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FY 1993 Progress Report

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Determining Uranium Speciation in Fernald Soils by Molecular Spectroscopic Methods

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by

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ABSTRACT

This progress report describes new experimental results and interpretations for data collected from October 1, 1992, through September 30, 1993, as part of the Characterization Task of the Uranium in Soils Integrated Demonstration of the Office of Technology Development, Office of Environmental Restoration and Waste Management of the US Department of Energy. X-ray absorption, optical luminescence, and Raman vibrational spectroscopies were used to determine uranium speciation in contaminated soils from the US Department of Energy's former uranium production facility at Fernald, Ohio (18 mi northwest of Cincinnati). These analyses were carried out both before and after application of one of the various decontamination technologies being developed within the Integrated Demonstration. The treatment technologies included soil washes with carbonate, citrate, Tiron, and Tiron/dithionite mixtures. This year the program focused on characterization of the uranium speciation remaining in the soils after decontamination treatment.

X-ray absorption and optical luminescence spectroscopic data were collected for approximately 40 Fernald soil samples, which were treated by one or more of the decontamination technologies. Results for the A-series soils from the Incinerator Area suggest that the treated soils can be divided into three sets. The first set comprises control samples that are little changed from the untreated soils. The second set encompasses most of the A-series samples. The uranium remaining in these soils appears to have a slightly higher ratio of tetravalent to hexavalent uranium than the untreated soils.

have. The third set consists of only A-11 soils that were treated by Tiron, carbonate, or both, but with no reducing agent. This set appears to have the highest ratio of tetravalent to hexavalent uranium remaining in the soil for any sample examined thus far. Observation of different x-ray absorption spectra in the second and third sets suggests that there are several uranium species—rather than a single intransigent species—left in the soils following treatment and that the treatment chemistry may be dictating the difference in the remnant species. The treated B-series soils from the Plant 1/Storage Pad Area are less easily categorized. However, from the usual x-ray absorption criteria, it appears that they retain primarily hexavalent uranium following the treatments.

The optical luminescence data demonstrate that there is a decrease in size (and probably quantity) of the particulate hexavalent uranium that gives rise to the green emission. Thus, all treatment technologies do seem to lead to a more dispersed, finer grained contamination. Some instances of particulate green emission still exist in these samples, and the spectral band structure suggests that this is attributable to a schoepite phase. An orange emissive phase, also seen in many samples, is probably attributable to a hexavalent uranium species, but its identity has not been confirmed.

New Raman and luminescence data for untreated soils and reference mineral phases have made it possible to identify the highly-structured green emissive phase as meta-autunite. This phase can be easily removed from a quartz particle by using deionized water, which suggests a possible reason for the lack of these structured emitters in the treated soils.

INTRODUCTION

The Fernald Environmental Restoration Management Company, formerly known as the Feed Material Production Center, is a US Department of Energy (DOE) facility that historically has served as one of the principal processing centers for pure uranium. Processing operations there were suspended in 1986, and the site is now undergoing remediation of uranium and other radioactive and toxic wastes. In 1991, the Fernald site was chosen by DOE's Office of Technology Development to serve as the host for the Uranium in Soils Integrated Demonstration (USID). The Integrated Demonstration (ID) concept is a cradle-to-grave approach for design, implementation, and assessment of remediation at a contaminated site. Although specific contaminants and remediation technologies are targeted for each ID, the intent is to develop remediation programs that can be successfully transferred to other sites with related contamination problems.

A key factor in the successful and timely remediation of this and other contaminated sites at DOE facilities is the availability of speciation information on the contami-

nants. The actinides (uranium, neptunium, and plutonium), in particular, can exist in myriad chemical forms, and their response to remediation technologies—particularly those based on chemical intervention—will vary as the speciation varies. If there is an *a priori* characterization of the speciation [that is, specification of the oxidation state, chemical form and structure, and physical state (surface precipitate, secondary mineral, or adsorbate)], several potential advantages accrue. The remediation technology can be devised with the specific form of the actinide in mind, which leads to more efficient and less drastic remediation measures and enhances the likelihood of leaving a viable soil substrate behind. In addition, it is possible to make a valid assessment of the long-term stability of the actinide contamination in its present form. This information is important in guiding the remediation effort and determining whether the contaminant site is stabilized with respect to transport and subsequent groundwater contamination.

We are now involved in determining the uranium speciation in contaminated soils at the Fernald site as part of the USID. Because many different processes were employed at the site, there are potentially many different source terms for uranium in the soils. Although uranium migration in general has not been extensive, the shallow subsurface requires significant remediation to bring the site into compliance with EPA (US Environmental Protection Agency) standards. We have employed molecular-level probes, including x-ray absorption spectroscopy and optical luminescence and Raman spectroscopies, to characterize the uranium speciation in samples from several different sites at the facility.

