CHARACTERIZATION OF THORIUM AND URANIUM CONTAMINATED SOIL FROM A NUCLEAR FUEL FACILITY

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ABSTRACT

This paper describes the utility of soil characterization using electron microscopy to support decontamination efforts of contaminated soil. Soil contaminated with thorium and uranium from the grounds of a nuclear fuel manufacturing facility was subjected to remediation efforts. A light acid leach was able to remove only 30% of the thorium suggesting that the thorium was present in two or more forms. Analytical electron microscopy determined that all of the thorium was present as ThO_2, but in a bimodal size distribution and occasionally closely associated with other minerals. Electron microscopy was useful in understanding the remediation data and demonstrates the need for characterization of contaminated soils.

SAMPLE HISTORY AND PREPARATION

The waste site is located on the grounds of a nuclear fuel manufacturing facility. The site was used for miscellaneous waste disposal from 1957 to 1966. Based on site characterization data, a sample of soil was selected which represented the worst-case contamination level for evaluation. The sample contained contamination levels of 2350 ppm uranium and 5670 ppm thorium. A series of scoping tests were performed to identify potential soil washing or leaching processes for the soil. The uranium contamination was amenable to a wide variety of decontamination reagents.

Promising thorium decontamination factors were achieved only through the use of strong mineral acids, although some of the thorium was amenable to a light mineral acid leach. Typical results for acid leaches are presented in Table I. A leachant to soil volume ratio of approximately 4 to 1 was maintained.

TABLE I
Typical Leaching Decontamination Factors for Thorium and Uranium After 4 Hours at 80°C

Lixiviant	%Th Leached	%U Leached
0.1M H_2SO_4/H_3BO_3	24.6	81.1
0.1M H_2SO_4	31.5	73.1
1M HNO_3	2.1	64.5
2M HNO_3	56.0	88.7
3M HNO_3	71.8	97.1
4M HNO_3	83.3	98.1

The light acid leaches were performed with and without boric acid. Boric acid was added to complex any fluoride in the matrix to help the dissolution of any thorium fluoride species. These tests indicated that the thorium was not present as the fluoride. In fact, later studies indicated that a small amount of fluoride present in the soil matrix enhanced the thorium dissolution. Based on site history, and these test results, it was concluded that the bulk of the thorium was present as the oxide and the rest of the thorium was present in less refractory forms, such as the hydroxide.

In an attempt to reduce the acid leach requirements, size and density separations were evaluated as a potential means of removing thorium oxide from the soil matrix. Table II presents a sieve analysis of the soil.

TABLE II
Soil weight Fractions as a Function of Sieve Size

Sieve size	Weight %
>8 Mesh	44.8
8 to 20 Mesh	3.9
20 to 40 Mesh	6.8
40 to 80 Mesh	10.0
80 to 200 Mesh	13.3
200 to 325 Mesh	3.1
<325 Mesh	58.0

Because of the large clay fraction present in the soil, the soil was dispersed prior to attempting the separations. A small amount of ammonium hydroxide was found to act as a good dispersing agent for the aqueous soil mixtures. Size separation methods were effective at removing thorium from the >200 mesh soil fractions with the thorium remaining in the <200 mesh size fractions. Because of the large weight fraction of the small mesh material (>58%); disposal of the fines is not a viable option. Finally, the small size fraction did not respond to density separation techniques.

The unexplained leaching behavior of this soil and the difficulties associated with its cleanup illustrate the need for characterization of radioactively contaminated soils (1). Without knowledge of the contaminant phases and size distribution, soil decontamination efforts cannot be optimized readily.

