

**ANALYTICAL ELECTRON MICROSCOPY EXAMINATION
OF URANIUM CONTAMINATION
AT THE DOE FERNALD OPERATION SITE***

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ABSTRACT

Analytical Electron Microscopy (AEM) has been used to identify uranium-bearing phases present in contaminated soils from the DOE Fernald operation site. A combination of optical microscopy, scanning electron microscopy with backscattered electron detection (SEM/BSE), and AEM was used in isolating and characterizing uranium-rich regions of the contaminated soils. Soil samples were prepared for transmission electron microscopy (TEM) by ultramicrotomy using an embedding resin previously employed for aquatic colloids and biological samples. This preparation method allowed direct comparison between SEM and TEM images. At the macroscopic level much of the uranium appears to be associated with clays in the soils; however, electron beam analysis revealed that the uranium is present as discrete phases, including iron oxides, silicates (soddyite), phosphates (autunites), and fluorite. Only low levels of uranium were actually within the clay minerals. The distribution of uranium phases was inhomogeneous at the submicron level.

INTRODUCTION

Technologies are under development for remediating the uranium-contaminated soils resulting from defense-related operations at the Fernald Environmental Management Project Site, OH. These remediation technologies begin with characterization of the nature and distribution of the uranium contamination, followed by the application of chemical and physical separation technologies (1). Analytical Electron Microscopy (AEM) is one tool that can be used to determine the nature of uranium interactions with the local environment at the submicron level. Such interactions, termed weathering, will affect the transportability of uranium in the groundwater system. Uranium weathering results in the transformation of the primary uranium-bearing phases into secondary minerals or incorporation of uranium into other phases (2). Such phases can be identified with the combination of techniques available with AEM, including imaging, electron diffraction, X-ray energy dispersive spectroscopy (EDS), and electron energy loss spectroscopy (EELS).

At Fernald, the contamination of the soil generally came from three sources; airborne uranium dust particles, aqueous uranium wastes, and solid uranium product spills (3). An extensive sampling program has identified the areas of major contamination, and current interest is on further analysis of selected samples from the site. In this investigation soil fractions taken from two different sampling positions (SP) have been analyzed. One fraction was analyzed from SP4 (Plant 1/Storage Pad Area) and was taken from a core sample from a depth of 8.5 cm. The contamination in this area resulted mainly from uranium product spills. The second sample SP10 (taken in the vicinity of the Fernald incinerator plant), had had its uranium content concentrated by a gravimetric method, and it was the concentrated sample which was analyzed by AEM.

The basic components of the contaminated soils had been earlier identified by SEM and x ray diffraction as various clays and quartz, and revealed the presence of uranium inclusions associated with the clay fraction of the soil, but a unique description of the phases was not provided (3). This paper describes the characterization of the uranium-bearing soil fractions from Fernald sites including both processed and untreated soil. The objective of the paper is to (a) describe the combination of optical microscopy, Scanning Electron Microscopy using Backscattering Electrons (SEM/BSE), and AEM as a coherent methodology to provide representative characterization data on the uranium-bearing phases within the contaminated soil, and (b) to identify discrete uranium phases found in Fernald soil fractions.

EXPERIMENTAL

The uranium-bearing phases in the contaminated soil samples were isolated using micromanipulation techniques assisted by polarizing light microscopy and SEM/BSE. Thin sections for Transmission Electron Microscopy (TEM) analysis were produced by ultramicrotomy. AEM was performed using a JEOL 2000FXII TEM operated at 200 kV.

Thin sectioning of isolated small particulates by ultramicrotomy is well described in the literature (4,5). Thin sections of soil constituents have been prepared using the microtome, but the technique has seen limited use in gross soil studies. Wada and Kakuto (6) have examined clays in soils by TEM, producing samples by embedding them in epoxy and then sectioning.

In studies where a representative sample of the bulk is required, it is necessary to show that one is observing the same regions in the SEM and the TEM. This has usually been a difficult task to accomplish, as it requires producing an intact sample section along a precise direction and over a specific area. Comparison of SEM and TEM images allows greater confidence in determining whether uranium-bearing phases are not just peculiarities, but true representations of the major uranium-bearing phases in the soil.

