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ABSTRACT

Electron beam techniques have been used to characterize uranium-contaminated soils from the Fernald Site in Ohio, and also plutonium-bearing "hot particles" from Johnston Island in the Pacific Ocean. By examining Fernald samples that had undergone chemical leaching it was possible to observe the effect the treatment had on specific uranium-bearing phases. The technique of Heap leaching, using carbonate solution, was found to be the most successful in removing uranium from Fernald soils, the Heap process allows aeration, which facilitates the oxidation of uraninite. However, another refractory uranium(IV) phase, uranium metaphosphate, was not removed or affected by any soil-washing process. Examination of "hot particles" from Johnston Island revealed that plutonium and uranium were present in 50-200 nm particles, both amorphous and crystalline, within a partially amorphous aluminum oxide matrix. The aluminum oxide is believed to have undergone a crystalline-to-amorphous transition caused by alpha-particle bombardment during the decay of the plutonium.

INTRODUCTION

The clean-up of radionuclide-contaminated sites is a major problem facing the U.S. Department of Energy (DOE). Knowledge of the soil and contaminant characteristics can greatly facilitate the identification of suitable remediation techniques during bench-scale tests, which otherwise must proceed by trial and error. More importantly, detailed characterization can allow the rejection of inappropriate technologies for a particular site on a sound scientific basis. At the DOE Fernald site in Ohio, several characterization techniques have been used to support the remediation efforts at both bench-scale and pilot-scale. These characterizations have described the exact nature of the uranium contamination and the effect that various chemical treatments had on the soil and contaminant (1). The application of electron microscopy in characterization studies at Fernald has been reported elsewhere (2-4). In this paper, further examples of soil characterization are presented, with emphasis on how they can benefit remediation efforts.

EXPERIMENTAL PROCEDURE

Soil characterization by analytical transmission electron microscopy (AEM) with electron diffraction provides the spatial resolution necessary to examine sub-micron phases. Using the combination of electron diffraction, X-ray energy dispersive spectroscopy (EDS), and electron energy loss spectroscopy (EELS), unknown phases can be identified. At Argonne National Laboratory (ANL) we have developed a small particle handling facility and analytical microscopy laboratory for the characterization of radioactive materials, soils, and residues. The facility uses micro-manipulation techniques to mount small particles and ultramicrotomy to prepare thin sections of the particles for AEM examination. The ultramicrotome is specially designed so that radioactive samples can be thin sectioned. A combination of optical microscopy and scanning electron microscopy (SEM) assures representative sampling.

Characterization Protocol

Soil characterization is divided into two tiers. In Tier I, the bulk physical soil characteristics are determined by particle sizing, separation, radiochemical and elemental analysis, optical microscopy, SEM, and X-ray

diffraction (XRD). More detailed characterization falls under Tier II studies. Here, the oxidation state and speciation of contaminant radionuclides are determined by techniques such as AEM and X-ray absorption spectroscopy (XAS), and, if necessary, atomic and molecular spectroscopies. Often it is the combination of techniques which provide the most useful information on the soil contaminant.

Analysis of Soil Samples by Electron Microscopy

Radionuclide-bearing soil samples were infiltrated with a water-soluble melamine resin for examination in the SEM. The radionuclide-bearing particles were located by SEM backscattered electron imaging. Individual particles were isolated by trimming away excess material from the SEM mount. Thin sections suitable for AEM examination were prepared by ultramicrotomy (2). The ultramicrotome has been specially adapted to handle radioactive materials. The instrument itself is located inside a hood and the operator is required to wear a respirator during operation. Monitoring is carried out after sectioning to ensure that there has been no contamination. This method of sample preparation allows direct comparison of SEM and TEM images, which enables characterization of TEM samples to be representative of the bulk sample. The samples were analyzed in a JEOL 2000 FXII TEM operated at 200 kV and equipped with X-ray energy dispersive spectrometers (EDS) and a parallel electron energy loss (EELS) spectrometer. Phases were identified by a combination of EDS, EELS, and electron diffraction.

