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Analytical Electron Microscopy Characterization of Fernald Soils

Annual Report
October 1993–September 1994

by E. C. Buck, N. R. Brown,
and N. L. Dietz

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ANALYTICAL ELECTRON MICROSCOPY CHARACTERIZATION OF FERNALD SOILS

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ABSTRACT

A combination of backscattered electron imaging and analytical electron microscopy (AEM) with electron diffraction have been used to determine the physical and chemical properties of uranium contamination in soils from the Fernald Environmental Management Project in Ohio. The information gained from these studies has been used in the development and testing of remediation technologies.

Most chemical washing techniques have been reasonably effective with uranyl [U(VI)] phases, but U(IV) phases have proven difficult to remove from the soils. Carbonate leaching in an oxygen environment (heap leaching) has removed some of the U(IV) phases, and it appears to be the most effective technique developed in the program. The uranium metaphosphate, which was found exclusively at an incinerator site, has not been removed by any of the chemical methods. We suggest that a physical extraction procedure (either a magnetic separation or aqueous biphasic process) be used to remove this phase. Analytical electron microscopy has also been used to determine the effect of the chemical agents on the uranium phases. It has also been used to examine soils from the Portsmouth site in Ohio. The contamination there took the form of uranium oxide and uranium calcium oxide phases. Technology transfer efforts over FY 1994 have led to industry-sponsored projects involving soil characterization.

I. INTRODUCTION

The Feed Materials Production Center, a former uranium processing plant located at Fernald in Ohio, was the starting point for weapons manufacturing in the United States during the Cold War years. Uranium ore was brought from mines in both North America and the Belgian Congo (Zaire) for processing at the Fernald plant [1], which was run by the National Lead Company of Ohio. Although the U.S. Department of Energy (DOE) suspended production there in 1986, the decades of uranium processing have left the soils around the Fernald plant contaminated with uranium. FERMCO, the DOE contractor, is remediating the site, which is now known as the Fernald Environmental Management Project.

To help remediation groups optimize their treatment methods, the site is being characterized in detail. For these remediation efforts to be successful (and for researchers to be able to predict the long-term behavior of uranium), it is necessary to identify the uranium-bearing solid phases that control the solubility of uranium in the environment. Many technologies for decontamination are available, but if the nature of the contamination is not understood (i.e., its physical and chemical characteristics), it becomes difficult to select the most suitable method for cleaning a particular site.

This report presents the results obtained in FY 1994 as part of the ongoing effort to characterize the uranium contamination in Fernald soils by means of electron beam methods. The goal of this project is to describe the types of uranium-bearing phases in Fernald soils, as well as the effect of chemical leaching agents on these phases. Detailed characterization has yielded interesting observations on the nature of uranium contamination at Fernald that have implications for treatment methods and the transportability of uranium in the environment.

Scanning electron microscopy (SEM) investigations over FY 1992-1993 have showed that these soils contain uranium particles ranging from 1 μm to 100 μm in diameter. Furthermore, AEM has shown that these uranium-rich regions are made up of discrete uranium-bearing phases. The identification of these phases has allowed a better understanding of the effect of treatment methods on the contaminated soil. The distribution of these uranium phases was found to be inhomogeneous at the microscopic level, a result that has implications for both bulk characterization methods and remediation techniques.

A. Use of Electron Microscopy in Characterizing Soil Contamination

Electron beam methods of analysis yield detailed information about the structure and composition of soil contaminants. High-energy electrons interact strongly with matter through a series of elastic and inelastic events. Elastic events result in backscattered electron imaging and electron diffraction, while inelastic events can produce characteristic X-rays and energy loss spectra. Both processes produce contrast that allows the sample morphology to be seen. Electron microscopy utilizes a fine, high-intensity probe to characterize materials with nanometer-scale resolution. In our characterization efforts, we combine analytical electron microscopy (AEM) with electron diffraction, microtomy methods for preparing thin sections of soils, and other microscopy techniques. This suite of techniques can provide important representative information that allows remediation efforts to be directed on a sound scientific basis [2]. In AEM, X-ray energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) are used to analyze samples.

By means of AEM combined with electron diffraction, the major uranium phases have been identified as calcium uranyl(VI) phosphate (meta-autunite), uranium(IV) oxide (uraninite), uranium(VI) calcium oxide, uranyl(VI) silicate, and uranium(IV) metaphosphate [$\text{U}(\text{PO}_3)_4$], although other uranium phosphorus phases have been found.

B. Other Characterization Studies at the Fernald Environmental Management Project

The Fernald plant is located 20 miles northwest of Cincinnati, by the Great Miami River. Radiological surveys of the site, conducted using a portable gamma spectrometer, located the regions of high uranium contamination [3]. A number of highly contaminated plumes were found, which had an average uranium concentration of 500 ppm, although some surface soils from these sampled regions had uranium contents up to 5000 ppm [4]. Detailed characterization efforts have been concentrated at three areas: the incinerator site soils (termed A11 and A14) and two storage pad site soils (termed SP2 and SP4). These areas were considered to be representative of uranium contamination over the whole site.

Lee and Marsh [3] used X-ray diffraction (XRD) to identify the major non-uranium-bearing phases in the soils as quartz, clays, calcite, and dolomite. Bertsch et al. [5] and Allen et al. [6] have used X-ray absorption spectroscopy (XAS) to determine the oxidation state of uranium in bulk soil samples from Fernald. The shift to higher energies of the X-ray absorption uranium L_{III} edge suggested that 80% of the uranium was in the U(VI) oxidation state. Furthermore, microbeam XAS by Bertsch et al. [5] suggested that in many of the soils the distribution of uranium-bearing particles was inhomogeneous because the signal varied as the focused beam was moved across the sample. However, in SP4 soils, uranium appeared to be uniformly distributed. This observation agreed with radiochemical analysis and particle sizing performed by Lee and Marsh [3]. Therefore, two separate techniques appeared to indicate that uranium occurred in a particulate form in incinerator site soils. These results indicated that characterization by electron microscopy would be representative, as all the contamination was in particulate form. Buck et al. [2,7,8], using electron microscopy techniques, also confirmed that most uranium in incinerator and SP2 soils was in the form of discrete particles but were unable to locate many uranium-bearing particles in SP4 soil samples.

Allen et al. [6] have determined U-O bond lengths by using XAS data to calculate radial distribution functions (RDF); however, as the data have not been corrected for phase shifts, the bond lengths may be in error.