To provide a representative characterization of uranium phases distributed in soil, a relatively large number of unaltered soil particles must be examined. This was achieved by mounting particles for SEM and examining polished cross sections with a backscattered electron detector. Because the objective was to use an embedding resin that would allow thin sectioning of a uranium-containing particle directly from the SEM mount, it was imperative to use a resin with optimum infiltration and sectioning properties.

Ultramicrotomy of soil particles is the most appropriate means of viewing the undisturbed spatial relationship of soil components. Section quality can be substantially improved by selecting a resin that has good cohesion and matched hardness with the sample, and several different embedding media were evaluated. The best improvement in infiltration was achieved with a water-soluble melamine resin, which is used to replace water in wetted soil particles. Frösch et al. (7) compared sections made of the polar melamine resin and a non-polar epoxide resin and found that the melamine resin produces much thinner and smoother sections. The soil particles were prepared for microtomy following a procedure similar to that used in the preparation of aquatic colloids (8).

The SEM results showed an improvement in the polished surface and in the infiltration of large particles with the melamine resin. Because the spatial relationship of uranium phases within the larger particles was well preserved, more uranium-containing areas could be isolated in a given field of view. The increased section quality made it possible to produce completely intact sections thinner than sections obtained with the epoxy and acrylic resins. Because of these improvements, the uranium phases identified in the TEM could be correlated with the corresponding areas in the SEM/BSE image.

In Fig. 1, structures from the same particle can be seen in both the SEM and TEM micrographs. The slight discrepancy in particle morphology between the SEM and TEM images is due to the sectioning process, which may occur over a depth of ~3 μm ; however, the overall structure of the particles is preserved.

"Place Fig. 1 here"

RESULTS AND DISCUSSION

While the general mineralogy of the soil samples has been described by Lee and Marsh (3), we sought to identify the specific phases in the current samples and thereby determine the distribution of uranium within the clay fraction of the soils. The TEM examination of the soils revealed two major components, quartz and clay. In Fig. 2, a quartz particle can be seen surrounded by clay particles. Clays mineral types in SP4 were identified as mica, chlorite, and smectite clay groups by selected area electron diffraction (SAED), EDS composition data, and clay morphology. However, specific clay minerals could not be identified with the method of analysis used.

"Place Fig. 2 here"

Clay minerals are known to have an affinity for uranyl species and take up uranium either by adsorption onto the surface of the clay or within interlayer sites (9). The affinity for cation sorption depends on the clay mineralogy and the nature of the cation which compensates for the negative surface charge. At Fernald, bulk analyses of soil samples has suggested that uranium is associated with clay phases, based on gross studies of the large soil fraction. In the present study, a mica group clay was found to contain no detectable uranium, but a small amount of uranium (<1 wt%) was found to be associated, on occasions, with a chlorite group clay. At times it appeared that a high concentration of uranium was present in the clay minerals, but this was later identified as a discrete uranium silicate phase (see Fig. 3). The SAED patterns from this phase were consistent with soddyite $[(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O}]$, a uranyl silicate commonly found as an alteration product both in laboratory-reacted and field-weathered uraninite (10, 11). The presence of this phase in the core soil sample SP4 suggests some weathering of the uranium.

"Place Fig. 3 here"

For sample SP4, calcium and uranium were detected together in a number of SEM analyses, which indicated that this phase was an important uranium-bearing phase (see Fig. 4) The calcium phase, though crystalline, consisted of many small crystallites, resulting in a powdered SAED pattern, which matched with fluorite. Compositional analysis by EELS confirmed that oxygen was not a major component of this phase.

"Place Fig. 4 here"

Amorphous uranium-bearing iron oxide phases were observed in many regions of sample SP4 (Fig. 5). This type of uranium phase had a different morphology compared to that of the calcium phase. It consisted of small (100 nm diameter) particles, which often appeared to be strung together into a much larger agglomerate. A higher concentration of uranium was found in the iron uranium oxide phase than in the calcium fluoride phase. The uranium concentration varied considerably, suggesting the adsorption of uranium on the iron oxide particles. Hsi and Langmuir have observed the pH-dependent adsorption of uranyl [U(VI)] on various iron oxides (12).