ELECTRON MICROSCOPY CHARACTERIZATION

Procedure

Methods developed at ANL (2) were used to characterize the <325 mesh soil. These methods allow for contaminated soil to be examined in cross section by scanning electron

microscopy, (SEM) followed by a detailed analysis in the analytical electron microscope, (AEM). The combination of SEM and AEM is crucial in assuring that representative samples are examined and to positively identify the phases *present*. These methods are also being applied to contaminated soil from Fernald (3) and the Johnston Atoll (4). Samples were mounted in a water soluble melamine resin and polished for cross sectional SEM analysis. SEM analysis was conducted at 30 kV on a Topcon ABT 60 equipped with an EDS detector and a Robinson backscatter detector. Many thorium containing particles were located using backscattered electron imaging. Backscattered electron imaging is highly sensitive to changes in average atomic number with high z containing particles appearing quite bright. Energy dispersive X-ray analysis (EDS) tentatively identified the particles, which fell into three categories. Due to the large excitation volume $>1\ \mu m^3$ and lack of structural information, SEM analysis is incapable of positively identifying the particles.

Particles selected for further examination, using the AEM, were then isolated by chipping away unwanted areas until only the area containing the particle remained. The remaining area of the polished black faces were approximately 100 μm by 100 μm. This area containing the particle of interest was then thin sectioned using an ultramicrotome equipped with a diamond knife. The sections were approximately 500 to 1000 Å thick and contain the particle of interest plus any adjacent soil constituents. Ten to fifteen sections were placed on a carbon coated copper grid and then examined in the AEM. AEM examination was conducted on a JEOL 200FX operating at 200 kV, equipped with two EDS detectors capable of detecting elements down to and including carbon. In addition to compositional information the AEM provides structural information through electron diffraction data. With compositional data and structural information AEM can positively identify the phases present.

RESULTS AND DISCUSSION

Six blocks of soil were examined in the SEM. Using backscattered electron imaging, the thorium-rich and uranium-rich particles were easily located. Over 15 uranium-rich and 50 thorium-rich particles were identified using EDS, while no thorium or uranium was detected in clays or other particles at low levels (>0.1 wt% detection limit).

Uranium Characterization

An SEM analysis was conducted on the uranium-rich particles. The particles ranged in size from approximately 2 μm to 15 μm in diameter. The particles consisted of uranium oxides and uranium nitrides. If leaching experiments indicated that it was warranted, AEM analysis would be necessary to positively identify the phases present. Interestingly, this uranium speciation is significantly different from the phases located at Fernald, which are primarily uranium phosphates and uranium calcium phosphates (5). An SEM micrograph of a uranium nitride particle, a small ThO_2 particle, and their SEM EDS spectra are presented in Fig. 1.

Thorium Characterization

Three distinct population groups of thorium-rich particles were noted; particles representative of these groups are shown in Figs. 2a-2c. The first group consists of particles containing only thorium and oxygen, which was later identified by AEM as ThO_2 (the SEM cannot determine the hydration state of the particles) and a size of approximately 1 μm in