RESULTS AND DISCUSSION

Assisting Remediation at Fernald, Ohio

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 in North America and from the Belgian Congo for processing at Fernald (5). The soils around the Fernald processing plant have become contaminated with uranium after decades of uranium processing, and efforts are now being made to remediate the site. The 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 plumes of high uranium contamination, typically around 500 ppm uranium. However, a number of highly contaminated regions were also found, where, in some instances, the uranium content was up to 5000 ppm (6). Efforts have been concentrated at two regions at Fernald; the incinerator site soils and storage pad site soils, as the soils from these regions were considered to encompass the range of contamination at the whole site. These soils all had an average uranium concentration of 500 ppm.

Lee and Marsh (6) identified by XRD the major non-uranium-bearing phases in the soils, which were quartz, clays, calcite, and dolomite. Buck et al. (2-4) identified the major uranium-bearing phases by AEM as calcium uranyl (VI) phosphate (tetragonal meta-autunite), uranyl (VI) silicate (soddyite), calcium uranium (VI) oxide, uranium (IV) oxide (uraninite), and uranium metaphosphate [monoclinic-$U(PO_3)_4$]. The uranium metaphosphate was only found in the incinerator site soils. Bertsch et al. (7) and also Allen et al. (8) have used XAS to determine uranium oxidation state of bulk soil samples from Fernald. A 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, micro-beam XAS by Bertsch et al. (7) suggested that the distribution of uranium-bearing particles in the incinerator site soils was inhomogeneous, as indicated by signal varying as the focused beam was moved across the sample. In contrast, in some storage pad soils, uranium appeared to be uniformly distributed through the soil. This observation agreed with radiochemical analysis and particle sizing performed by Lee and Marsh (6) and observations made by SEM and AEM (2-4).

Carbonate leaching has been selected as the most appropriate method for removing the uranium from Fernald soils. However, the U(IV) phases (uraninite and uranium metaphosphate) in bench-scale tests were not removed. Uraninite can be leached by carbonate according to the scheme (9);

$$UO_2 + 1/2O_2 + 3CO_3^{2-} + H_2O \rightarrow [UO_2(CO_3)_3]^{4-} + 2OH^- \quad (1)$$

In other words, as long as an oxidizing agent is present, uraninite will be attacked. 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. Chemical methods for adding this oxygen such as hydrogen peroxide and potassium permanganate are either expensive and/or increase the amount of pollution. Permanganate, however, was used in the bench-scale tests, after TEM analysis had shown that uranium(IV) phases were still present in soils that had been treated with carbonate. Addition of the oxidizer was found to improve uranium extraction during carbonate leaching.

The technique used in the mining industry for the recovery of metals, termed "Heap leaching," may be an attractive alternative for introducing oxygen. The nature of the Heap, where soil is heaped (or piled) onto an impermeable pad, can allow some aeration. In the Heap-treated samples (see Fig. 1), there was evidence from TEM of uraninite dissolution (although some uraninite was still present in the treated samples); however, no evidence was found of dissolution of the uranium metaphosphate phase, and a number of uranyl phosphate phases were still present.

Characterization of "Hot Particles" from Johnston Island

Johnston Island, located in the Pacific Ocean, 1330 km southwest of Honolulu, became contaminated in 1962 when the Island was used for launching missiles to test the effects of high-altitude nuclear bursts (10). In a number of instances problems occurred with the Thor missiles and the nuclear devices were intentionally destroyed by chemical explosives. One intentional destruction 59 sec after launching deposited plutonium- and uranium-contaminated debris throughout the atoll, while a second destruct of a missile on the launch pad contaminated a smaller land area but to much higher levels. Plutonium was dispersed by the explosive high temperatures and pressures generated by the explosion. The growth of the plutonium daughter product ^{241}Am has permitted isolation of "hot spots" by gamma detection.

Tier I size sieving studies and radiochemical analysis by Wolf et al. (11) demonstrated that 96.5% of the activity was located in the 2 to 0.063 mm range. Most of the activity was localized in small "hot particles" in the coral sand. Bramlitt has also indicated that some of these "hot particles" were magnetic. This suggests that they might be closely associated with iron (10). A mechanical soil sorting method has been developed by Moroney et al. (12), termed the segmented gate system, that screens out "hot particles" automatically by using NaI gamma detectors. Improvements in this system have helped to reduce the contaminated volume of soil by 98%. The clean soil has a total alpha radioactivity from the plutonium and americium of less than 500 Bq/Kg.