Allen et al. [6] have suggested that schoepite (uranyl oxide hydrate) is an important phase in Fernald soils, although they present no evidence for its existence. There are two types of schoepite, hydrated and dehydrated, which have characteristic XRD reflections (7.37 Å and 3.59 Å for hydrated schoepite, 5.11 Å and 3.43 Å for dehydrated schoepite). Lee and Elles [9], who have used XRD extensively, have not reported the existence of schoepite in Fernald soils. In addition, schoepite is likely to be unstable in Fernald soils, relative to uranium phosphate, silicate, and carbonate phases. However, there was tentative evidence of becquerlite group uranium phases, which are structurally similar to the uranyl oxide hydrates. The difficulty with identifying uranium phases in bulk soil with only limited structural data and no compositional data to match is that there are a large number of possible uranium minerals in the literature. A "fingerprint" technique will require one to compare experimental data with standards obtained from all the listed minerals. However, the one uranium phase (uranium metaphosphate) which was of importance at Fernald is not a commonly known uranium mineral [2]. This result clearly demonstrates the advantage of AEM over fingerprint methods. Table 1 lists the various techniques used to characterize Fernald soils and the type of information they can provide. The luminescence and Raman spectroscopic methods used by Allen et al. [6] are unreliable techniques for performing this type of analysis, although once the phases have been established by using AEM, these methods might be used to estimate the relative amounts of phases in bulk soil. (These methods will still be subject to errors due to the large size of some uranium phases and interference from other phases in the soils.) Indeed, luminescence and Raman data matched

Table 1. Comparison of Characterization Techniques

Technique	Bulk	Trace Phases	Structural Analysis	Compositional Analysis	Fingerprint Method
AEM/SEM	x	x	x	x	No
XRD	x		x		No
XAS	x		x	x	--
Luminescence Spectroscopy	x	x			Yes
Raman Spectroscopy	x	x			Yes

well with the values expected for meta-autunite, supporting the AEM identification of this uranium phase as a major phase in SP2 and incinerator soils [6,7]. However, many other uranium minerals would have similar vibration spectra fingerprints, as all the phases contain UO_2^{2+} and phosphate groups [10].

II. EXPERIMENTAL METHODS AND DEVELOPMENT

Fernald soil samples were placed in polyethylene capsules and infiltrated with a few milliliters of a water-soluble melamine resin. The details of the sample preparation method are described elsewhere [11]. The sample block was polished and examined by SEM with backscattered electron (BSE) imaging and by X-ray energy dispersive spectroscopy. Uranium-rich particles were located by using atomic number contrast through BSE imaging. The uranium-bearing particles were isolated and made into thin sections by ultramicrotomy. The resulting sections were suitable for observation by transmission electron microscopy (TEM). This method of sample preparation allowed direct comparison between BSE images and TEM images. This enabled characterization of TEM samples to be representative of the bulk sample, because a much larger volume of soil can be examined in detail by this SEM/AEM combination than by AEM alone. Analysis by AEM is necessary because it provides the resolution required to probe the composition and structure of the small uranium phases that are within a matrix of other soil components. The TEM thin sections of uranium phases were analyzed in a JEOL 2000 FXII TEM operated at 200 kV and equipped for EDS and parallel EELS. Some images were collected by using a slow-scan charge-coupled device (CCD) camera because this instrument has excellent light sensitivity. Quantification of EDS analysis results was performed by using experimentally determined k-factors that were obtained by using 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 by a combination of EDS, EELS, and electron diffraction.

III. RESULTS AND DISCUSSION

By examining the samples with the SEM, we determined that uranium was contained within particles typically 1 to 10 μm in diameter in the incinerator and SP2 soils, although some particles were up to 100 μm or more in diameter. We also found uranium particles in the storage pad (SP4) soils, but they were much rarer in these soils. We found a surprising variety of uranium phases, some of which suggested that weathering and redistribution of uranium had occurred, resulting in the formation of a number of secondary uranium-bearing phases similar to those observed at naturally occurring weathered uranium deposits [7]. However, considering the wide variety of sources from which Fernald uranium came, this result should not be totally unexpected. The natural uranium deposits would have undergone some alteration. For example, the deposits in Zaire were in an oxidizing environment and would have led to the formation of silicates and oxide hydrates. Table 2 presents the distribution of uranium phases in the incinerator soils (A11 [including density-fractionated samples] and A14), as determined by a combination of SEM and AEM. Although the total amount of U(VI) phases in the soils was around 60-80% for both A11 and A14 samples, the distribution of the uranium phases was inhomogeneous.

The relative contributions of each phase to the total uranium content have been estimated on the basis of the area of the uranium phase observed in the polished SEM samples. (Density differences in the different uranium phases have been accounted for.) However, this method of estimating the contribution of each phase to the total uranium content is subject to errors: because the uranium contamination in Fernald soils was inhomogeneous, samples sometimes contained too few particles to allow generalization. However, because the same volume of soil was examined by all characterization methods performed at the different laboratories (i.e., XAS, XRD, and SEM/AEM), it is likely that all methods will be subject to these errors. The general agreement between the different techniques suggests that representative data have been obtained. It is also likely that treatability studies on similarly small samples will be highly variable as well. Therefore, the best extraction may depend, not on the best conditions, but on the most favorable (in terms of leaching) soil sample. The larger scale operations, such as the heap leaching studies, will be much more representative [12].

Table 2. Distribution (Percentage) of Uranium Phases in Incinerator Soils

	Autunite [U(VI)]	Uranium Metaphosphate [U(IV)]	Uraninite [U(IV)]	Uranium Calcium Oxide [U(VI)]	Uranium Silicate
Soil A11, Total	31	20	7	20	22
Heavy Sand	45	10	10	—	35
Medium Sand	3	37	1	58	1
Heavy Silt	24	32	14	16	13
Medium Silt	47	47	—	6	—
Soil A14, Total	55 - 80	10 - 34	5 - 8	0	2-5
Total Area of Uranium Phases, μm^2	27,675	17,700	6010	16,905	19,930

The specific uranium phases, as well as other non-uranium-bearing phases, in both the treated and untreated soil samples were identified by using TEM. This examination provided information on the effect of treatment technologies on the Fernald soils.