The FY 1993 effort has focused on characterization of Fernald soils following the application of one or more decontamination technologies that are based on chemical and/or physical-chemical extraction now being developed within the Decontamination Task of the USID. This report summarizes recent results for Phase 1 and preliminary Phase 2 studies that used the molecular spectroscopic characterization tools described in the FY 1993 Characterization Plan (MORRIS, 1994). The focus of our Phase 1 efforts has been on characterizing the speciation in bulk samples that have not undergone rigorous size and/or density separations in S. Y. Lee's laboratory at Oak Ridge National Laboratory (ORNL). These samples include specimens treated by the Los Alamos National Laboratory Decontamination Task project (J. R. Brainard, principal investigator) and the ORNL Decontamination Task project (C. Francis, principal investigator). Phase 2 characterization efforts also started at the end of the year; these studies involve treated samples that have undergone size and/or density fractionation at ORNL. The Phase 2 samples were size-fractionated specimens from the ORNL Decontamination Task project.

We are attempting to obtain speciation information about the uranium that is left behind in the soils following soil-washing treatment(s), including specific issues/concerns such as whether the soil-washing selectively removes certain uranium species, whether the treatment alters all or most uranium phases, and how the treatment affects the dominant physical forms of the uranium. (For example, do the particulates decrease in size and/or become redistributed?). These data are important to the Decontamination Task group's effort to understand and fine-tune soil-washing technologies. There also have been minor efforts this year to enhance our uranium species identification capabilities through the collection and analysis of luminescence and Raman spectra for a suite of uranium mineral phases.

BACKGROUND

To adequately specify uranium speciation, we need techniques that probe structure at the molecular level. Elemental specificity (for example, as provided by inductively-coupled plasma atomic emission or x-ray fluorescence spectroscopies), although important, is insufficient by itself. We also need techniques that are applicable to opaque samples such as solids (for example, soils and mineral assemblages) because these samples frequently possess challenging optical properties. Two general approaches satisfy these criteria. The first—based on molecular spectroscopic methods that probe the vibrational and electronic properties of the system—is the approach undertaken by Los Alamos and described in this report. The second approach is based on analytical microscopies as practiced for the USID by J. Cunnane and co-workers at Argonne National Laboratory. Each method has relative merits and the optimal applicability of either depends on a variety of factors, including the chemical and physical characteristics of the system and the level of speciation detail required. Some of the specific strengths of the molecular spectroscopic approach are delineated below. However, the experience gained in the USID suggests that the best protocol for uranium speciation is one that employs both approaches—thereby taking advantage of their complementarity.

No single molecular spectroscopic method is readily able to provide a detailed speciation description for uranium or other contaminants of interest. A combination of spectroscopic techniques is generally required to achieve a detailed description. We have identified four core methods that, when used in combinations of two or more, are sufficient for actinide speciation studies in subsurface matrices: x-ray absorption spectroscopy (XAS), optical luminescence spectroscopy, photoacoustic spectroscopy, and Raman vibrational spectroscopy. These methods (1) are complementary in the information they provide and (2) span an analyte concentration range from ~1% to ~100 parts per trillion and below (that is, the relevant regime for the

Fernald site). When these core methods are supplemented with ancillary analytical methods, a precise description of speciation is possible.

Of the four core methods, x-ray absorption spectroscopy is the most incisive (KONINGSBERGER AND PRINS, 1988). It provides oxidation state information [for example, U(IV) vs U(VI)] directly. It also provides a "snapshot" of the local coordination environment about the target (uranium) ion. Thus, the identity and number of coordinating atoms (from ligands and/or surfaces) and their bond lengths can be quantified. Optical luminescence spectroscopy is a very valuable probe for the speciation of hexavalent uranium moieties (that is, UO_2^{2+} species) and other emissive species (CHISHOLM-BRAUSE *et al.*, 1992a and b). This method has excellent sensitivity, and because of the often distinct, species-specific nature of the hexavalent uranium emission spectrum, the method can be used as a "fingerprint" for speciation. Photoacoustic spectroscopy is the ideal complement to optical luminescence because species that are not emissive tend to yield excellent photoacoustic spectra (PATEL AND TAM, 1981). Thus, the speciation of uranium in the nonemissive or weakly emissive oxidation states (that is, 0, +3, +4, and +5) can be probed by using photoacoustic spectroscopy to measure the electronic spectra. Of the four core methods, photoacoustic spectroscopy is the most sensitive. Dissolved species concentrations of 10^{-8} moles/ ℓ can be probed routinely (TAIT *et al.*, 1994). The final core method, Raman vibrational spectroscopy, provides molecular structure information explicitly by means of the number, energy, and intensity of the observed vibrational transitions (LONG, 1977). This method can also be used as a "fingerprint" for species identification because of the distinctive nature of the Raman spectrum. However, of the four methods, this is, in general, the least sensitive.

