The TEM thin sections of uranium phases were analyzed in a JEOL 2000 FXII TEM operated at 200 kV and equipped with EDS. The results from EDS analyses were quantified on the basis of experimentally determined *k* factors obtained from glass and mineral thin-film standards. The uranium *k* factor for the L X-ray line was determined from synthetic soddyite and uranophane minerals. Phases were identified using a combination of EDS, selected area electron diffraction (SAED), and convergent beam electron diffraction (CBED). The SAED camera lengths were calibrated with a polycrystalline aluminum sample. The SAED patterns for d-spacing estimation were made with a steadfast eucentric height and objective lens current as well as with the brightness control defocused.

Results

SEM Observations. The SEM examination showed that uranium was contained within particles typically 1–10 μm in diameter in the incinerator and SP2 soils, although some particles were up to 100 μm in diameter. Uranium particles were found in the SP4 soils but were much rarer. A surprising variety of uranium phases were found in the soils, some of which suggested that weathering and redistribution of uranium had occurred, resulting in the formation of secondary uranium-bearing phases similar to those observed in naturally occurring deposits of weathered uranium (9).

Estimates of the relative contributions of each phase were based on the area of the uranium phase observed in the polished SEM samples and accounting for the density differences among the different uranium phases (see Table 1). Estimating the contribution of each phase to the total uranium content using this method is subject to some error, as the sample volumes were small. Uranium contamination in Fernald soils was inhomogeneous, and occasionally there were not a large enough number of particles in each sample for accurate analysis. Nevertheless, the same volume of soil was examined by all characterization methods performed at the different laboratories (i.e., XAS, XRD, and TEM/SEM). As there was reasonable agreement between the different techniques, it is believed that representative data were obtained.

It should also be noted that treatability studies, based on similar small samples, would produce variable results from bench-top leaching studies. Therefore, a technique capable of probing how a chemical leaching agent is affecting a particular contaminant phase will provide important information. This will allow an assessment of treatment technologies to be more accurate.

One of the objectives of the AEM studies (discussed below) was to identify the specific uranium phases as well as other non-uranium-bearing phases, in both treated and untreated soil samples. This would help us to determine the effect of treatment technologies on the Fernald soils.

The SEM analyses were also used to determine the major soil components as quartz, phyllosilicates, calcite, and feldspars. Non-uranium-bearing minor phases found in the soil samples included rutile, ilmenite, maghemite, apatite, cerium phosphate, yttrium phosphate, and zircon. The identification of these phases was confirmed using TEM. The distribution of non-uranium-bearing phases is important because it may affect the efficiency of the treatment methods. For example, the large amount of calcite in Fernald soils prevents the use of acid leaching agents. Furthermore, acid leaching will also cause dissolution of the complex aluminosilicates, hence alkaline leaching was selected as one possible remediation route.

Characterization of Uranium-Bearing Minerals Using AEM and Electron Diffraction. In AEM analyses, uranium oxide particles were fairly common in untreated soil samples (Figure 1a). [Uranium oxide particles were identified as uraninite using electron diffraction (Figure 1b).] The uraninite (UO_2) was a nonstoichiometric phase (UO_{2+x}) possessing a fluorite structure. Uraninite readily undergoes oxidation (10), increasing the unit cell parameters that can be measured using XRD (1, 11) or electron diffraction (12). Most often the UO_2 particles were 50–200 nm in diameter, which should make them amenable to chemical leaching. However, the particles tended to occur in larger clumps, sometimes 10 μm in diameter.

The most abundant uranium phase found in the Fernald soils was a calcium uranyl phosphate that was identified using EDS and electron diffraction as meta-autunite [$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$]. The presence of phosphate phases in soils may not be considered surprising as tributyl phosphate (TBP) was used to purify uranium at Fernald, and similar precipitates may have occurred during product spills. Precipitation of uranium phosphates during TBP extraction is a common problem (13). Figure 2 shows a uranium phosphate phase found in SP2 site soils. The phase was identified as tetragonal calcium uranyl phosphate (meta-autunite), ideally $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. Meta-autunite is a greenish-yellow uranium mineral with a layered structure. As is common with many U(VI) minerals, the phase consisted of spiny needles that are seen in the BSE images (Figure 2a). The electron diffraction pattern was taken along the [001] zone axis and indicates that the phase is tetragonal (Figure 2c).