"Place Fig. 5 here"

Uranium oxide particles were found in both the processed soil from SP10 and, less frequently, in the core samples from SP4. The SAED of uranium oxide phases found in SP4, located in the vicinity of the calcium fluoride phase described earlier, matched that of fluorite. A uranium phosphate phase was found in one group of particles in SP4. The phase was crystalline judging from the morphology; however, SAED analysis failed to detect any signs of crystallinity. The uranium phosphate particles were elongated and micrographs appeared to display lattice fringes. In SP10 the second major phase found was a uranium phosphate phase. In Fig. 6, long fibrous particles of the uranium phosphate phase can be observed. The uranium phosphate phase appeared to be connected to the uranium oxide, suggesting, that the uranium phosphate was an alteration product. The phase was identified, based on SAED data, as a tetragonal meta-autunite, uranyl phosphate hydrate $[M^{2+}(UO_2)_2(PO_4)_2 \cdot xH_2O]$, an alteration product of uraninite (2). Figure 6c displays an SAED pattern taken down the $\langle 001 \rangle$ zone axis of the uranium phosphate phase. The SAED identification of the uranium-bearing phase has also indicated that the uranium is in the uranyl state [U(VI)].

"Place Fig. 6 here"

The application of optical microscopy, SEM, and AEM techniques provided a clearer picture of uranium contamination at Fernald. The evidence suggests that some of the weathering processes at Fernald have resulted in the alteration of the initial uranium-bearing phases, and that soluble uranium interacted only slightly with the clay phases in the soil substrate, based on the detection limit for the EDS system. Effective removal of uranium from the Fernald soils will depend on detailed knowledge of the chemical and physical characteristics of the waste and its environment. The characterization methods described above, in combination with other methods under development (1), will allow remediation technology groups to find a more direct and efficient route to removing the contamination. These techniques are intended to be transferred for implementation throughout the contaminated sites of the DOE and private sector. For example, at Johnston Atoll (13) and Hanford (14) are areas where similar techniques may be applied.

CONCLUSION

Selected soil samples from SP4 and SP10 were examined using optical microscopy combined with SEM and AEM. With these methods we were able to isolate and characterize discrete uranium-bearing phases in the Fernald soils. With optical

microscopy, no large uranium-bearing secondary minerals were observed. With SEM, however, clumps of uranium-rich regions were identified. Upon further examination with AEM, these regions were found to be composites of finely dispersed phases, which were both crystalline and amorphous. Little uranium was associated with the clay substrate itself. The types of uranium-bearing phases observed at Fernald are similar in many cases to those found in other environments, such as the amorphous uranium iron oxides phases and the altered uraninite. While it is still necessary to show the applicability of these results to larger soil samples, the utility of using multiple techniques for uranium phase identification and characterization has been demonstrated.

Further studies are underway of core and processed samples from Fernald to investigate the effectiveness of separation processes by characterizing the uranium bearing phases isolated.

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Figure 1. (a) SEM/BSE micrograph showing round particles, which can also be seen in the (b) TEM image. The uranium-contaminated regions are identified by the white BSE contrast. The particles are similar in shape because the SEM mount has been sectioned nearly parallel to the plane of the paper.