A number of experimental advantages are specifically associated with these molecular spectroscopic probes for uranium speciation in soils. For example, spatial ranges from $>1 \text{ cm}^2$ to $<100 \text{ }\mu\text{m}^2$ (that is, 6 orders of magnitude change in area) can be probed by changing the degree of focus of the excitation source, which gives these methods a "zoom lens" capability for examining the heterogeneity in speciation. In addition, no sample preparation is required before implementation of any of these methods. All methods can be used on opaque samples like the Fernald soils, and all methods are noninvasive (that is, the sample is not altered by the spectroscopic probe). This, in particular, contrasts with conventional analytical methods like inductively-coupled plasma atomic emission spectroscopy or mass spectrometry, in which soil samples must be dissolved before investigation, thereby potentially altering the speciation information. In addition, all of these spectroscopic probes work equally well with amorphous samples and/or submonolayer coatings. For example, we successfully investigated the speciation of uranyl ions on layered clay minerals

(CHISHOLM-BRAUSE *et al.*, 1992a and b). Finally, all of these methods can be implemented in a temporally resolved mode by using pulsed excitation and/or gated detection. This mode enables better distinction between various uranium species and isolation of signal from background (that is, impurity) constituents, and it enables real-time investigations of the kinetic and mechanistic aspects of the decontamination technologies being developed within the USID.

It is important to reiterate that, although many of the advantages described above are not shared by speciation methods based on analytical microscopies, these microscopy-based probes are still of great value. Furthermore, they have many advantages not shared by the molecular spectroscopy-based approach. For example, the analytical microscopies can be operated in electron-diffraction modes that enable precise identification of crystalline uranium phases on the basis of established diffraction patterns.

EXPERIMENTAL

Samples

Phase 1 and Phase 2 samples are listed in Tables 1 and 2, respectively. Specific details concerning the decontamination treatments (for example, reagent concentrations, pH, contact times, solid-to-liquid ratios) are provided in the recent report from the Decontamination Task group (FRANCIS *et al.*, 1993). To briefly summarize the strategies and differences associated with these decontamination methods, the LANL group is investigating strong chelators that target U(IV) species. Tiron is a catecholate-like organic ligand analogous to naturally occurring siderophores. Dithionite, a common reducing agent, is being investigated as a catalyst to convert hexavalent uranium to tetravalent uranium for chelation by Tiron. Dithionite is also being investigated for its potential ability to liberate uranium that is strongly associated with Fe(III) in the soil matrix. Carbonate and citrate are two common uranium complexants employed in the metal mining industry. Other samples discussed in this report include the original, untreated "SP" series (particularly SP2 from the Plant 2/3 area) collected by S. Y. Lee of ORNL (LEE AND MARSH, 1992) and specimens from the library of high-purity uranium-bearing minerals maintained by the University of New Mexico (Professor Rodney Ewing, Department of Earth and Planetary Sciences, Albuquerque, New Mexico). These samples are valuable because they expand the database of luminescence and Raman spectra we use in studies of Fernald soils.

Instrumentation

Uranium L_{III} x-ray absorption spectral data were obtained on air-dried, powdered samples at both the National Synchrotron Light Source (NSLS) at Brookhaven

Table 1. Phase 1 Characterization Samples

<i>Treatment</i>	<i>Incinerator</i>		<i>Plant 1/Storage Pad</i>	
	<i>A-11</i>	<i>A-14</i>	<i>B-16</i>	<i>B-24</i>
LANL				
Untreated	B	B	B	B
De-ionized water		B		
Tiron	B	B		B
Dithionite		B		
Tiron/Dithionite	B	B		B
Carbonate	B	B		
Tiron/Carbonate	B			
Tiron/Dithionite / Carbonate	B			
ORNL				
Carbonate		<20 mm	<20 mm	
		20-75 mm	20-75 mm	
Citrate		<20 mm	<20 mm	
		20-75 mm	20-75 mm	

B = bulk phase (that is, unfractionated).

Table 2. Phase 2 Characterization Samples

<i>Treatment</i>	<i>Incinerator</i>		<i>Plant 1/Storage Pad</i>	
	<i>A-11</i>	<i>A-14</i>	<i>B-16</i>	<i>B-24</i>
ORNL				
Untreated	<2 mm	<2 mm	<2 mm	<2 mm
	2-5 mm	<20 mm	<20 mm	2-5 mm
	5-15 mm			5-15 mm
Dithionite	<2 mm			<2 mm
	<20 mm			<20 mm
Carbonate		<2 mm	<2 mm	
		<20 mm	<20 mm	
Citrate		<2 mm	<2 mm	
		<20 mm	<20 mm	

National Laboratory and the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University. All data were collected under ambient temperature and pressure. Absorption was detected in either transmission or fluorescence mode. Calibrations of the U L_{III} edge were obtained either simultaneously or between sample runs. We will provide additional experimental and data reduction details in a forthcoming manuscript.