We also used AEM to identify the major soil components, which were quartz, phyllosilicates, calcite, and feldspars. Other non-uranium-bearing phases found in the soil samples included rutile, ilmenite, maghemite, apatite, cerium phosphate, yttrium phosphate, and zircon. The identification of these phases was confirmed by AEM and was discussed in our FY 1993 annual report [8]. The distribution of non-uranium-bearing phases will affect the efficiency of the treatment methods. For example, the large amount of calcite at Fernald prevented the use of acid leaching agents. Furthermore, acid leaching would also cause dissolution of complex aluminosilicates; hence, alkaline leaching is a more favorable remediation route.

A. Uranium Minerals Found in Fernald Soils

The large number of uranium phases present at Fernald was described in the FY 1993 annual report [8]. In this section, the types of uranium phases commonly found are discussed with reference to new samples, and data are given on some new uranium phases, which may have been produced by the action of chemical remediation agents.

The uranyl silicates and uranyl calcium oxides (becquerlite) found in Fernald soils may have been present in the feed material from ores from oxidizing environments such as the Congo (Zaire) uranium deposits. However, the phosphorus-bearing uranium phases probably formed at Fernald with phosphates present in the soils and from the plant.

After repeated analyses, we could recognize particular uranium phases by BSE imaging alone, which permitted us to determine the distribution of uranium phases more rapidly, although there were always a few uranium phases which could not be identified without the high resolution and electron diffraction capabilities of TEM.

1. Uraninite and Calcium Uranium Oxide

Uraninite (UO_2) is normally a nonstoichiometric phase (UO_{2+x}) possessing a fluorite structure. UO_2 will readily undergo oxidation, which results in an expansion of the unit cell parameters that can be detected by use of XRD [1] or electron diffraction [13]. Uranium oxide particles were fairly common in all the Fernald soil samples (Fig. 1a). Most often the particles were 50-200 nm in diameter, which should make these particles amenable to chemical leaching; however, they tended to occur in clumps, which were sometimes $\pm 0.1 \mu\text{m}$ in diameter. Uranium oxide particles were identified as uraninite by electron diffraction. The diffraction patterns show a number of larger d-spacings in the nonstoichiometric uranium oxide that are due to the creation of an oxygen superlattice by excess oxygen. Such reflections were absent in most of the analyses performed (Table 3). With the image resolution of the TEM, it is possible to see spatial relationships between phases in the soils. In Fig. 1b, a calcium uranium oxide phase can be seen embedded inside a pyroxene phase. The uranium-bearing phase was identified by the electron diffraction pattern taken along a major zone axis. Other calcium uranium oxide phases have also been found, which matched well with becquerlite, a calcium uranium oxide hydrate [U(VI) phase] (Table 4).

2. Uranyl Phosphate (Meta-Autunite)

The most abundant uranium phase found in Fernald soils was a calcium uranyl phosphate, which was identified by EDS and electron diffraction as meta-autunite. The presence of phosphate phases in soils may not be considered surprising because Fernald used tributyl phosphate (TBP) to purify uranium. Precipitation of uranium phosphates during the TBP

Fig. 1.

TEM CCD Image of (a) Uranium Oxide Particles and (b) Calcium Uranium Oxide Particle Embedded within Pyroxene Phase, with (c) Electron Diffraction Pattern from the Calcium Uranium Oxide Phase

Table 3. Electron Diffraction from Uranium Oxide Phase

Experimental d-Spacings, Å	UO ₃ (JCPDS 15-0201), Å	UO ₂ (JCPDS 5-550), Å
3.23	3.25	3.16
2.77	2.79	2.735
1.98	1.99	1.934

Table 4. Electron Diffraction from Calcium Uranium Oxide Phase

Experimental d-Spacings, Å	Experimental d-Spacings (Dithionite/Tiron), Å	Becquerlite (JCPDS 29-389), Å
6.14	---	6.25
3.47	3.44	3.45
	3.37	3.38
3.29	---	---
	3.17	3.18, 3.16
	2.70	2.72
	1.97	1.99
	1.88	1.87
	1.68	1.68

extraction process is a common problem. Figure 2 is a BSE image of a uranium phosphate phase found in incinerator site soils, which was identified by electron diffraction as tetragonal calcium uranyl phosphate (meta-autunite), ideally $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$ (in fully hydrated autunite, $x = 10$) (Table 5). As is common with many uranium minerals, the phase tended to consist of spiny needles, which could sometimes be recognized in the BSE images. An electron diffraction pattern taken along the [001] zone axis confirms the tetragonal nature of the phase (Fig. 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 [10]. Another group of uranyl phosphates, phosphuranylites, which have a U:P ratio of 3:2, were observed occasionally. Evidence from EELS indicated that meta-autunites containing ammonium may be present in the soils (Fig. 3). Autunites are weathering products of uraninite sometimes found in natural systems, and, indeed, there was evidence of some alteration of uranium-bearing phases in Fernald soils [7]. Uranyl phosphates were found attached to uranium oxide particles, as is observed in natural uranium deposits that have been exposed to oxidizing conditions. However, at Fernald, uranyl phosphates were most often found isolated from uraninite, possibly because they had precipitated from a phosphate-rich solution. Uranyl phosphates will control the uranium concentration in groundwaters, because they have solubilities below those of uranyl silicates and carbonates [14]. In groundwaters, where

$$\lg \frac{[\text{CO}_3^{2-}]}{[\text{PO}_4^{3-}]} > -3.5, \quad (1)$$

uranyl phosphates will dominate.

Fig. 2. Analysis of Uranyl Phosphate Phase: (a) BSE Image, (b) Electron Diffraction Pattern, and (c) EDS Analysis

Table 5. Electron Diffraction from Uranyl Phosphate Phase

Experimental d-Spacings, Å ^a				Autunite (JCPDS 12-418), Å	
---	---	5.80	5.80, 5.99	---	---
5.02	---	4.95	---	4.95	4.96
4.42	---	4.53	4.42	---	4.48
4.13	4.17	---	---	---	---
3.15	---	---	---	3.38	3.33 Å, 3.23
---	3.00	3.095	---	---	3.09
2.65	---	---	2.89	2.69	2.65
2.58	---	---	---	---	---
2.29	2.25	2.16	---	2.33	2.25, 2.19, 2.14
2.00	---	---	---	---	2.04
---	1.69	1.63	1.69	---	1.73, 1.64

^aFrom five samples with similar composition.

Fig. 3.