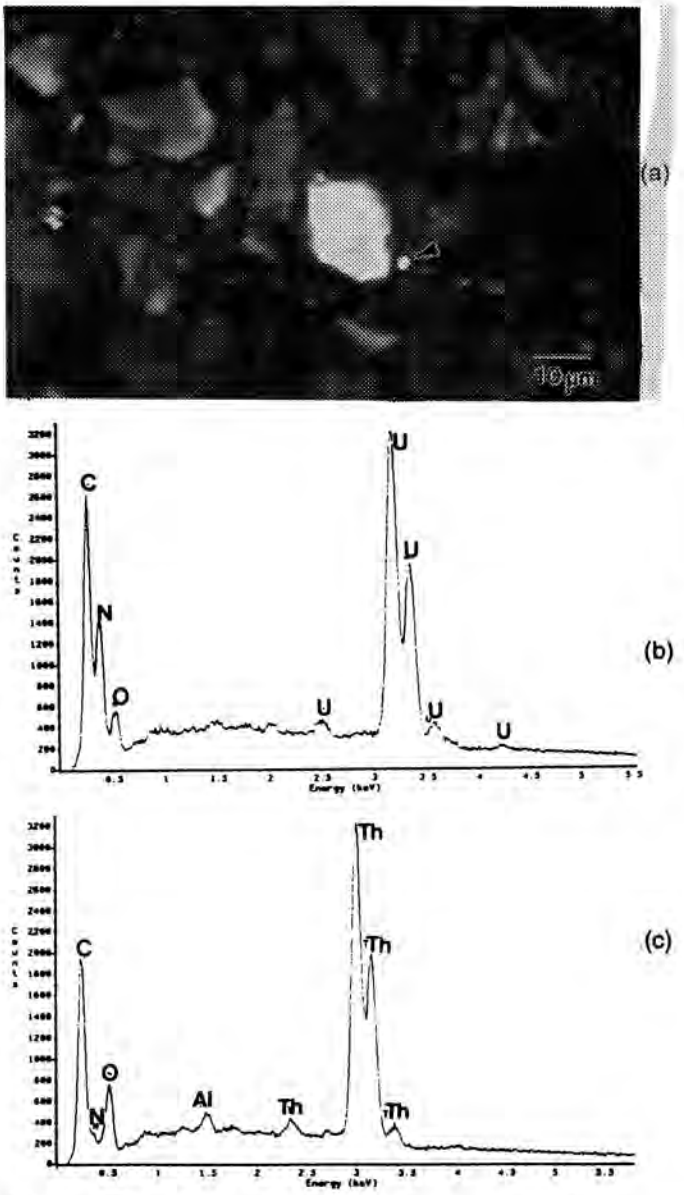

Fig. 1. SEM micrograph a) of a large uranium nitride particle. Also present is a small ThO_2 particle (arrow). The low energy EDS spectra are also presented. The uranium particle contains nitrogen b) while the ThO_2 does not c).

diameter. The second group of particles are also ThO_2, but are approximately 10 μm in diameter. While a full particle size distribution would require the examination of many more particles, it does appear that the discrete thorium particles exist in a bimodal size distribution. The third type of thorium containing particles appear as large clusters of small thorium particles held together by a calcium, silicon and aluminum phase. SEM examination is unable to determine the actual composition and phase of the thorium containing particles due to possible EDS signals from underlying regions. (The SEM EDS probe excites a region about 1 μm^3.)

Particles from each group were examined in the AEM. From EDS analysis in the AEM all of the thorium was found to be present in the form of thorium oxide. Selected area electron diffraction, (SAED) identified the phase as ThO_2.