We collected luminescence and Raman data by either continuous wave argon-ion laser excitation (Spectra-Physics Model 2040) or monochromatized light from a xenon arc lamp. For the laser-excited experiments, data were collected on a SPEX Industries Model 1403 double monochromator. For the arc-lamp experiments, data were collected on a SPEX Industries Fluorolog system. In all cases, we used a photomultiplier tube to detect the emitted light. In the laser-excited experiments, we used near ultraviolet lasing lines at 336, 351, and 364 nm. We varied the focus of the beam from ~50 μm to ~2 mm to change the spatial resolution of the probe on the sample. The samples, contained in glass vials in their heterogeneous form, were manually rastered so that the excitation beam probed different sites and features within the samples. In the arc-lamp experiments, we focused the exciting light to illuminate large portions of the sample and obtained no spatial resolution. The excitation wavelength was chosen to optimize the emission intensity. In some cases, the arc-lamp experiments were conducted with the samples (in sealed capillary tubes) in a liquid helium cryostat (~10 K) in an attempt to mitigate the quenching of the uranium luminescence and to sharpen the spectral features.

X-ray powder diffraction patterns were collected on a Phillips Model XRG 3100 computer-controlled x-ray diffractometer using $\text{Cu K}\alpha$ radiation. Data points were collected at 0.02 steps/degree 2θ with an integration time of 150 s/step. Crushed powder samples were contained in aluminum sample holders. Scanning electron microscopy data were collected on an International Scientific Instruments Model ISI-SX-40 unit interfaced to a Tracor Northern Pulse Processing and Detector Electronics package.

RESULTS AND DISCUSSION

X-Ray Absorption Data on Treated Samples

We have collected x-ray absorption data on all of the LANL-originated Phase 1 samples and four of the ORNL-originated Phase 1 samples. The remaining Phase 1 and the Phase 2 samples underwent XAS more recently, and these data will be discussed in another report. Note that even though we suspect some of these samples have uranium contamination removal of ~90% (for example, the Tiron + dithionite treatment), adequate signal-to-noise was still achievable by x-ray absorption. All untreated soil samples (A-11, A-14, B-16, and B-24) yield nearly identical edge and near-edge x-ray absorption spectra (Fig. 1) and Fourier-transform representations of the extended x-ray absorption fine structure (EXAFS) region. Furthermore, these spectra are essentially the same as those found previously for the untreated SP series from the Incinerator Area (SP9), the Plant 1/Storage Pad Area (SP4), and the

Plant 2/3 Area (SP2). We have shown previously that, based on both the edge position of the absorption and the occurrence of a pronounced EXAFS peak corresponding to the UO_2^{2+} moiety, most of the uranium in these soils (80 to 90%) exists in the hexavalent oxidation state (TIDWELL *et al.*, 1993). These results indicate that the bulk uranium oxidation state (that is, averaged over all species) in the A- and B-series soils from these sites is fairly constant, and the homogenization process (KNEFF *et al.*, 1993) did not affect this parameter to a significant extent.

On the basis of the x-ray absorption data, the treated A-series soils fall into three distinct categories. The first and simplest set comprises the "control" samples that were treated with deionized water or with dithionite only. These samples yield x-ray spectral data that are quite similar to those of the untreated samples, which indicates that neither water washing nor a reducing agent significantly changes the bulk uranium speciation in the soils in the absence of a chelator. The analytical data on these samples also suggest that very little uranium is removed (FRANCIS *et al.*, 1993).

Fig. 1. Uranium L_{III} x-ray absorption spectra for homogenized but otherwise untreated soils from the Incinerator Area (A-11 and A-14) and the Plant 1/Storage Pad Area (B-16 and B-24).

The second set of soils includes the A-14 soils treated with Tiron only, Tiron plus dithionite, carbonate only, and citrate only, as well as the A-11 soils treated with Tiron plus dithionite and Tiron plus dithionite plus carbonate. These soils all yield nearly identical x-ray absorption edge and near-edge signals and comparable EXAFS Fourier-transform representations. However, in these cases, the x-ray absorption data are markedly different from those seen in the untreated samples. Figure 2 shows the new characteristics of the x-ray absorption spectrum for this second set of soils, including a relative increase in the amplitude of the white line at ~ 17.18 eV and the loss of the characteristic shoulder in the near-edge region (~ 17.19 keV). However, the initial EXAFS feature remains at about the same energy (~ 17.22 keV) in this set of samples as in the untreated samples.

The third set includes the A-11 soils treated with Tiron only, carbonate only, and Tiron plus carbonate. These three samples also have nearly identical x-ray absorption edge and near-edge signals and comparable EXAFS Fourier-transform representations. However, the x-ray absorption data for this set differ from those in both the second set and the untreated samples. There are some similarities to the data for the second set samples in that the white line intensity is increased relative to the intensity for untreated samples, and the characteristic shoulder at ~ 17.19 keV is also

Fig. 2. Comparison of the uranium L_{III} x-ray absorption spectrum of an untreated sample to that from the second set of treated samples. The soil specimen for both spectra is A-14.