EELS Analysis of Ammonium-Containing Phase, Possibly an Autunite-Type Mineral Phase

Finch and Ewing [15] believe that the formation of 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). This condition may have occurred in Fernald soils. Apatite controls the PO_4^{3-} concentration in many natural waters and will keep phosphate levels below 10^{-7} M when the pH exceeds 7. In the Fernald soils, we found calcium phosphate and iron phosphate, which are sources for phosphorus in soil. Some of this phosphate may have come from fertilizers used in farming or from weathering of rocks, although much must have come from the TBP used in uranium purification. According to Lee and Marsh, the soil pH was around 8 for all soil samples [3], which suggests that $[\text{PO}_4^{3-}]_{\text{aq}}$ concentrations will be low and favoring precipitation.

Autunites possess a sheet-like structure composed of $(\text{UO}_2\text{PO}_4)^n$ layers in which each U^{6+} ion is six-coordinated. The U-O bond lengths in the calcium uranyl(VI) meta-autunite are 1.79 and 1.99 Å, and the four U-O(P) distances are 2.32 Å [10]. Allen, using uncorrected RDF data, reports bond lengths for U-O of around 1.1 to 1.3 Å [6].

3. Uranium Metaphosphate

During the TEM characterization of uranium contamination in Fernald incinerator site soils, we observed a ceramic-like phase that was stable under the electron beam and contained uranium and phosphorous. This phase did not possess the fine needles that were characteristic of uranyl phosphates. Figure 4 shows examples of the ceramic-like phase from incinerator site soil samples. The diffraction patterns were very stable even under a condensed beam, which tended to amorphize natural uranium minerals rapidly. The phase was identified as uranium metaphosphate $[\text{U}(\text{PO}_3)_4]$ by electron diffraction (Table 6). The experimental values from the different particles are quite consistent, and the match with a monoclinic uranium metaphosphate is reasonable. Uranium metaphosphates may have been formed within the incinerator at temperatures over 400°C and then deposited in the surrounding area through emissions from the stack. Uranium metaphosphates $[\text{U}(\text{PO}_3)_4]$ exist in several structural varieties, all of which require high temperatures and fairly harsh reaction conditions to form. All are greenish, and all have uranium in the (IV) oxidation state, coordinated with polyphosphate chains. Each U^{4+} ion is eight-coordinated with a distorted square antiprismatic array of oxygen atoms around it. The PO_4 tetrahedra are connected to form phosphate chains coiled in double spirals. The average U-O distance is 2.356 Å [10]. Allen et al. [6] report U-O bond lengths from RDF data of ~2.8 Å (although the data were not corrected for phase shifts). This general type of structure is typical of polyphosphate glasses and crystals that contain phosphate chains and highly charged metal ions with small radii. Uranium metaphosphate is very stable and completely nonhygroscopic, which may explain its stability in the electron beam (hydrated phases tend to amorphize rapidly in the electron beam). It is virtually insoluble in cold mineral acids, only dissolving slowly in H_3PO_4 on prolonged heating [10].

4. Uranyl Silicate

Uranyl silicate phases were relatively rare, although they were so large that they accounted for a significant amount of uranium in some of the soil samples (Fig. 5). The phase in Fig. 5 was identified as boltwoodite ($a = 7.07$ Å, $b = 7.06$ Å, $c = 6.64$ Å, and $\beta = 105.6^\circ$) on the basis of the electron diffraction pattern. The phase had the spiny crystal morphology typical of uranium minerals.

Table 6. Electron Diffraction from Uranium Metaphosphate Phase

Experimental d-Spacings, Å			Uranium Metaphosphate (JCPDS 16-0225), Å
4.51	4.48	4.42	4.41
3.51	---	3.54	3.53
2.37	2.38	2.34	2.47
2.25	2.23	2.22	2.22
---	1.91	1.93	---
1.77	---	1.77	1.79
1.63	---	---	---

Fig. 4.

BSE Images of Uranium Meta-phosphate Phase in (a) A11 Heavy Sand, (b) A11 Medium Sand, and (c) A11 Heavy Silt Soil Fractions; (d) Electron Diffraction Pattern from Phase Taken along $[011]$ which Indicated that the Phase was Monoclinic with $\beta = 96^\circ$; and (e) EDS Analysis of Phase

Fig. 5. AEM Characterization of a Uranyl Silicate Phase: (a) BSE Image, (b) TEM CCD Image, (c) Electron Diffraction Pattern Taken along the $[111]$ Zone Axis, and (d) EDS Analysis

B. Supporting Soil Remediation

Efforts over FY 1994 have concentrated on characterizing treated samples and providing information on these phases (through meetings and monthly reports) to the remediation groups working at Fernald and other national laboratories.

1. Carbonate Leaching

Because Fernald soils are thought to contain around 80% U(VI) phases (on the basis of the XAS results of Bertsch et al. and Ailen et al. [5,6] and SEM/AEM results [Table 2]), carbonate leaching was expected to be an efficient method for removing uranium from the soils. This approach was taken at the SP4 site with success [4]. At the incinerator site and SP2 site, carbonate leaching was not as effective, because the distribution of uranium phases was different in these samples. The uranyl phosphate phase still remained in the treated soils. Uranyl-type phases can be leached by carbonate according to the scheme [16]

As TEM analysis showed, much of the uranium in SP2 and incinerator site soils was in the form of uranyl phosphates, which are more insoluble than uranyl carbonate complexes. Many of the uranyl phase particles ranged in size from 1 to 10 μm ; they were elongated and had large surface areas, which could allow rapid dissolution. In carbonate-treated incinerator soil samples, 72% of the uranium was solubilized [12]. Using TEM, uranyl phosphates were shown to be substantially reduced, but not completely removed. Two types of U(IV) phases remained, uraninite and uranium metaphosphate, as well as some other uranyl phases. It is the variety of uranium-bearing phases that has made removal by one chemical process difficult.

Uraninite can be leached by carbonate according to the scheme [16]

In other words, as long as an oxidizing agent is present, uraninite will be attacked.

Allen et al. [6] have shown a change in RDF data with chemical leaching, which appears to indicate the removal of U(VI) phases, in agreement with the AEM investigations.

2. Heap Leaching

Effective oxidation of tetravalent uranium can be achieved with molecular oxygen in carbonate solution, with the rate of oxidation being proportional to the oxygen partial pressure. Chemicals that can provide this oxygen, such as hydrogen peroxide and potassium permanganate, are either expensive and/or will increase the amount of pollution. Hence, the mining technique of heap leaching may be an attractive alternative for introducing oxygen.