The uranyl phosphates constitute a very diverse group of uranium-bearing minerals. The most common type, autunite, is characterized by a U:P ratio of 1:1 (14). Another group of uranyl phosphates, phosphuranyls, has a U:P ratio of 3:2 and was observed occasionally in the Fernald soil samples. Autunites are a weathering product of uraninite sometimes found in natural systems (10), and indeed, there was evidence of some alteration of the

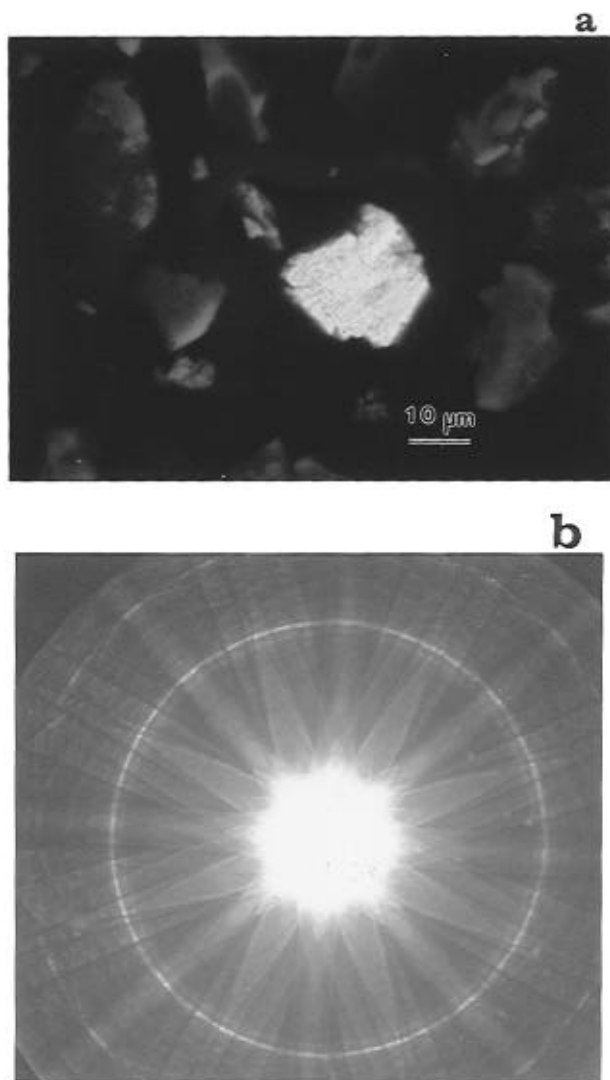


FIGURE 1. Electron beam analysis of uraninite found in Fernald soils: (a) BSE image of uranium oxide particle and (b) a CBED pattern, showing 4-fold symmetry, taken along the [100] zone axis from this sectioned sample.

uranium-bearing phases in Fernald soils (8). However, at Fernald, uranyl phosphates were most often found isolated from uraninite in both SP2 and incinerator site soils. Uranyl phosphates will control the uranium concentration in groundwaters when $\log \{[\text{HPO}_4^{2-}]/[\text{HCO}_3^-]\} > 1 \times 10^{-3}$. Under these conditions, uranyl phosphates have solubilities below those of uranyl silicates and carbonates (15).

It is interesting to note that Ewing and Finch (9) found that autunite requires the presence of a lead-containing uranyl hydrate, curite, which acts as a catalyst for the formation of uranyl phosphate, at least in groundwaters with a low phosphate concentration. However, uranyl phosphates will precipitate if a high phosphate concentration exists ($\sim 10^{-2}$ M). High $[\text{PO}_4^{3-}]$ concentrations may have been present in Fernald soils. Apatite controls the $[\text{PO}_4^{3-}]$ concentration in many natural waters and keeps phosphorous levels below 10^{-7} M when the pH exceeds 7. In the Fernald soils, calcium phosphate and iron phosphate are often observed. Some of this phosphate may have come from fertilizers used in farming or during weathering of rocks, although much must have come from the TBP used in the uranium purification attempts at Fernald. Although the soil pH was around 8 for all soil samples (4), suggesting

TABLE 2

Electron Diffraction Analysis of Uranium Metaphosphate Phase

experimental d-spacings (nm)	JCPDS 20-1348 d-spacings for $\text{U}(\text{PO}_3)_4$ (nm) ^a
0.664	0.627
0.513	0.513
0.440	0.441
0.383	0.385
0.365	0.366
0.272	0.270
0.317	0.314
0.296	0.295
0.221	0.220
0.180	
0.215	0.216
0.202	0.202

^a Ref 16.

that the $[\text{PO}_4^{3-}]_{\text{aq}}$ concentrations are low, significant precipitation of uranyl phosphate phases has occurred in the Fernald soils.