Fig. 3. Comparison of the uranium L_{III} x-ray absorption spectrum of an untreated sample to that from the third set of treated samples. The soil specimen for both spectra is A-11.

absent. However, note that for the third sample set (Fig. 3) the initial EXAFS feature has decreased in energy by ~ 150 eV. The differences between the untreated (and first set), second, and third sets of treated A-series soils are well illustrated in Fig. 4 by the Fourier-transform representations of the EXAFS data.

In a prior, mid-year report (DONOHOE *et al.*, 1993), we noted that for all A-series samples treated with effective treatment technologies (that is, those that removed substantial amounts of the uranium), the x-ray absorption data were very similar. We made the tentative suggestion that this similarity might reflect the fact that the same intractable uranium species or mixture of species remained in all the samples. The x-ray absorption data collected since the release of that report, particularly those for the treated A-11 soils, clearly suggests that this early conclusion was erroneous. The obvious differences in x-ray absorption data between the second and third sets of samples, all of which have substantial amounts of uranium removed from them, indicate that the remnant uranium species do vary between some samples, depending on the treatment technology. The data shown in Fig. 4 also suggest that there may be an emerging trend in the oxidation-state distribution of the remnant uranium species. The progressive shift to higher r -values for the initial EXAFS peak—from untreated (and first set) to second set to third set samples—could be interpreted as a

Fig. 4. Fourier-transform representations (radial structure functions) of the extended x-ray absorption fine-structure data for untreated, second-set, and third-set samples for soil A-11. Spectra have not been corrected for phase shift.

general increase in the relative abundance of tetravalent uranium *vs* hexavalent uranium. We are currently seeking a quantitative estimate of the relative abundance of tetra- and hexavalent species.

Note that the A-11 soils treated with Tiron plus dithionite and Tiron plus dithionite plus carbonate produce x-ray spectral data that are indistinguishable from those seen for similarly treated A-14 soils, whereas the A-11 soils treated by procedures that did not include dithionite (that is, the third set) are different. This fact perhaps suggests that differing chemical processes are at work with and without the reducing agent, but that these processes have only been manifested thus far for the newer A-11 soil lot. It has also been suggested that the reactivity of the dithionite may have been different between the trials with A-14 and A-11 soils as a result of pH variations,* which could account for the lack of observable differences in the A-14 soils with and without dithionite. However, this observation does not help to reconcile the fact that the samples that were not treated with the reducing agent appear to have the greatest abundance of tetravalent uranium as the remnant form, as was noted above (Fig. 4).

The x-ray absorption data for the B-series of soils that were treated are less clear cut at this point—in part because the sample set is smaller, which makes comparisons more difficult, and in part because the concentration of uranium in these samples after treatment appears to be much lower than in the A-series (consistent with other reports such as FRANCIS *et al.*, 1993), leading to much lower signal levels and poorer signal-to-noise ratios. For example, we have been unable to obtain meaningful EXAFS data from these samples. Nonetheless, we have acquired x-ray absorption edge and near-edge spectra, and examples are shown in Fig. 5. Note that the spectra for the treated samples retain the shoulder feature in the near-edge region, but there is considerable variability in the position of the initial EXAFS feature. Based on the edge position and the persistence of the near-edge shoulder, it is likely that the remnant uranium in these treated samples is still predominantly hexavalent. However, additional data is warranted. It would be useful to treat these B-series soils with stoichiometrically-limited amounts of remediation solutions to deliberately leave behind more uranium.

*Information received from J. R. Brainard, Los Alamos National Laboratory, Los Alamos, NM 87545.

Fig. 5. Uranium L_{III} x-ray absorption spectra comparing untreated (B-24) and treated (B-16 and B-24) soils from the Plant 1/Storage Pad area.

Optical Spectroscopic Data on Treated Samples

All of the Phase 1 soil samples, except the LANL-originated A-11 and B-24 samples, and all of the Phase 2 samples that are listed in Tables 1 and 2 have been screened for optical luminescence activity. The most notable result from these investigations is that the treated soil samples show a substantial decrease in the quantity and size of the particulate uranyl species that give rise to the green and orange luminescence spectra reported previously. In fact, in no instances have we observed the highly structured green emission spectrum seen in the SP9 and SP2 samples (TIDWELL *et al.*, 1993) that we now assign to a uranyl phosphate species (see below). We have employed the complete range of experimental perturbations for these studies, including either a tightly focused laser excitation source or large-area laser and continuous-wave excitation sources and using either microscopic imaging or manual rastering of the sample in the excitation beam. There are, however, some green and orange luminescent species seen in the treated samples, which are most likely attributable to hexavalent and/or mixed-valent uranium species. Table 3 summarizes these occurrences.