On the basis of SEM/AEM analysis of the uranium-bearing phases in the carbonate-treated soils, the majority of the uranium (60-75%) was in the form of uranium metaphosphates, about 20% was uranium oxide (UO_2), and the remainder was uranyl phosphate. Wet chemical analysis showed that 45-70% of uranium was removed from Fernald soils by

carbonate leaching alone. With the addition of an oxidizing agent (potassium permanganate), more than 80% was removed [4], suggesting that some U(IV) phases had been leached. The uranium concentration in SP2 and incinerator soil samples was reduced significantly, but it was still above the regulatory target level of 20 ppm.

In the heap-treated samples, there was evidence from TEM images of uraninite dissolution; however, there was no evidence of dissolution of the uranium metaphosphate phase (Fig. 6a). Table 7 shows the results of SEM/AEM analysis of the heap leaching samples. There is a suggestion that U(VI) phases were removed in the lower portions of the column. Electron diffraction analysis of the sample indicated that uraninite had been oxidized (Table 8). However, crystalline autunite phases still remained in the treated soil samples, as confirmed by electron diffraction (Table 9). Using the [001] zone axis pattern, the phase was identified as tetragonal meta-autunite, as it was difficult to separate the phases based solely on d-spacings. As the uranium metaphosphate phase appears to be insoluble and leach-resistant, it could be left in the treated soil indefinitely, without any further release of uranium into the environment. However, treated soils will need to be tested with rainwater to see if further weathering will occur.

3. Tiron/Dithionite Process

A very different approach to the removal of uranium in Fernald soils involved the use of a synthetic analogue of microbially produced complexing agents, termed Tiron [4]. In this method of soil remediation, a catalyst (dithionite) is used to reduce the uranyl ion to U(IV), which is removed from solution by chelation with Tiron. The technique is effective at removing uranium from soil contaminated with an oxide hydrate (schoepite) in laboratory tests [4], but it is only slightly effective at dissolving uranyl phosphates, which are major U(VI) contaminants in both Fernald incinerator site soils and SP2 soils. In Fig. 7, a meta-autunite (calcium uranyl phosphate) phase has been attacked by the dithionite/Tiron mixture, but a core of crystalline uranyl phosphate remains, and the surrounding phosphorous-rich amorphous area is only slightly depleted in uranium (see Table 10). Fluorescence optical images taken by Allen et al. [6] indicated substantial reduction in the size of the uranium meta-autunite phase; however, AEM examination demonstrated that the uranium phase had been altered and had lost its ability to fluoresce to the same degree as the crystalline phase. The treatment has removed both uranium and calcium from the crystalline meta-autunite. The dithionite/Tiron leaching method was not effective at removing the uranium phases in Fernald soils. Table 11 shows electron diffraction analysis of a uranium metaphosphate phase. This phase was found to be unaffected by dithionite/Tiron treatment. The composition of the phase was determined to be approximately UP_3O_x by AEM.

4. Aqueous Biphasic Separation Process

Particles from the aqueous biphasic (ABP) separation process were examined. Optical microscopy was used to determine the distribution of quartz and clay material in the separation columns. Knowing the distribution of these phases was critical to understanding whether the column was operating correctly. The ABP process appeared to reduce the uranium concentration significantly in contaminated soils. The uranium concentration in treated samples was found to be reduced from 500 ppm to 70 ppm [17]. SEM/AEM analysis revealed that most of the particles remaining were uraninite phases around 1 μ m in diameter (Fig. 8). It is important to evaluate the application of this process after chemical soil washing to see whether the process can separate out the particulate U(IV) phases.

Fig. 6. Effect of Heap Leaching on the Surface of Uraninite Phase: (a) TEM CCD Image of Oxidized Uranium Oxide (Uraninite) Phase, (b) Electron Diffraction Pattern from the Phase; and (c) TEM CCD Image of Uranium Metaphosphate Phase Showing No Alteration.

Table 7. Distribution of Uranium Phases from the Heap Leaching Process

Sample Number	Autunite [U(VI)]	Uranium Metaphosphate [U(IV)]	Uraninite [U(IV)]	Uranium Calcium Oxide [U(VI)]	Other Uranium Phases
Column #1	46	1	53	---	---
Column #2	72	1	22	---	4
Column #3	---	8	46	46	---
Total area (μm^2)	21,825	365	15,100	600	3200
Total %	53	1	37	1	8

Table 8. Electron Diffraction from Uranium Oxide Phase from Heap Leaching

Experimental d-Spacings, Å	Experimental d-Spacings, Å	UO ₃ (JCPDS 31-1418), Å	UO _{2+x} (JCPDS 13-225), Å
8.84	---	8.31	---
---	6.57	7.16	---
5.71	5.31	5.86, 5.10	---
5.02	4.79	4.80	---
---	3.54	3.58	---
3.38	---	3.40	---
3.23	3.23	3.25	---
---	3.09	3.10	3.09
---	2.93	2.93	---
---	2.65	2.66	2.68
---	2.48	2.49	---
---	2.29	2.29	---
---	2.15	2.17	---
1.99	1.90	---	1.90
---	1.76	---	---
---	1.67	---	1.62

Table 9. Electron Diffraction from Calcium Uranium Phosphate Phase from Heap Leaching

Experimental d-Spacings, Å	Autunite (JCPDS 12-418), Å	Meta-Autunite (JCPDS 14-73), Å
6.81, 6.75	6.67	6.57
5.23	5.19	5.30
4.95	4.96	4.81
3.66	3.58	3.51
3.09	2.91	2.93, 3.10
2.30	2.30	2.20
1.94	1.92	1.92

(a)

(b)

Fig. 7. Effect of Dithionite/Tiron Treatment on the Uranyl Phosphate (Meta-Autunite) Phase: (a) BSE Image and (b) TEM Image

Table 10. Composition of Uranyl Phosphate (Meta-Autunite) Phase in Dithionite/Tiron-Treated Incinerator Soil Samples

Element	Amount of Element in Crystalline Uranium Phosphate, wt% ^a			Amount of Element in P-Rich Phase, wt%
P	20.1	15.5	17.3	42.7
U	59.1	73.6	66.9	47.5
Ca	20.7	10.9	15.8	9.8

^aComposition analyzed at three different regions in the crystalline material.