During the TEM characterization of uranium contamination in Fernald incinerator site soils, a ceramic-like crystalline uranium- and phosphorus-bearing phase was found (Figure 3). This phase was electron beam stable and did not possess the fine needles characteristic of the uranyl phosphates. The diffraction patterns were very stable even under a condensed beam that tends to amorphize natural hydrated U(VI) minerals rapidly. The phase was identified as uranium metaphosphate (actually a phosphite) $[\text{U}(\text{PO}_3)_4]$ using electron diffraction (see Table 2 and Figure 2b) (16). The uranium metaphosphate may have formed within the incinerator at temperatures over 400 °C and then have been deposited in the surrounding area after leaving the incinerator stack. There are several structural varieties of $\text{U}(\text{PO}_3)_4$, all of which require high temperatures and fairly harsh reaction conditions to form (14). The phase at Fernald was determined using electron diffraction to be monoclinic with $a = 0.89$ nm, $b = 1.49$ nm, $c = 0.69$ nm, and $\beta = 96^\circ$. Uranium metaphosphates are all greenish with uranium as U(IV), coordinated with polyphosphate chains. The polyphosphate chains consist of PO_4 tetrahedra connected with bridging oxygen atoms. Each tetrahedron has two oxygen atoms that are shared with adjacent tetrahedra. The two other oxygen atoms are coordinated with a uranium ion in such a way that each U(IV) ion is surrounded by eight nonbridging oxygen atoms. This general type of structure is typical of polyphosphate glasses and crystals that contain phosphate chains and highly charged metal ions with small radii. Heating of uranium compounds with phosphoric acid or ammonium phosphate to 900–1000 °C results in the formation of $\text{U}(\text{PO}_3)_4$ regardless of the initial uranium oxidation state. Indeed, this process has been recommended for the gravimetric determination of uranium. Uranium metaphosphate is very stable and is completely nonhygroscopic, which may explain its stability in the electron beam. Uranium metaphosphate is insoluble in all cold mineral acids, only dissolving slowly in H_3PO_4 on prolonged heating. However, when heated with solutions of alkali metal carbonates in air, it will gradually dissolve (14). After repeated analyses, it was possible to recognize particular uranium phases with the SEM alone. This capability permitted us to determine the distribution