Table 3. Occurrence of Luminescent Uranium Species in Treated Soils

Soil	Source	Treatment	Size	Emission Color	
				Green	Orange
Phase 1					
A-14	LANL	Tiron	B	X	
A-14	LANL	Carbonate	B	X	
A-14	ORNL	Carbonate	20-75 mm	X	X
A-14	ORNL	Carbonate	<20 mm		X
B-16	ORNL	Carbonate	<20 mm		X
Phase 2					
A-14	ORNL	Carbonate	<2 mm		X
A-14	ORNL	Carbonate	<20 mm	X	X
A-14	ORNL	Citrate	<20 mm		X
B-16	ORNL	Untreated	<2 mm	X	
B-16	ORNL	Citrate	<2 mm		X
B-16	ORNL	Citrate	<20 mm		X
B-24	ORNL	Untreated	<2 mm		X
B-24	ORNL	Untreated	5-15 mm		X
B-24	ORNL	Dithionite	<2 mm		X
B-24	ORNL	Dithionite	<20 mm		X

B = bulk phase (i.e., unfractionated).

The green luminescence we observed in five of these samples produces approximately the same spectrum in each case. Examples are provided in Fig. 6. The particle size from which this emission emanates is, in all cases, much smaller than we generally observed in the SP series. Note that these spectra are very similar in energy and band shape to those from a naturally occurring, well-crystallized schoepite sample (Fig. 6) but quite distinct from those for freshly precipitated uranyl hydroxides (TIDWELL *et al.*, 1993). This suggests that the uranyl species producing the spectra in these treated samples are not simply reprecipitation products that result from hydrolysis of dissolved uranyl species during the course of the treatment processes.

The orange emitters are much more prevalent in these treated samples than the green emitters, as is indicated in Table 3. Similar orange-emissive particles have been found in the SP series of samples—frequently in intimate contact with the structured green uranyl phosphate phase (Fig. 7 shows example spectra). In the SP series, we observed what appeared to be two distinct classes of orange emitter. The first, we assume from Raman data, is possibly associated with a carbonate matrix and is

Fig. 6. Comparison of the optical emission spectra for green hexavalent uranium particulates in treated A-14 (Incinerator Area) soils with that from a well-crystallized schoepite mineral sample $[\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}]$ obtained from the University of New Mexico mineral collection. All spectra were excited with point-focused 364-nm laser radiation.

Fig. 7. Examples of the optical emission spectra for the photochemically stable (A: SP2-3, Plant 2/3 Area) and unstable (B: carbonate-treated B-16, Plant 1/Storage Pad Area) orange emissive phases of hexavalent uranium found in Fernald soils. All spectra were excited with point-focused 364-nm laser radiation.

photochemically stable (Fig. 7, spectrum A). This phase has an intense low-energy shoulder in the emission profile. The second class is photochemically very unstable with respect to 364-nm laser excitation and does not appear to have an intense low-energy shoulder. It is this second class that dominates the occurrence of orange emitters in the treated samples (Fig. 7, spectrum B). Obtaining an exact identification of these orange emitters is problematic because the spectral bandshapes vary from occurrence to occurrence; they do not yield Raman data; and their physical size is small, making manual concentration difficult. Some additional data are provided below for the orange emitting phases that are isolated from the SP series of soils. Nonetheless, the photochemical instability is suggestive of uranyl species complexed by organic ligands because the uranyl-organic complexes are notorious for their photochemical instability (RABINOWITCH AND BELFORD, 1964), and this generally results in complete degradation of the original hexavalent species.

The diminished occurrence of uranyl emission in the treated samples clearly is consistent with the preliminary analytical results, which show that as much as ~90% of the uranium can be removed from the soils (Francis *et al.*, 1993). However, other factors must be operating as well because the signal-to-noise of our results in

unwashed soils was much greater than 20:1, suggesting that we should easily see the remaining 5 to 10% of the uranium in the soils. (Note that the x-ray absorption data indicate that hexavalent uranium is still prevalent in most samples. Therefore, complete oxidation-state conversion to nonemissive uranium(IV) can be excluded for most samples.) Furthermore, even those samples for which the treatment was not particularly effective (such as dithionite-only and deionized-water-only treatments) yielded samples with diminished uranyl luminescence. It is possible that, as a result of all treatments, the uranium may be more evenly spread along the surface of the soil matrix rather than existing as micrometer-size particulates. Such an effect may be caused by dissolution, followed by reprecipitation and/or attrition to smaller particle sizes, followed by redistribution. This final effect might be promoted by the LANL team's ball-milling process, which was used in the pretreatment protocol in some of their early experiments. The more homogeneous distributions of uranium resulting from either of these mechanisms would lower the uranyl luminescence relative to the broad emission background from organics or iron species that remain in the soil, making it more difficult to locate and isolate the emissive uranyl species for spectroscopic characterization. Alternatively, after dissolution/redistribution, the uranium may become sorbed onto the surface of iron oxide particles—especially goethite—or organic-coated particles. In these cases, the uranyl luminescence may be effectively quenched.