Table 11. Electron Diffraction from Uranium Metaphosphate Phase Resulting from Dithionite/Tiron Treatment

Experimental d-Spacings, Å	Uranium Metaphosphate [18], Å
6.40	6.256
5.30	5.13
4.50	4.41
4.13	4.04
3.87	3.84
3.64	3.64
3.21	3.21
2.76	2.77
2.63	2.62
2.24	2.24
2.13	2.16
1.88	
1.84	

Fig. 8. BSE Image of Uranium Particles Remaining in Soil after ABP Processing

5. Acid/Bacterial Digestion

Bacterial leaching for the recovery of metals has been practiced for well over a century. Treatment of uranium ores in this fashion came about after it was observed that the Uregerica uranium mill in Portugal was not achieving its expected uranium yield. The uranium was being leached by rain water in a reaction catalyzed by bacteria. The most effective leaching conditions have been found to be pH = 1.1 to 2.8, 35°C, and a good oxygen supply [16]. In soil, acid will be consumed by reaction with calcite and dolomite, and may lead to the dissolution of clays. Fernald soils that have undergone the process of acid and bacterial digestion were examined by SEM/AEM techniques. The acid/bacterial process failed to remove the major types of uranium phases (meta-autunite as well as uranium(IV) phases [Fig. 9]). The report on this work is attached as Appendix B. It is likely that a heap leaching operation may have some bacterial action which may assist in leaching uranium in a full-scale plant.

C. Characterization of Portsmouth Site Soils

We have used SEM/AEM techniques to determine the distribution and identity of contaminant phases in the soil from the former gaseous diffusion plant at Portsmouth in Ohio. This study will continue through FY 1995. The majority of the particles were uranium oxides and calcium uranium oxides, although a number of other types of phases were found (Table 12 and Figs. 10 and 11). Phosphates were extremely rare in the soils, although the fluorine-bearing particles we expected were not observed. A thorium-uranium-silicon phase and uranium-iron-tin phase were also found by SEM. Characterization by AEM will be required to determine the exact nature of these phases. The errors involved in determining the distribution of particles was explored by plotting the size distribution of phases found by BSE imaging. The graph in Fig. 12 illustrates that a non-Gaussian distribution of particles was examined. This suggests that the smaller particles may have been missed, as larger particles accounted for a larger portion of the total uranium found.

(a)

(b)

Fig. 9. BSE Images of (a) Uranyl Phosphate (Meta-Autunite) Phase and (b) Uranium Metaphosphate Phase from Acid/Bacterially Digested Samples from the Incinerator Site

Fig. 10. BSE Images of Uranium Phases Found in Portsmouth Soil Samples

(a)

(b)

Fig. 11. AEM Characterization of Uranium Oxide Particles from Portsmouth Soils: (a) TEM Image and (b) Electron Diffraction

Fig. 12. Size Distribution of Phases Found by BSE Imaging of Portsmouth Soils

Table 12. Distribution of Uranium Phases in Portsmouth Soil Samples

	Phase Identified by SEM				
	Uranium Phosphate	Uraninite	Calcium Uranium Oxide	Uranium Iron Oxide	Other Types of Uranium Phases
Area of Phase, μm^2	100	3614	6080	1225	1875
Relative %	1	28	47	15	10

IV. SUMMARY AND RECOMMENDATIONS

A. Using Characterization for Developing Remediation Approaches

Our AEM investigations have shown that many types of uranium phases are present in Fernald soils. This diversity may be due to the broad range of sources of uranium and the variety of processes employed at Fernald. The range of contamination has had implications for the remediation efforts at Fernald, because no single chemical process has been able to remove all uranium without totally destroying the soil. However, carbonate heap leaching has managed to remove a majority of the uranium phases, leaving only the uranium metaphosphate phase (which is only present at the incinerator site). Although not the most technologically advanced of processes, it does appear that heap leaching is the most effective. However, given the relatively large phosphate concentration in Fernald soils, the risk of reprecipitation of uranium should be considered in scaled-up remediation. Dithionite/Tiron treatment does leach some uranium from meta-autunite phases but is not completely effective against these U(VI) phases. Acid/bacterial digestion was ineffective at removing many of the uranium phases, and, in addition, it tended to destroy the soil composition. The uranium metaphosphate phase, which has not been removed by any of the chemical techniques, may be affected by the ABP process. In FY 1995, we will further investigate samples from the ABP extraction columns. Because the properties of the uranium metaphosphate phase are known, it may be reasonable to leave this phase in the soil.

Effective removal of uranium from the Fernald soils can be enhanced by detailed knowledge of the chemical and physical characteristics of the waste and its environment. Unless a characterization technique can determine the exact nature of the contaminant phase, incorrect interpretations of data could lead to the selection of inappropriate remediation methods. Using a technique that provides both compositional and structural data makes it easier to determine the correct phase. Luminescence and Raman spectroscopy provide only a fingerprint, which must be distinct from all other phases for accurate identification. There are at least 21 types of uranium phosphates, as well as many uranium carbonate, silicate, oxide, and hydroxide phases, all of which must be compared to the experimental result, if one has no reliable compositional data.

The characterization methods described above, in combination with XAS and XRD, will allow remediation technology groups to find more efficient ways of removing contamination. Characterization has been criticized as providing esoteric information; however, the results of characterization studies at Fernald can be used to demonstrate effectiveness of remediation technologies, select appropriate cleanup methods, reject inappropriate ones, or introduce alternative approaches.

B. Technology Transfer Efforts

Efforts have been made to find alternative customers for soil characterization, particularly from that part of the commercial sector that is engaged in developing and testing soil treatment technologies. Ecotech, Inc. (now Advanced Recovery Systems) funded a study of thorium- and uranium-contaminated soil surrounding a nuclear facility [19]. In addition, the AEM characterization group has been funded to support studies at Johnston Island in the Pacific Ocean [20] and studies of plutonium-contaminated incinerator waste from the Rocky Flats Plant and Los Alamos National Laboratory [21].

C. Summary

Uranium has been found in a number of different forms in Fernald soils, including calcium uranyl phosphate (meta-autunite), uraninite (uranium oxide), calcium uranium oxide, uranium metaphosphate, and uranyl silicate (boltwoodite). Although uranium is known to have a strong affinity for adsorption onto iron oxides, particularly amorphous iron oxyhydroxides, uranium 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 (50 nm) particles of uraninite [11]. Observations by micro-XAS methods supported this finding [5].

The diversity of uranium particulate phases at Fernald has been established by utilizing a combination of electron beam methods. This variety of phases is partially due to the range of operations that were conducted at Fernald and also possibly due to weathering and redistribution of the uranium over time. This diversity of uranium phases may impede cleanup efforts, because any single remediation technique cannot remove all the different forms of uranium in the soils. Indeed, Harrington [1] writes that insoluble uranium phases were often encountered during the operation of the Fernald plant. Electron beam analysis of these contaminated soils has provided information on the uranium present that is useful for developing innovative cleanup technologies. This study has demonstrated the utility of AEM for determining the nature of contaminant phases in environmental samples. With the combination of diffraction and composition data with fine probe resolution, complete unknowns can be identified. By combining AEM and electron diffraction studies with SEM, and preparing samples by ultramicrotomy, detailed characterization can be carried out quickly and efficiently. The combination of microscopies has also allowed representative characterization of particulate phases in the samples.