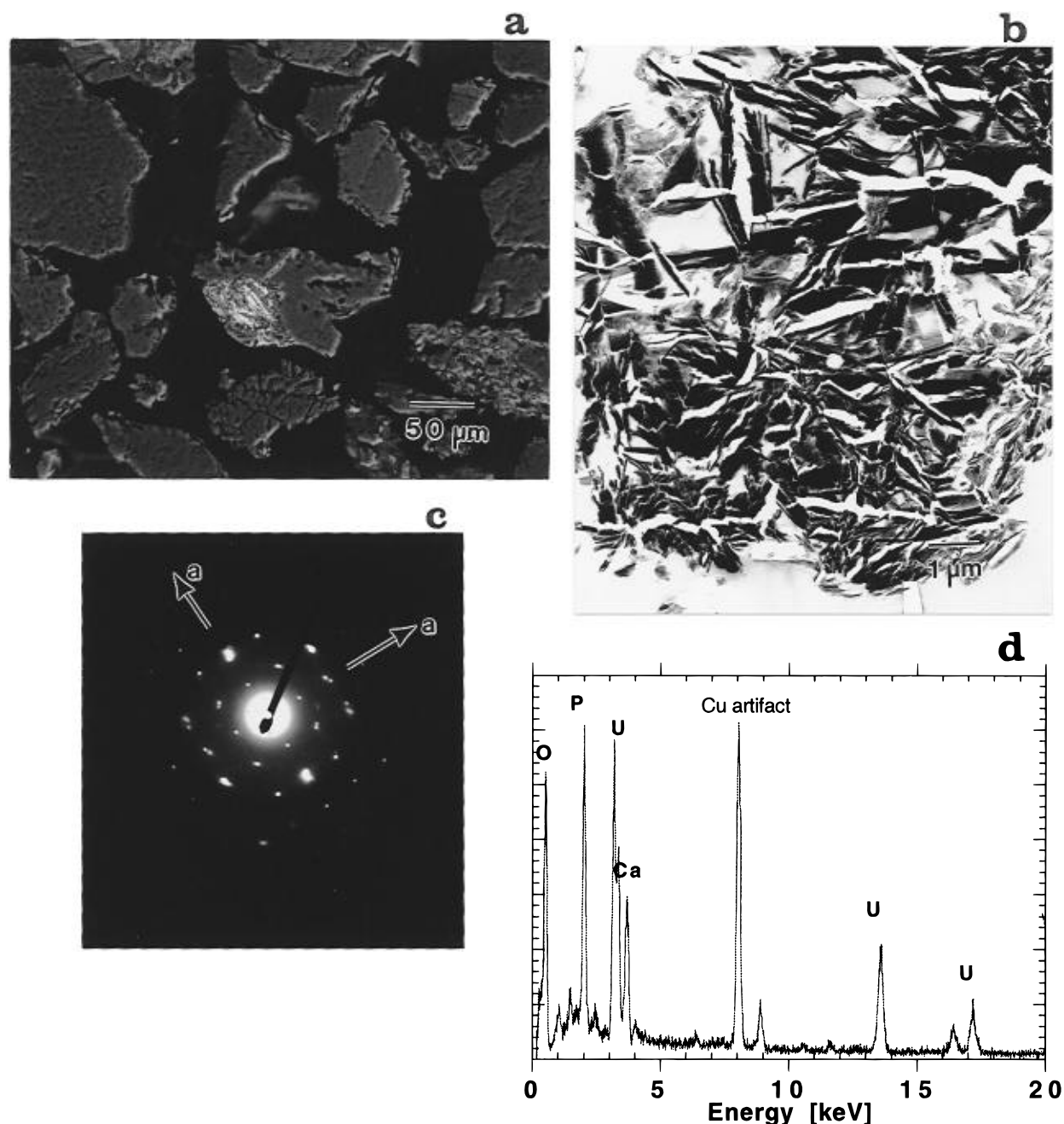


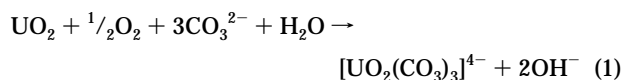
FIGURE 2. Electron beam analysis of meta-autunite phase found in Fernald SP2 site soils: (a) BSE image showing isolated nature of particles, (b) TEM image of the elongated crystals, (c) SAED pattern of the tetragonal crystal taken along the [001] zone axis, and (d) TEM/EDS compositional analysis.

of uranium phases more rapidly, although there were always a few uranium phases that could not be identified without the high resolution and electron diffraction capabilities of TEM. Other uranium-bearing phases have been found including uranium calcium oxide, uranium silicide, and uranyl silicate (7, 8).

Treatability Studies. In the next two sections, the results of characterization of samples obtained from bench-scale testing will be presented. Other types of treatment were conducted at the Fernald site; however, only two types will be discussed.

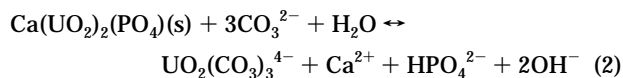
Carbonate-Treated Soils. As Fernald soils contain around 80% U(VI) phases, carbonate leaching was expected to be an efficient method for removing uranium from the soils, and indeed this was accomplished at the SP4 site (17). Uraninite, a U(IV) phase, can also be leached by

carbonate according to the scheme (1)



In other words, as long as an oxidizing agent is present, uraninite will be attacked. Analyses using TEM demonstrated that much of the uranium in SP2 soils and incinerator soils was in the form of uranyl phosphates, which are less stable than uranyl carbonate complexes. Although most of the particles were large ranging in size from 1 to 10 μm , they were elongated with large surface areas that should allow rapid dissolution. In carbonate-treated incinerator soil samples, uranyl phosphates were substantially reduced, although two types of U(IV) phases remained: uraninite and uranium metaphosphate. The uranyl phosphates may

react with carbonate according to



resulting in aqueous carbonate complex formation. Bicarbonate must be added to prevent re-precipitation of the dissolved uranium with the hydroxyl ion. Uranyl ions have a strong tendency to form carbonate complexes in neutral and alkaline waters, which can account for high uranium solubility (15).