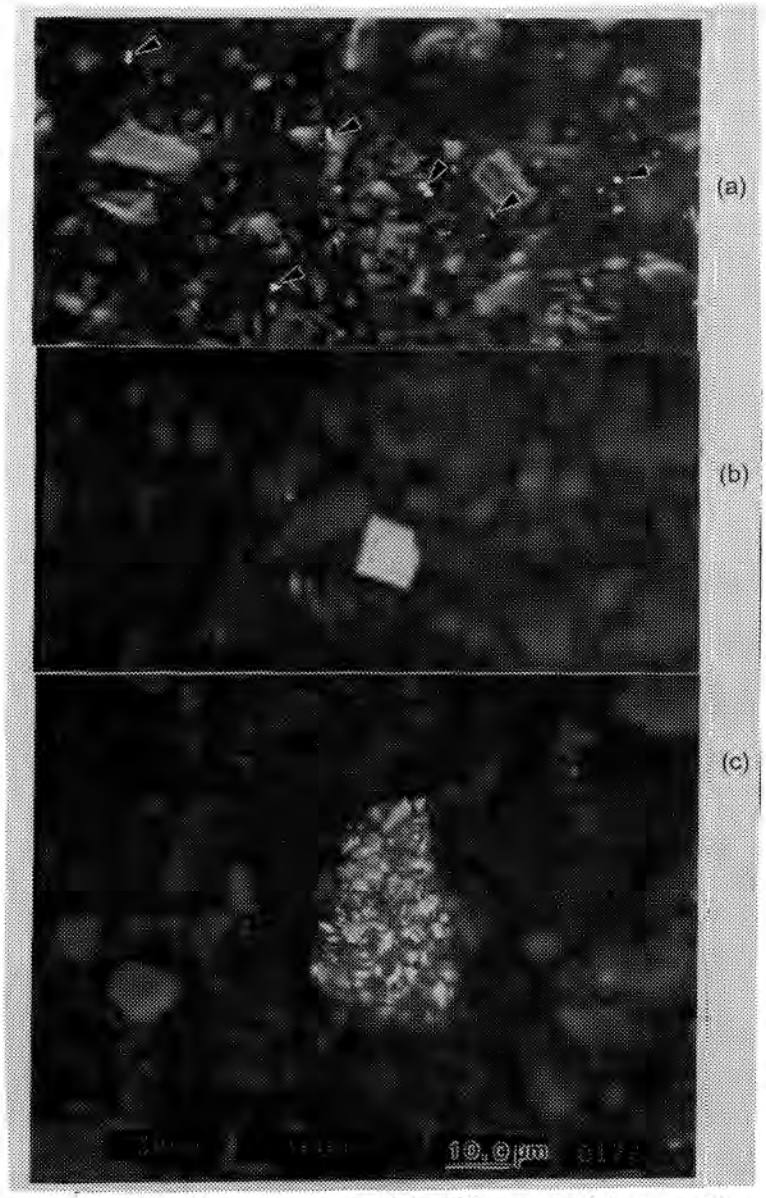

Fig. 2. SEM micrographs of the different particle types. The images are taken in backscattered imaging mode, with the thorium-rich regions appearing bright. a) many very small ThO_2 particles, b) a typical large ThO_2 particle, c) a large conglomeration containing Th, Al, Si and Ca.

The expected lattice spacings and experimentally determined spacings are presented in Table III.

EDS spectra from the SEM and AEM of the thorium-rich regions of the particle presented in Fig. 2c are presented in Fig. 3. The SEM EDS spectra clearly indicate that a large amount of Ca, Si and Al is present with the thorium even at the smallest probe size of 1 μm. The much higher resolution of the AEM EDS (<20 nm) indicates that the thorium rich regions are thorium oxide with no Ca, Si or Al present. Selected area electron diffraction confirms that the thorium is present as ThO_2 in this particle as well. An AEM micrograph of the conglomerated particle is presented in Fig. 4.

TABLE III
Experimental and Theoretical Lattice Spacings for Thorium Oxides

KHL Plane ThO_2	Measured (nm)	ThO_2 (nm)	ThO (nm)
(111)	0.323	0.3234	0.3063
(200)	0.280	0.2800	0.2654
(220)	0.191	0.1980	0.1870
(311)	0.167	0.1689	0.1429