It is our conclusion that heap leaching with carbonate has the best chance of removing uranium from the contaminated soils around the Fernald plant. Observations at the microscopic level by TEM indicate that heap leaching does attack the uraninite and uranyl phosphates in the soil.

ACKNOWLEDGMENTS

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APPENDIX A.

TERMINOLOGY

A14	soil sample from incinerator site
A11	soil sample from incinerator site
ABP	aqueous biphasic [separation process]
AEM	analytical transmission electron microscopy (term used to cover imaging, diffraction, and compositional analysis on TEM)
BSE	backscattered electrons (Rutherford scattering which is proportional to the square of the atomic number of analyzed element)
CCD	charge-coupled device (for real-time imaging and low light intensities)
EDS	X-ray energy dispersive spectroscopy (for elemental analysis)
EELS	electron energy loss spectroscopy (superior energy resolution and sensitivity for many more elements than EDS)
dithionite	reducing agent
heap	open-type leaching method common in the mining industry
RDF	radial distribution functions
SEM	scanning electron microscopy
SP2	core soil sample, storage pad area
SP4	core soil sample, storage pad area
TBP	tributyl phosphate
TEM	transmission electron microscopy
Tiron	complexing agent for uranium-based or microbial agents
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction

APPENDIX B.

**CHARACTERIZATION BY AEM/SEM OF
BACTERIA-TREATED SOILS**

ARGONNE NATIONAL LABORATORY**Chemical Technology Division****9700 South Cass Avenue, Argonne, Illinois 60439-4837**

January 17, 1994

Dr. Gretchen Mattern
Centers for Bioprocessing and
Environmental Assessment
EG&G, INEL
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Dear Dr. Mattern:

Subject: Analysis of INEL Soil Samples Summary

Two sample sets of soil were examined for uranium distribution and soil composition. They were labeled 930212-027, incinerator site, and B12, storage pad area. The samples were examined in the untreated, partially treated and fully treated conditions. No particulate uranium was located in the B12 soil sample, which is consistent with results from LANL (Dave Morris) for this soil, who noted that the X-ray absorption spectra were different for 'A' series and 'B' series soil. The untreated 930212-027 soil contained three main uranium bearing phases, uranium metaphosphate, autunite and uranium oxide. The analysis of the partially treated soil indicates that the uranium metaphosphate, $U(PO_3)_4$ was not removed while the other phases were. No uranium bearing particles were located in the fully treated sample.

EDS analysis of the soil samples indicate that the treatment process is removing calcium and magnesium from the soil. This is probably the result of dissolution of calcite and dolomite particles.

Sample Information

We received two sample sets of soil from INEL. They are labeled 930212-027 and B12. Both sets of samples were sent in untreated, partially treated and fully treated conditions. The untreated 930212-027 soil from the incinerator area was described as containing 490 ppm U while the B12 soil from the storage pad area contained 390 ppm. The partially treated soil was described as having had approximately 50% of the contamination removed. The fully treated soil was described as clean. The treatment consisted of leaching with a dilute sulfuric acid solution containing the bacterium *Thiobacillus ferrooxidans* at a pH of 2.3.

The untreated soils arrived damp, the partially treated soils were quite wet and the fully treated soils were dry. Samples were embedded in nanoplast in the as received condition, but the resin did not cure properly. Next the samples were dried at 40°C for 3 days. The resulting dry soil consisted of large clumps that were broken apart and further dried for 1 day at 40°C. The samples were then successfully embedded for SEM and TEM examination.

Soil Composition

Several large area EDS probes were taken of the soil in the untreated and in the treated condition to determine if the treatment resulted in noticeable compositional differences. The EDS spectra for different areas of the same soil type matched up quite well, indicating that at the probe size of 2 cm by 1.5 cm, the soil is nearly homogeneous. Results were normalized to 100% for the analyzed elements.

INEL 930212-027 Soil
Atomic % of analyzed elements

	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe
untreated	0.7	7.8	77.7	1.2	2.3	4.2	1.9	1.0	3.1
partially	0.4	7.4	80.6	0.5	2.2	4.1	1.0	1.0	2.8
fully	0.4	7.5	76.0	3.6	1.5	4.9	0.5	0.8	4.7

The standard deviations for the Mg content of the soils are 0.06, 0.09, 0.13 for the untreated, partially treated and fully treated soils respectively. They are 0.3, 0.26, 0.07 for Ca concentrations. The sulfur content also varies, perhaps due to the soil washing after treatment. Also, the Fe content varies, but since this is not a systematic variation it is presumed to be due to sampling statistics.

INEL B12 Soil
Atomic % of analyzed elements

	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe
untreated	2.4	9.8	58.5	2.0	4.0	4.5	14.0	0.7	4.2
partially	1.1	11.0	58.8	9.3	1.7	4.4	8.3	0.9	4.6
fully	0.9	9.9	53.4	11.8	3.8	4.9	8.7	0.7	6.0

The standard deviations for the Mg content of the soils are 0.25, 0.2, 0.34 for the untreated, partially treated and fully treated soils respectively. They are 1.34, 0.13, 0.38 for the Ca concentrations. The sulfur content also varies, perhaps due to the soil washing after treatment. Also, the Fe content varies, but since this is not a systematic variation it is presumed to be due to sampling statistics.

Based upon these observations the clay in the soils was examined to determine if it had been affected by the soil washing. No noticeable differences were observed in the compositions or relative amounts of the clays for the differing sample conditions. This would suggest that individual calcite and dolomite particles are being dissolved in the treatment process.

In order to determine if the treatment process had resulted in preferential dissolution of the smaller particles, the polished surfaces were examined to determine a size distribution. Unfortunately, large amounts of conglomerations were present in all of the samples, making this determination quite difficult with much room for error.

Uranium-Bearing Phases

Using back scattered electron imaging the samples were examined for uranium bearing phases. Location of uranium in the 'B12' soil sample (storage pad area) in both the untreated and treated conditions has proven to be quite difficult. This is in contrast to the 'A' series soil (incinerator site) where particulate uranium is easily located. This observation is consistent with D. Morris's (LANL) results who has observed a difference in the X-ray absorption spectra between the A and B series soil. One particle, approximately 1 by 2 μm , containing U was located in a large clay conglomeration, Figure 1.