Effective oxidation of tetravalent uranium can be achieved with molecular oxygen in carbonate solution, with the oxidation rate being proportional to the oxygen partial pressure (1). Chemical methods for oxidizing U(IV) phases, such as hydrogen peroxide and potassium permanganate, either are expensive and/or increase the amount of pollution. Hence, the mining technique of heap leaching appeared to be an attractive alternative for assisting the oxidation of U(VI). In heap leaching, soil is piled on top of an impermeable pad, and an overhead sprinkler system is used to distribute the solubilizing solution, in this case, carbonate, over the heap. The nature of the heap allows for aeration, allowing reaction 2 to proceed. Permanganate, however, was used at the bench scale (17), after analysis using TEM showed that U(IV) phases were still remaining in the carbonate-treated soils. The heap-treated samples showed evidence of uraninite dissolution (see Figure 4). However, analysis by electron microscopy found no evidence of uranium metaphosphate dissolution, and a number of uranyl phosphate (meta-autunite) phases were still present.

The SEM/TEM analysis of the uranium-bearing phases in the carbonate-treated soils revealed the following: the majority of the uranium (60–75%) was in the form of uranium metaphosphates [$\text{U}(\text{PO}_3)_4$], about 20% was uraninite, and the remaining was uranyl phosphate. Wet chemical analysis showed that 45–70% of uranium was removed from the Fernald soils with just carbonate leaching. With the addition of an oxidizing agent (permanganate), >80% of the uranium was removed (17), suggesting that some U(IV) phases had been leached. While the uranium concentration in SP2 and incinerator soil samples was reduced significantly, it was still above the target level of around 20 ppm.

Dithionite/Tiron-Treated Soils. A very different approach to the removal of uranium in Fernald soils involved the use of a synthetic analog of microbial-produced complexing agents, termed Tiron (17). In this method of soil remediation, dithionite reduces the U(VI) species to U(IV), and then these reduced species are removed from solution through chelation with Tiron. In laboratory tests, the technique was effective at removing uranium from an oxide hydrate (schoepite)-contaminated simulated soil (17), but is only slightly effective at dissolving uranyl phosphates, which are a major U(VI) phase in both Fernald incinerator site soils and SP2 soils. In Figure 5, a meta-autunite (calcium uranyl phosphate) phase is shown that has been attacked by the dithionite/Tiron mixture. However, a core of crystalline uranyl phosphate remains, and the surrounding phosphorous-rich amorphous area is only slightly depleted in uranium. As this phase is now amorphous, it may be more soluble and more susceptible to leaching than crystalline meta-autunite. The composition of this material was determined using TEM/EDS (see Table 3) at several