Ancillary Data on Treated Samples

We collected x-ray diffraction data for only a subset of the Phase 1 samples: no data were collected on the A-11 or B-24 samples. The x-ray diffraction (XRD) powder patterns of the untreated soils identified quartz, feldspars (Ca, Na, and K), dolomite, and calcite as the principal minerals present; quartz contributed the dominant pattern. Neither clay minerals nor apatites were important features, and we found an unassigned peak at $2\theta = 37^\circ$. Many of the XRD features of the treated soils that were examined remained the same: quartz is still the dominant constituent in all of the XRDs, feldspars also contribute [especially albite (Na) and anorthite (Ca)] in carbonate-washed samples, and orthoclase (K) became relatively less abundant. Furthermore, calcite and especially dolomite became more prominent in the treated samples, especially those treated with carbonate and citrate. XRDs showed that of all the samples, the small-size fraction from the ORNL carbonate treatment changed the most—the former showing dolomite and calcite becoming more predominant in the pattern. The unknown peak at 37° remained in all samples after treatment. We discounted the formation of any amorphous phases during the washing process because no broad scattering band is found in any of the XRDs. Several samples developed a new peak at 3.5° . Because of the large d-spacing implied by this peak ($23\text{\AA}$), this species is likely to be a clay mineral, possibly a weathered product from original

feldspars. It is very encouraging that these XRD data for the treated samples indicate that the treatment processes don't significantly alter the native soil characteristics.

Untreated Soils and Reference Uranium Minerals

We continue our efforts to identify precisely the various forms of uranium in the Fernald soils. To this end, we are examining untreated samples in search of new uranium species and more precise spectroscopic data (for example, Raman vibrational spectra) for previously identified species. We are also continuing our studies of reference uranium minerals and compounds. Most notably, we established a collaboration with R. Ewing of the University of New Mexico that enables us to access the extensive collection of uranium minerals in their mineral library. Substantial new luminescence and Raman spectroscopic data collected on oxy-hydroxide, carbonate, phosphate, and silicate minerals is being compared to the Fernald soil data.

The luminescence and Raman data from the reference uranium minerals have enabled us to identify with high confidence the uranyl species in the SP2 and SP9 soil samples that produce the highly structured emission. Specifically, we were able to isolate a small quartz-like particle (~0.5-mm diam) from the SP2 sample that clearly had a uranyl mass adhering to it. This uranyl mass produced the characteristic structured emission spectrum (see Fig. 8, spectrum A) that is very similar to the spectrum seen for the uranyl phosphate minerals meta-autunite, meta-ankoleite, and phosphuranylite. (The meta-autunite spectrum is shown in Fig. 8, spectrum B). Although these three uranyl minerals have nearly indistinguishable emission spectra, their Raman spectra in the region of the totally-symmetric uranyl stretch and the phosphate stretches are very distinct. Fortunately, we were able to obtain Raman spectral data for the uranyl-coated quartz mass isolated from the SP2 sample. As is shown in Fig. 9, the spectrum from the soil sample has numerous bands that match extremely well with those from meta-autunite. On this basis, we are confident in identifying the uranyl species on the quartz mass (and those seen elsewhere in bulk SP2 and SP9 samples) as meta-autunite.

In a separate experiment, we subjected this uranyl-coated quartz particle to gentle washing with ~5 ml of deionized water. (The process involved minimal attrition because the particle was merely rotated gently in a small glass vial.) We then re-examined the particle by both luminescence and Raman spectroscopy. The emission spectrum did not change in form, but it did decrease significantly in intensity, which allowed us to estimate that the washing process removed 90 to 95% of the uranyl contamination from the particle. The Raman spectrum is shown in Fig. 9.C. Note that the bands seen in the meta-autunite spectrum (Fig. 9 A) and the unwashed

Fig. 8. Optical emission spectra for (A) the emissive uranyl mass adhering to a quartz particle isolated from soil SP2-3 (Plant 2/3 Area), and (B) meta-autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$ obtained from the Smithsonian collection. All spectra were excited with point-focused 364-laser radiation.

quartz particle (Fig. 9 B) have disappeared from the washed-particle spectrum. This observation validates our assumption that these bands in the unwashed-particle spectrum belong to a meta-autunite phase on the particle.

It is interesting that the deionized water was so effective in removing the uranyl phosphate phase. Phosphate phases are thought to be quite insoluble in water; however, if—as this result suggests—these phases can be removed fairly easily, this may explain why we were unable to see the structured green emission in the treated soil samples (see earlier discussion). If deionized water can remove the phosphate phase from this quartz particle, then perhaps all of the treatment methods do the same for the bulk soils. Additional work using pure meta-autunite is under way to verify this result.