A Tier II study was undertaken to describe the nature of the plutonium and uranium contamination in the "hot particles" present in the contaminated soils, so that the movement of plutonium at Johnston Island can be explained and further dispersion into the environment predicted. In some sites plutonium has migrated to depths over 1.5 m, and the mechanism by which this has occurred is unknown. In addition, the fate of uranium is unclear.

The AEM examination showed that plutonium is not in direct contact with the coral but is present in "sols" of plutonium and uranium (50-200 nm in diameter) within a micro-crystalline (partially amorphous) aluminum oxide, as well as with other components such as iron. Plutonium-bearing iron particles

may account for the magnetic effects observed by Bramlitt (10). Beryllium, a typical bomb component, which can be detected by EELS, was found in some samples. Particles enriched in gallium and plutonium and 50 nm in size were also found. Gallium is often alloyed with plutonium, but the levels found in some of the discrete 50 nm particles exceeded normal alloying levels. In Fig. 2, "sols" of plutonium and uranium can be seen contained within the partially amorphous aluminum oxide matrix. The nature of the aluminum oxide is in itself unusual; the amorphization of aluminum oxide may have occurred by the decay of the plutonium. Alpha decay of ^{239}Pu would cause the most damage, though ^{239}Pu with a half-life of 2.411×10^4 years, may have produced the amorphization of the aluminum oxide within 30 years. The plutonium content in the aluminum oxide varied between 0.5 and 3 wt%. This would produce only 1×10^{13} to 6×10^{13} alpha-events/mg. Assuming that each alpha-recoil event displaces 1500 atoms, the dose delivered would be 0.5×10^{-3} to 3×10^{-3} displacements per atom (dpa). Metamictization in some ancient mineral phases typically occurs after $>1.0 \times 10^{16}$ alpha-events/mg (~1 dpa) (13).

PLACE FIG. 2 HERE

The crystalline-to-amorphous (c-a) phase transformation can be induced by variety of processes such as particle irradiation or inter-diffusion reactions. Elastic softening and volume changes of the lattice often results from the loss of atomic order. The softening effect meant the microtome was able to produce large continuous thin sections of the aluminum oxide. A completely crystalline or amorphous material would have exhibited deformation and/or fracturing. Furthermore, if expansion of the lattice occurred in the partially amorphous aluminum oxide, then this might have allowed the entry of carbonate-bearing water. However, no evidence of any carbonate precipitates was detected in the aluminum oxide thin sections. Alternatively, incorporation of plutonium in aluminum oxide may result in a c-a transition through stabilization of the amorphous structure.

We speculate that an explanation for the distribution of radionuclides in Johnston Island soils to be the following. The aluminum and other metals (iron, magnesium, etc.) used in the bomb casing and bomb materials (plutonium, uranium, gallium, etc.) underwent rapid oxidation when the missile firing was aborted. The plutonium and uranium was deposited in the form of fine droplets which became embedded in the larger amount of aluminum and iron components. Some of the uranium crystallized, which may have made it less susceptible to weathering. Over time plutonium was leached in the surrounding matrix, leaving uranium enriched globules surrounded by a matrix of amorphous aluminum oxide containing small amounts of plutonium. This plutonium was then able to leach into the calcium carbonate coral, where it moved rapidly over the coral surfaces.

The Tier II characterization of Johnston Island "hot particles" suggests that the segmented gate system will be effective at removing the plutonium, and that chemical soil washing will not be necessary. Most of the plutonium and uranium is mainly contained in oxide particles, although some plutonium is spread throughout the aluminum phase. In addition, the uranium also appears to be contained within the "hot particles," suggesting that removal of these particles will also remove any uranium in the soil.

CONCLUSIONS

These AEM investigations have shown a large variety of different contaminant phases in examined soils. These variations result from the broad range of sources of uranium and plutonium, and also the different chemical processes employed at sites such as Fernald. The range of uranium-bearing phases at Fernald has impeded the remediation efforts, as no single chemical process has been able to remove all the uranium without totally destroying the soil. However, carbonate Heap leaching has managed to remove a majority of the uranium phases, only leaving the uranium metaphosphate phase.