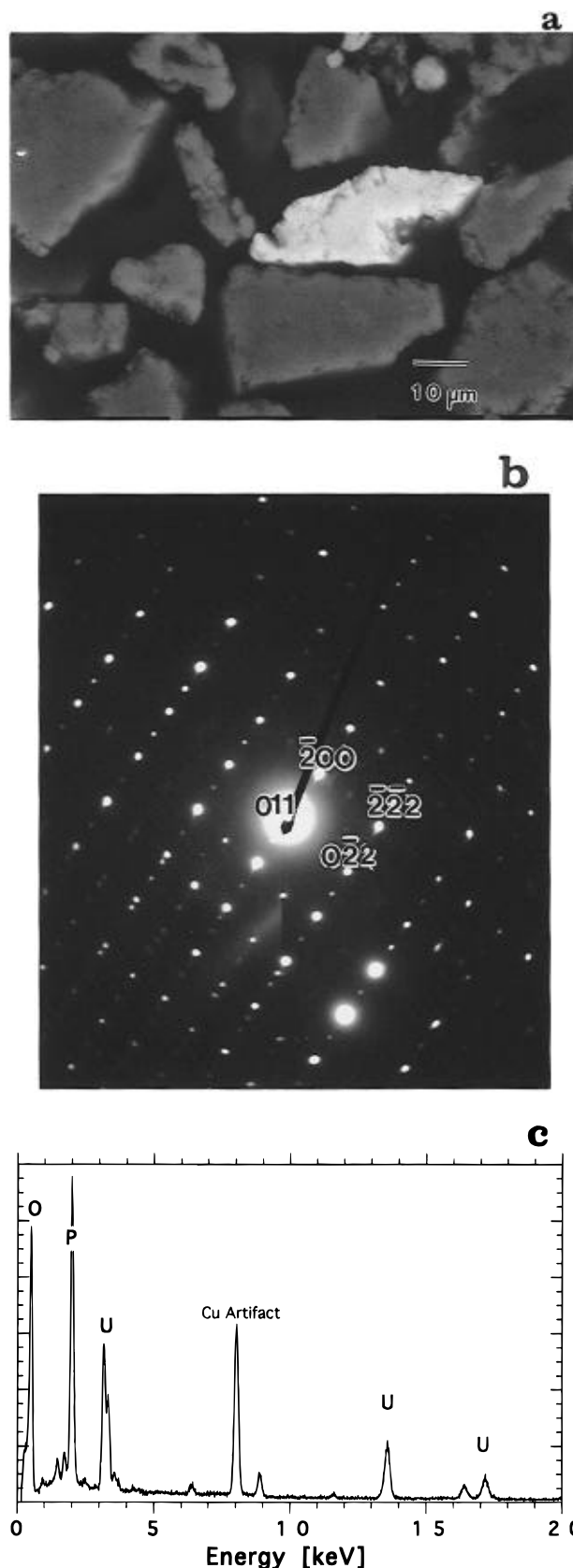


FIGURE 3. Electron beam analysis of uranium phosphite phase found in citrate-treated incinerator-site soils: (a) BSE image of phase, where bright contrast is related to atomic number; (b) SAED pattern of phase taken along the [011] zone axis; and (c) EDS analysis of phase. The phase is monoclinic with $\beta = \sim 96^\circ$.

points through the thin section. Both uranium and calcium were leached, but the uranium was reduced by only 20–

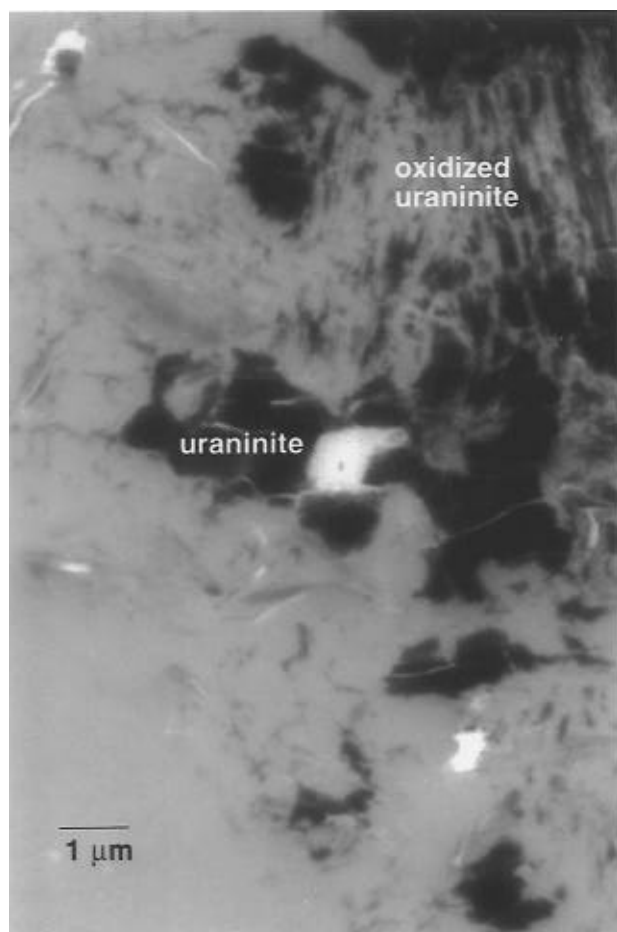


FIGURE 4. TEM image showing the dissolution of uraninite in heap-leaching processes. The periphery of the uraninite particles has been etched, and a uranium oxide hydrate has started to form as the uranium is oxidized and leached from the parent phase.