It is important to note that the occurrence of green emission in the SP series of soils is generally consistent with several co-existing emissive phases. For example, as we have shown previously (TIDWELL *et al.*, 1993), structured spectra such as in Fig. 8 A appear to also have an underlying broad-band uranyl emission. Oxyhydroxide (for example, schoepite) and carbonates (for example, rutherfordine) are

Fig. 9. Raman vibrational spectra for (A) meta-autunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 2\text{-}6\text{H}_2\text{O}]$ obtained from the Smithsonian collection, (B) the emissive uranyl mass adhering to a quartz particle isolated from soil SP2-3 (Plant 2/3 Area), and (C) the emissive uranyl mass adhering to a quartz particle following gentle washing with deionized water. All spectra were excited with point-focused 364-laser radiation.

such broad-band emitters. The presence of schoepite has been confirmed by XRD data from a hand-concentrated sample of the green-emitting particulates. The energy dispersive SEM of the concentrated Fernald green emitters showed both silicon- and phosphorous-containing anions (any carbon or oxygen would not be detected because of their low emission energy), as well as calcium, potassium, and magnesium cations, so a possible combination of phosphates and silicates can not be eliminated. The crystal habit of the green emitters in the Fernald soil can be described as platy, which is consistent with an oxyhydroxide (for example, schoepite) and/or a phosphate phase (for example, autunite), whereas silicates (for example, sklodowskite) tend to have acicular crystal habits.

We have also attempted to identify the orange emitters found in the SP2 samples. Two reddish minerals from the library samples, kasolite (lead uranyl silicate) and curite (hydrated lead-oxide uranate), showed no emission from the bulk phase, but we noted orange impurity emissions. The impurity in curite is similar (but not identical) to that found in the orange emitter from Fernald SP2. On the basis of previous studies, it has been suggested that orange and red uranium emitters are

uranate " UO_3 " structures such as ianthinite rather than uranyl ($[\text{UO}_2]^{2+}$) structures, but many historically " UO_3 " structures have been re-formulated as uranyl structures. Finally, alkyl-phosphate uranium compounds emit orange to red when optically excited. The SP2 samples are among the samples that exhibit the orange-red luminescence, and these were also taken near the Plant 2/3 area where tributyl phosphate was used in the PUREX process. To check this hypothesis, we are presently pursuing luminescence spectra from a series of known U-phosphate complexes.

The energy dispersive SEM for hand-concentrated orange emitters is much simpler than for the green emitters: silicon is greatly reduced in importance; phosphorous is not present at all; and the cations Mg and Ca are almost absent. In fact, the only cations in abundance are K and Al, and trace Fe is also present. Clearly, the orange emitters present in small quantities in untreated Fernald soil are not phosphates, nor are they likely to be silicates. This contrasts with circumstances of the green emitters, in which uranyl species containing these anions are likely candidates for the structured emission. The lack of Ca and Mg in the orange emitting phases is especially strange because nonluminescent particles that get picked out with the orange emitters look like calcite/dolomite under a microscope and contain a carbonate peak (not calcite) in the Raman spectrum. In any case, the XRD spectrum from hand-concentrated Fernald orange emitters is consistent with the ianthinite species, which would also account for the lack of anions and cations associated with this uranium phase. This identification is questionable, however, as these peaks are also present in the hand concentrated green emitters and may therefore be from the soil matrix rather than a uranium species.

SUMMARY

We have collected x-ray absorption and optical luminescence spectroscopic data for approximately 40 Fernald soil samples that have undergone treatment by one or more of the decontamination technologies being developed in the USID. Results for the A-series soils from the Incinerator Area suggest that the treated soils can be divided into three sets. The first set comprises control samples that are little changed from the untreated soils. The second set encompasses most of the A-series samples. The uranium remaining in these soils appears to have a slightly higher ratio of tetravalent to hexavalent uranium than the untreated soils. The third set consists only of A-11 soils treated by Tiron, carbonate, or both, but with no reducing agent. This set appears to have the highest ratio of tetravalent to hexavalent uranium remaining in the soil for any samples examined thus far. The observation of different x-ray absorption spectra in the second and third sets suggests that, contrary to previous preliminary conclusions, there are several uranium species left in the soils following

treatment, rather than a single intransigent species, and the treatment chemistry may be dictating the difference in the remnant species. The treated B-series soils from the Plant 1/Storage Pad Area are less easily categorized. However, based on the usual x-ray absorption criteria, they appear to retain primarily hexavalent uranium following the treatments.

The optical luminescence data demonstrate that there is a decrease in size and probably quantity of the particulate hexavalent uranium that gives rise to the green emission. In particular, the highly structured emissive phase seen in the untreated SP2 and SP9 soils was never seen in treated samples. Thus, all treatment technologies do seem to lead to a more dispersed, finer-grain contamination. Some instances of particulate green emission still exist in these samples, and the spectral band structure suggests that this is attributable to a schoepite phase. An orange emissive phase is also seen in many samples that is probably attributable to a hexavalent uranium species, but its identity has not been confirmed.

New Raman and luminescence data for untreated soils and reference mineral phases have enabled us to identify the highly structured green emissive phase as meta-autunite. We have also shown that this phase can be easily removed from a quartz particle by using deionized water, which suggests a possible reason for the lack of these structured emitters in the treated soils.

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