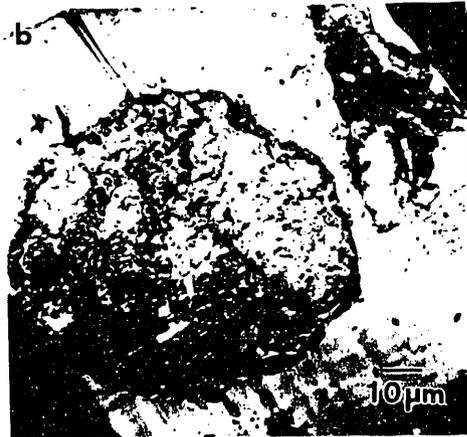
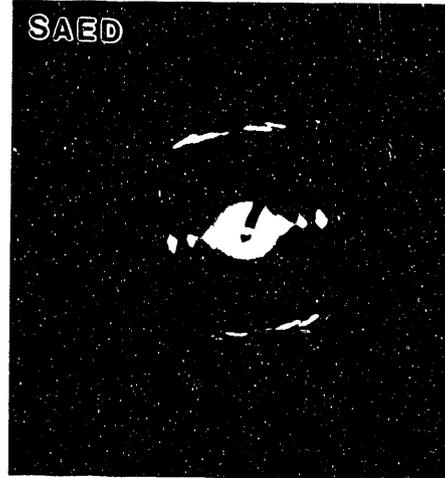
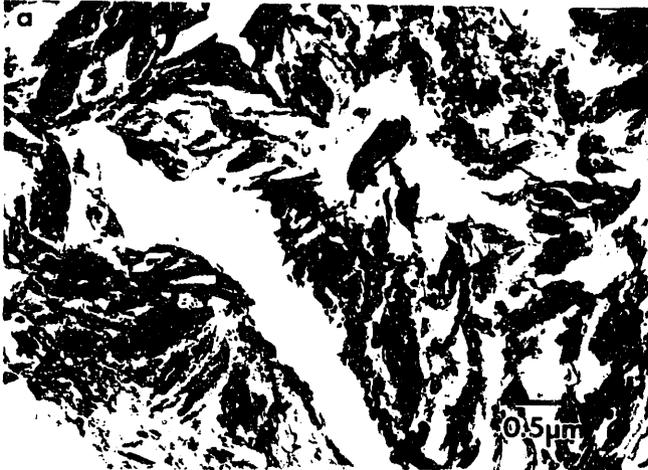


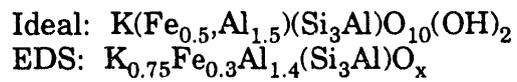
Figure 2. (a) Low magnification micrograph of sectioned soil sample showing clays and quartz (arrow). Electron diffraction of sectioned clays often revealed textured patterns (b), in this case, a chlorite type clay. Lattice images of (c) illite and (d) chlorite (vermiculite) with c-axis spacings of $\sim 10\text{\AA}$ and $\sim 13\text{-}14\text{\AA}$, respectively.



Illite



Compositions



Chlorite

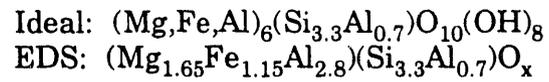


Figure 3. Within the clay phases, uranium-rich silicate phases (arrow) were found (a) and identified as a uranyl silicate by SAED and (b) EDS compositional analysis.