TABLE 3

Composition of Dithionite/Tiron-Treated Uranyl Phosphate (Meta-Autunite) Phase in Incinerator Soil Samples^a

	element wt %			
	crystalline uranium phosphate			P-rich phase
P	20.7 ± 2.1	16.6 ± 1.8	17.9 ± 2.0	42.9 ± 4.5
U	60.4 ± 12.2	73.2 ± 15.1	67.8 ± 14.2	48.4 ± 10.2
Ca	18.9 ± 1.9	10.2 ± 1.2	14.3 ± 1.6	8.6 ± 1.1

^a Treated soils were leached of both calcium and uranium. There were some compositional variation in the crystalline regions, which suggested some leaching without loss of structural integrity.

30%. The dithionite/Tiron leaching method was found to be ineffective at removing the types of uranium phases present in Fernald soils.

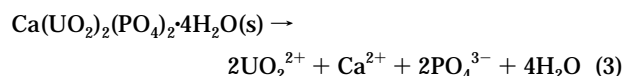
Conclusions

These electron beam investigations have shown a large number of different types of uranium phases in the Fernald soils. The major phases were identified as calcium uranyl phosphate (meta-autunite), uraninite (uranium oxide), and uranium metaphosphate [$U(PO_3)_4$] as with minor amounts of uranyl silicate (soddyite), uranium calcium oxide, uranium silicide (USi_{2-x}), and uranium associated with calcium fluoride and with iron oxides (7). Although

uranium is known to have a strong affinity for adsorption onto iron oxides, particularly amorphous iron oxyhydroxides, it was most often found to be in the form of particulate uranium phases in incinerator site and SP2 soils. In SP4 soils, uranium was found associated with iron oxides and as small particles of uraninite (7). Observations using micro-XAS methods supported this finding (5).

The diversity of uranium particulate phases is partially due to the range of operations that were conducted at Fernald and also possibly weathering and redistribution of the uranium over time. The mineral phases such as meta-autunite may have precipitated in the soil, whereas the ceramic particles, such as the metaphosphate, formed at high temperatures in the site incinerator and then were deposited in the surrounding area. This diversity of uranium phases may impede cleanup efforts, as any single remediation technique may be unlikely to remove all the different forms of uranium in the soils. However, carbonate heap leaching has managed to remove most of the more mobile uranium phases, only leaving the uranium metaphosphate.

Knowledge of the type of uranium-bearing phases left in the soil (either deliberately or by ineffective remediation) will be necessary to determine the partitioning of uranium between crystalline phase and aqueous solution. The solubility equilibrium for a number of uranyl phosphates has been determined by Sandino and Bruno (15). The reaction describing the dissolution of meta-autunite in aqueous solution is



where $\log K_{sp}$ (the solubility product at 25 °C) = -48.5 (15).

The low solubility of uranium phosphate phases suggests that dissolution of uranium-bearing phases in Fernald soils by carbonate leaching may result in some re-precipitation of uranium through complexation with phosphate. Uranium phosphate phases may be unique to Fernald because of the large use of phosphorus in chemical processes at the plant. Radionuclide-bearing phases present in contaminated soils at other former weapons processing sites may also depend on the types of operations conducted.

The characterization methods described in this paper, in combination with XAS and XRD, allow remediation technology groups to find more efficient ways of removing contamination. It has been shown that removal of uranium from the Fernald soils can be improved by detailed knowledge of the chemical and physical characteristics of the waste and its environment. The carbonate leaching process was improved by adding a step to induce oxidation of the uraninite after AEM characterization identified this phase as remaining in the treated soils. Electron beam techniques have also been used to characterize uranium-, plutonium-, and thorium-contaminated soils from other facilities and sites (18). The fact that uranium metaphosphate is resistant to oxidative dissolution implies that this phase could be left in the soil without substantial risk of uranium release to the environment. Indeed, on-site disposal has recently been suggested as an alternative method for dealing with radionuclide-contaminated sites (19). Recently, Ma et al. (20) have proposed a method for immobilizing lead in soils using phosphate-bearing rocks. A similar process could be conducted at Fernald using