The uranium in the sample 930212-027 (incinerator site) was present in particulate form. Particles were easily located in this soil sample. A summary of the area percentages of the uranium minerals located to date is presented below. The particles are tentatively divided into categories on the basis of SEM / EDS analysis. At Argonne, we have examined many of these particles by SEM and AEM in previous studies for Fernald Characterization. This experience enables us to identify these phases through a combination of morphology and SEM EDS composition. If warranted AEM analysis will be conducted on future samples.

**Area Percent of Observed Phases
Soil Sample 930212-027**

	U(PO ₃) ₄	UPCa	U Only	UCaFe	Undetermined
Untreated	12	70	17	-	1
Partially Treated	88	-	-	10	3

These results suggest that the partial washing process is effective at removing all of the uranium contamination except for the U(PO₃)₄, uranium metaphosphate, contamination. Confirmation of this observation could be obtained through X-ray absorption spectroscopy. Other groups have had a similar problem in the removal of this ceramic like phase. Figure (2) is an SEM micrograph of a typical U(PO₃)₄, uranium meta-phosphate, particle and its SEM EDS spectra. The semi-quantitative results of the standardless EDS analysis indicate a uranium to phosphorus level of approximately 4:1 as would be expected for this mineral. This is in agreement with TEM analysis of similar particles that positively identified this phase through a combination of electron diffraction which provides information about the crystal lattice spacings and EDS compositional analysis.

Previous analytic electron microscopy analysis, conducted at Argonne, of particles similar to the UPCA particles in this soil sample positively identified this group as autunite and meta-autunite minerals. Autunite has a composition of the form Ca(UO₂PO₄)₂·10-12 H₂O while meta-autunite has a chemical composition of the form Ca(UO₂PO₄)₂·0-6 H₂O. Other elements, such as iron can also be present. These phases are readily identified in the SEM due to their needlelike morphology. Figure (3) is an SEM micrograph of a typical autunite particle from the 930212-027 incinerator site soil and its SEM EDS spectra.

The uranium only phase is probably a uranium oxide. Previous AEM analysis, done at Argonne, of uranium oxide particles from the incinerator site found the uranium oxide to be UO_{2+x} . Figure (4) is an SEM micrograph of a typical uranium oxide particle from the 930212-027 soil. The UCaFe particle was not identified but similar particles from other soil samples were found to be conglomerations of the various oxides, when analyzed with the analytic electron microscope. It is not considered to be a major constituent.

Finally, a cursory search was conducted for any uranium bearing particles in the fully treated soil, none were located. A more exhaustive search can be conducted on samples of great interest.

AEM analysis can be conducted on these or future samples if necessary to more positively identify the uranium phases present.

Conclusions

The results indicate that the treatment process is removing most of the uranium bearing phases with the uranium metaphosphate, $\text{U}(\text{PO}_3)_4$, phase being the last to be dissolved. In addition the treatment process is removing calcium and magnesium from the soil, probably due to the dissolution of calcite and dolomite particles.

Sincerely,

Neil R. Brown
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Figure 1. SEM micrograph of a small uranium bearing particle located in a clay and quartz conglomeration, from the partially treated B12 soil. The particle contains U, P and Fe but due to its small size, resulting in EDS signal overlap, the phase could not be determined.

Figure 2. SEM micrograph of two typical uranium metaphosphate, $\text{U}(\text{PO}_3)_4$, particles and an accompanying EDS spectra, from the 930212-027 soil sample.

Uranium metaphosphate $U(PO_3)_4$

Label: Uranium metaphosphate $U(PO_3)_4$
 Livetime : 71.0 Sec.
 Technique: Peak Location

Chi-sqd = 1.28   Livetime = 71.0 Sec.

Standardless Analysis

Element	Rel. k-ratio	Net Counts
O -K	---	5071 +/- 99
P -K	0.29735 +/- 0.00267	30157 +/- 271
U -M	0.70265 +/- 0.01248	27247 +/- 484
U -L	---	2862 +/- 158

PROZA Correction 30.00 kV 44.42 deg
 No. of Iterations = 4

Element	k-ratio	Z	A	F	Atom %	Wt %
P -K	0.21305	0.836	2.107	0.991	81.99	37.20
U -M	0.50342	1.163	1.073	1.000	18.01	62.80
Total						100.00 %

Figure 3. Two typical autunite particles from the 930212-027 soil sample. Notice the fine needlelike structure lacking in the other phases.

Label: blk f253 inel-027 unt nrb225
 Livetime : 81.0 Sec.
 Technique: Peak Location

Chi-sqd = 2.45   Livetime = 81.0 Sec.
 Standardless Analysis

Element	Rel. k-ratio	Net Counts
C -K	---	5817 +/- 103
O -K	---	5886 +/- 134
Si-K	0.00268 +/- 0.00086	684 +/- 219
P -K	0.13323 +/- 0.00158	30246 +/- 358
U -M	0.73905 +/- 0.00920	62069 +/- 773
Ca-K	0.11945 +/- 0.00207	21210 +/- 367
Fe-K	0.00559 +/- 0.00177	641 +/- 203
U -L	---	5201 +/- 242

PROZA Correction 30.00 kV 37.81 deg
 No. of Iterations = 3

Element	k-ratio	Z	A	F	Atom %	Wt %
Si-K	0.00207	0.803	3.004	0.987	1.35	0.49
P -K	0.10316	0.832	2.373	0.988	50.05	20.14
U -M	0.57226	1.153	0.987	0.995	20.97	64.83
Ca-K	0.09249	0.822	1.843	0.999	26.89	14.00
Fe-K	0.00433	0.856	1.452	0.995	0.74	0.54
Total						100.00 %

Figure 4. SEM micrograph and EDS spectra of uranium oxides from the 930212-027 soil sample.

uranium oxide

Label: INEL-027 untreated blkf253

Livetime : 52.0 Sec.

Technique: Peak Location

INEL-027 untreated blkf253

Chi-sqd = 3.95

Livetime = 52.0 Sec.

Standardless Analysis

Element	Rel. k-ratio	Net Counts
C -K	---	5222 +/- 110
O -K	---	2472 +/- 120
U -M	0.99636 +/- 0.01078	79986 +/- 865
U -L	---	9930 +/- 282

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