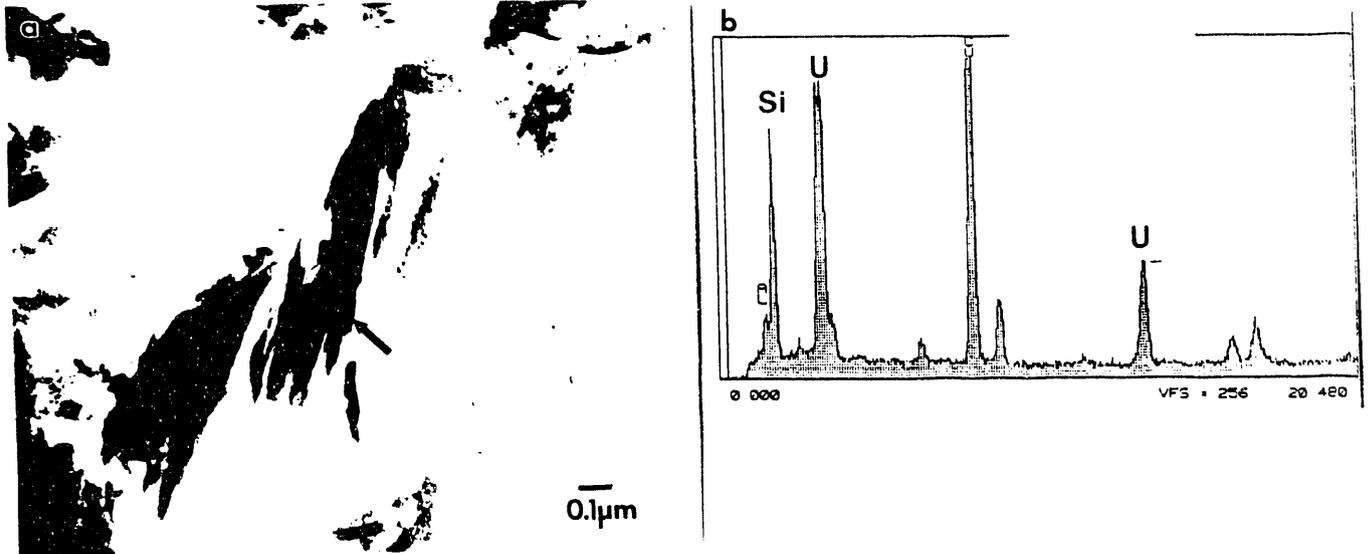


Figure 4. Bright-field micrograph of uranium-bearing phases, (a) which were identified as fluorite by (b) SAED and (c) EELS analysis which shows the Ca-L_{2,3} edges and F-K edge.

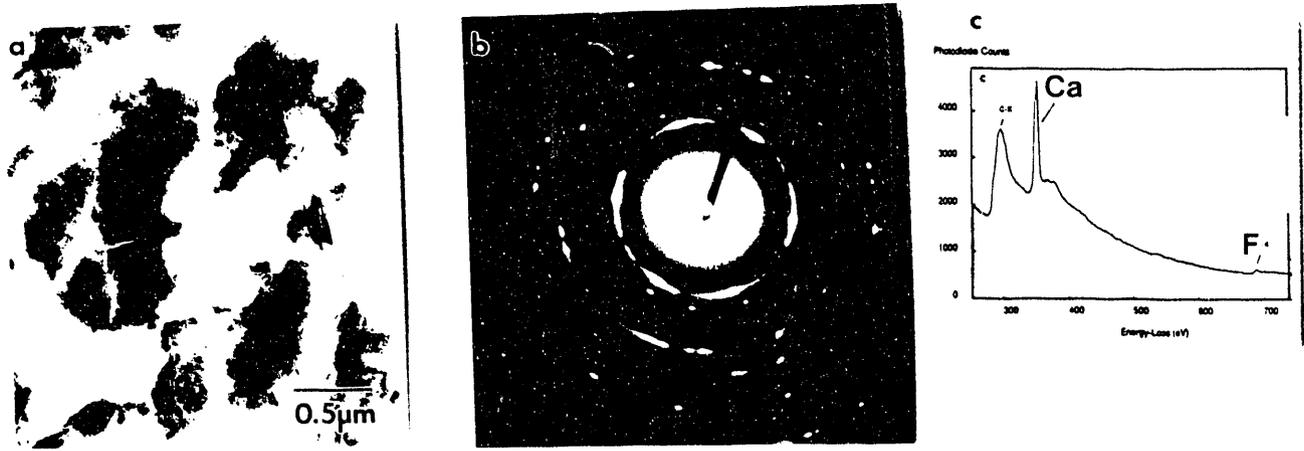


Figure 5. (a) Amorphous iron oxide phase (arrow) found in SP4 in close proximity to clay. The EDS compositional analysis is shown in (b).