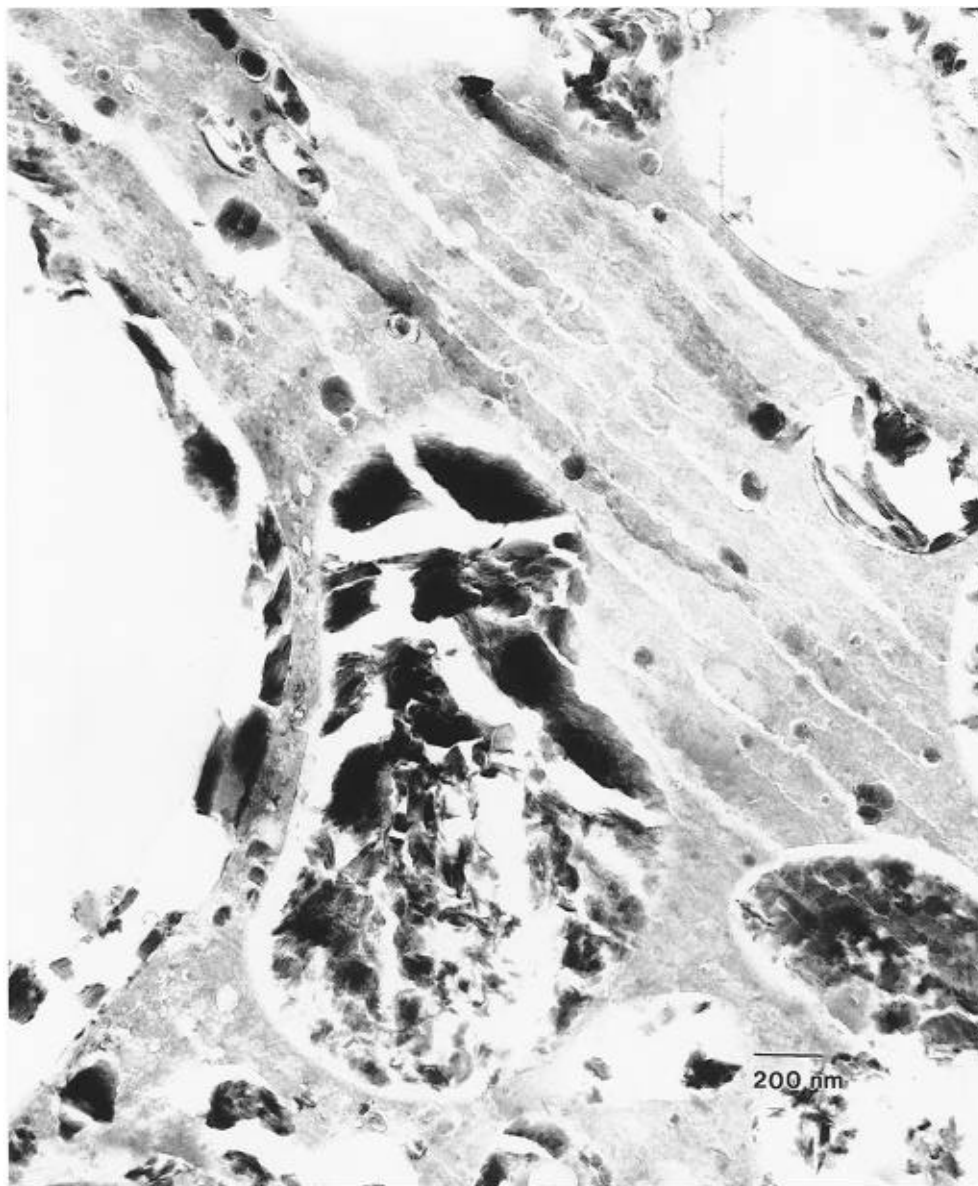


FIGURE 5. A TEM image showing the effect of the dithionite/Tiron process on uranyl phosphate phase. The chemical agents have leached uranium from the phase, leaving a core of crystalline *meta*-autunite surrounded by an amorphous phosphorous-rich phase. See Table 3 for the composition of the material.

phosphates or vanadates to produce insoluble uranium phases. However, it should be noted that phosphates are already in abundance at the Fernald site, yet uranium is still mobile. Therefore, the type of uranium phosphate phase formed will be important, if the uranium is to be left *in situ*. Geochemical modeling, using the EQ6 code (21), should be used in performance assessment at Fernald, utilizing the characterization information supplied from this study. In this paper, we have demonstrated that detailed characterization can provide pertinent information on the form of uranium contamination in soils. Electron microscopy, which provides both structural and compositional data with high spatial resolution, is one of the most useful techniques for providing accurate information on the form of particulate uranium contamination in environmental samples. Characterizing the soil before and after treatment allows one to say how effective the treatment was and what phases, if any, are resistant to treatment. This knowledge allows one to tailor the treatment to dissolve that specific phase if necessary.

Acknowledgments

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