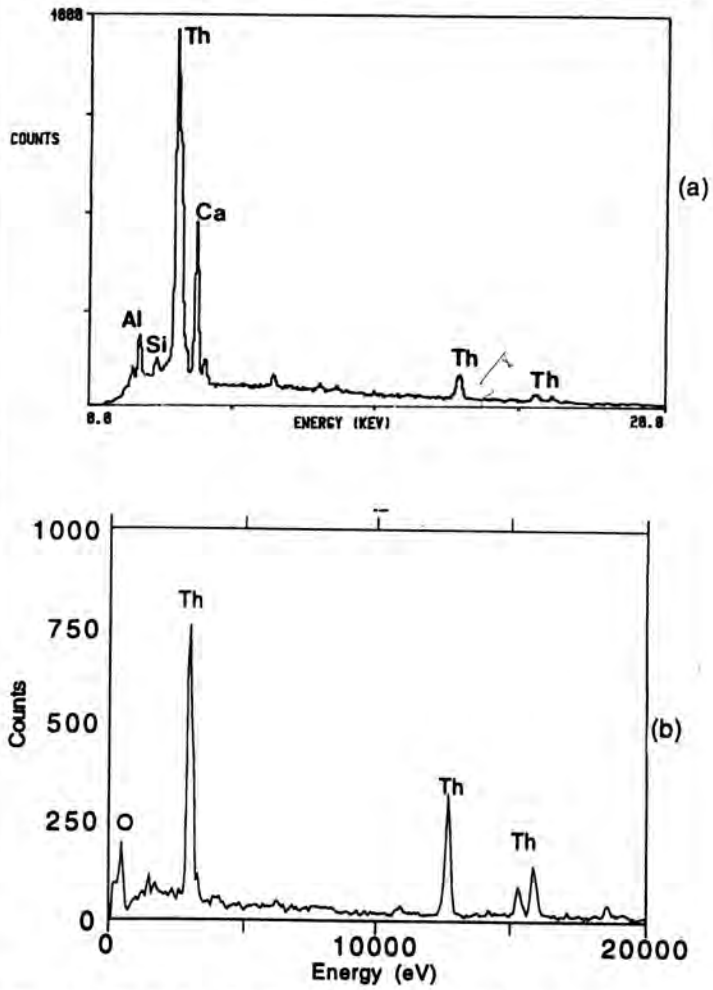

Fig. 3. SEM (a) and AEM (b) EDS spectra from the thorium rich regions of the conglomeration shown in Fig. 2(c). Notice the considerable amount of Al, Ca, and Si present in the SEM spectra and their absence in the AEM spectra. The thorium rich regions were identified as ThO_2 by AEM.

CONCLUSIONS

The utility of the analytical electron microscope is evident in the amount and quality of the information gathered. With knowledge that all of the thorium is present in the oxide form, selection of leachate solutions can be optimized. SEM analysis indicated that some of the thorium was present in particles containing silicon, calcium and aluminum. The high resolution of the AEM was able to determine that the thorium was present in these conglomerations as ThO_2. The bimodal

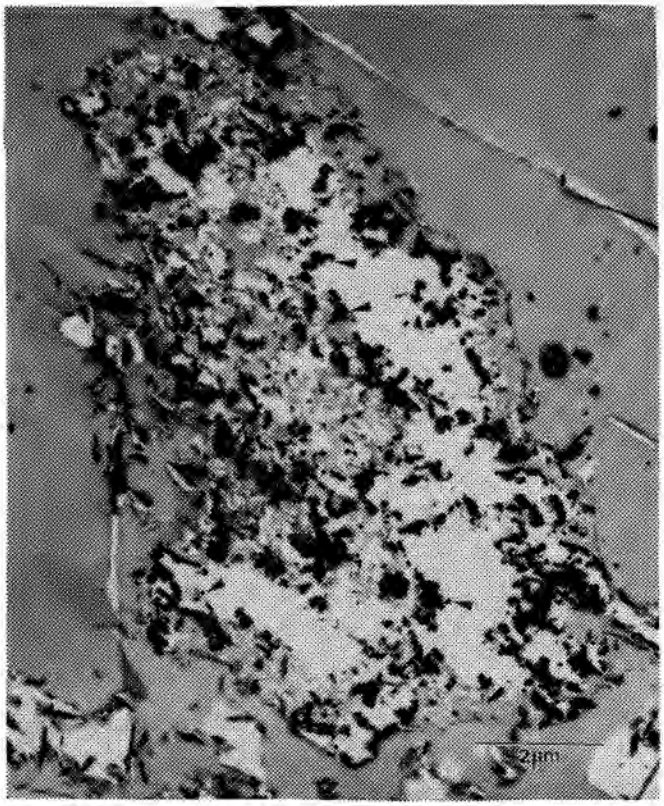

Fig. 4. Low magnification AEM micrograph of the conglomeration containing Th, Al, Ca and Si presented in Fig. 1(c). Due to the particles large size some fracturing occured during ultramicrotoming. Arrows indicate small ThO_2 particles, some as small as 75 nm, contained in the conglomeration. The matrix consists of Al, Ca and Si oxides.

particle size distribution observed during characterization explains the leaching behavior of the thorium.

ACKNOWLEDGMENTS

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