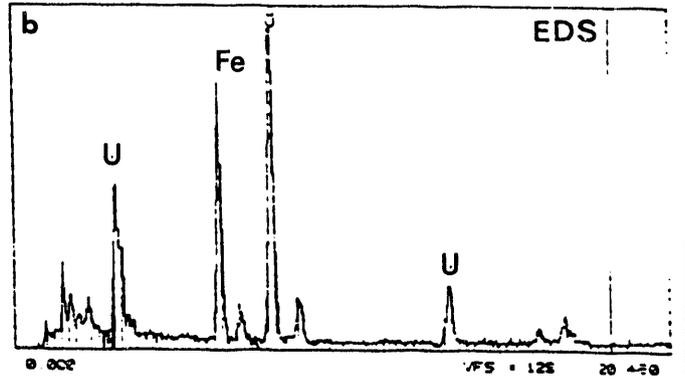
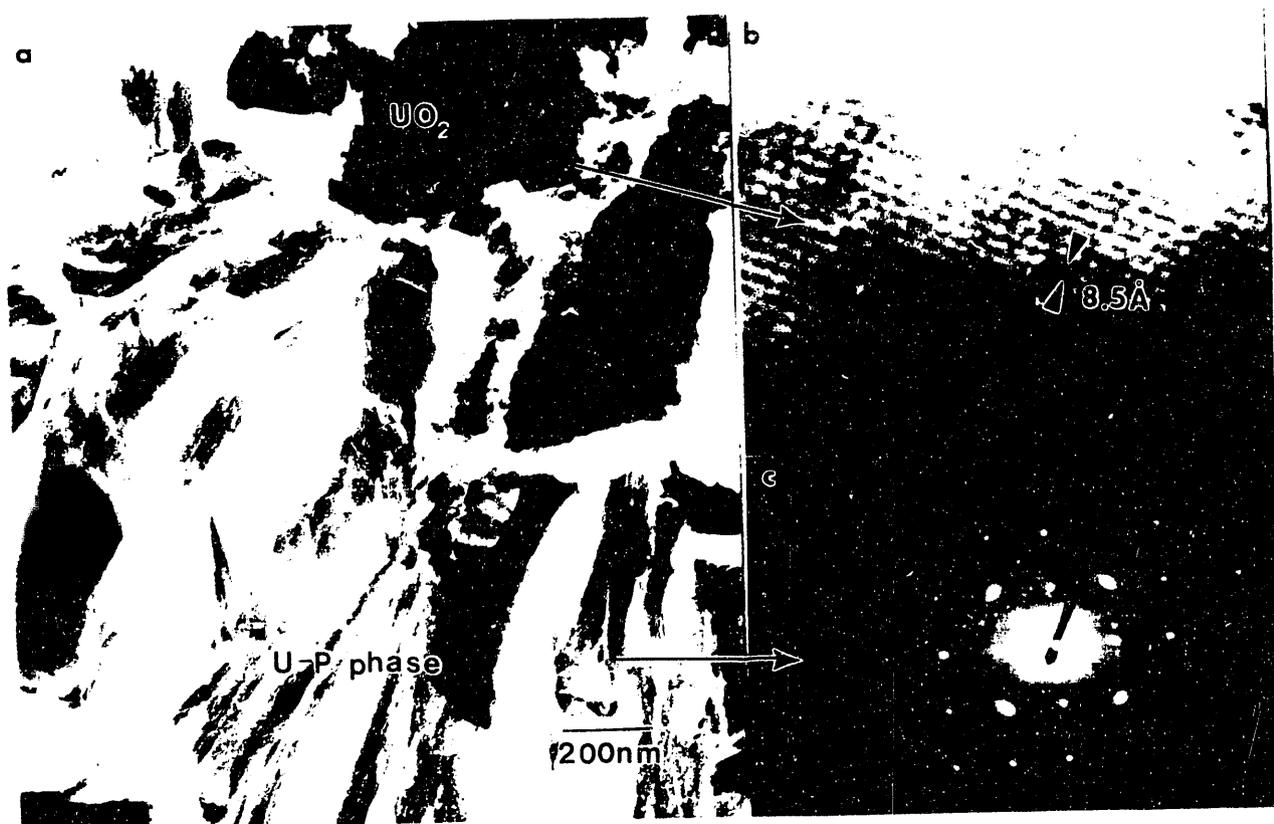


Figure 6. Density separated uranium contaminated soils (SP10) contained two major phases (a), a uranium oxide and uranium phosphate. The darker clumps were identified as uranium oxide (UO_{2+x}). (b) A lattice image taken down a major pole shows spacings from the nonstoichiometric oxide, and attached to these were uranium phosphate crystallites. AEM determined the phosphate phase to be a tetragonal autunite, uranyl phosphate hydrate, by (c) SAED taken down the $\langle 001 \rangle$ zone axis.



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