Removal of uranium from the Fernald soils and elsewhere can be made easier by detailed knowledge of the chemical and physical characteristics of the waste and its environment. A characterization technique must be able to determine the exact nature of the contaminant phase, as incorrect interpretations of data could lead to the selection of inappropriate remediation methods. A technique which provides both compositional and structural data, such as AEM, is advantageous because it can determine the chemical form of unique phases. At Fernald, the identification of the ceramic-like uranium metaphosphate phase is a good example of this capability.

At Johnston Island, AEM studies have confirmed that removal of plutonium using the segmented gate system will be effective and that it will also remove the uranium from the site, as the uranium is contained in the "hot particles." The characterization methods described above, in combination with other techniques such as XAS and radiochemical analysis, allow remediation technology groups to find more efficient ways of removing contamination. Characterization has been criticized as providing esoteric information. However, when used in the role of problem solving, it can provide information which improves the rate at which bench-scale testing can proceed to full-scale remediation.

The small particle handling facility and microscopy laboratory developed at ANL is equipped to handle radioactive materials for soil and residue characterization. The facility also includes radiochemical analytical instruments, inductively coupled plasma-mass spectroscopy for elemental analysis, and secondary ion mass spectroscopy for surface profiling of radioactive materials. We are currently engaged in establishing commercial sector projects for developing and testing soil and residue treatment technologies.

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FIGURE CAPTIONS

Figure 1. Effect of Heap Leaching on the Surface of Uraninite Phase, Showing an Oxidized Uranium Oxide Phase Identified by Electron Diffraction.

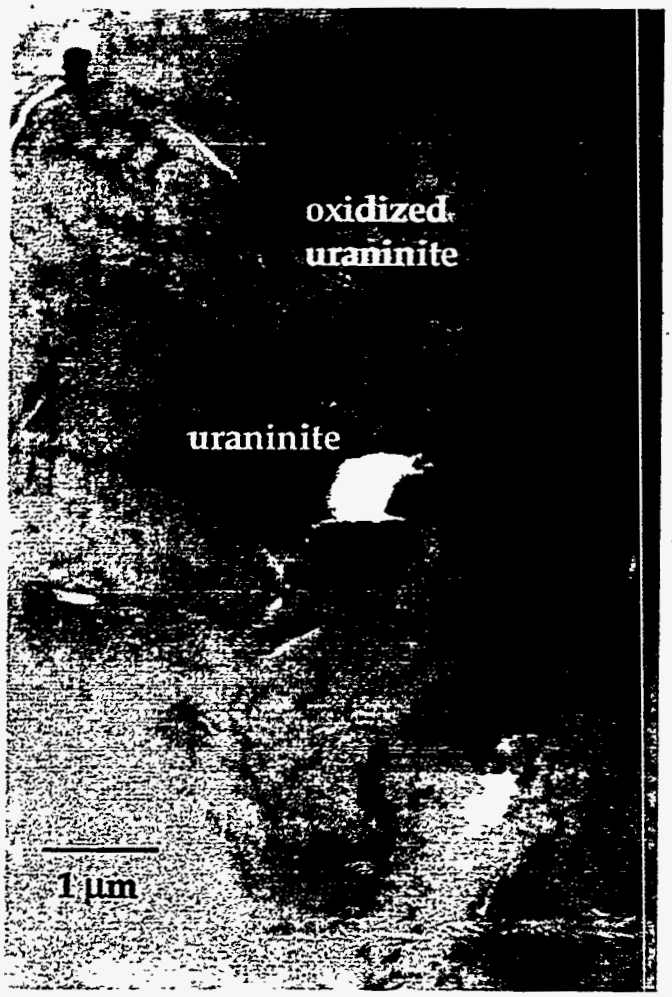

Figure 2. (a) TEM Images of Plutonium-Uranium Particles Contained within the Aluminum Oxide Matrix. (b) EDS analysis of 'sol' particles showed the presence of gallium in one particle. Electron diffraction from the crystalline uranium and plutonium phases identified the particles as PuO_2 and UO_2 oxides.