Project Number: 73691

Project Title: Direct Investigations of the Immobilization of Radionuclides in the Alteration Phases of Spent Nuclear Fuel

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Number of Undergraduate Students Involved: 10

RESEARCH OBJECTIVES

In a moist oxidizing environment, such as in the proposed geological repository at Yucca Mountain, rapid alteration rates are expected for spent nuclear fuel. Laboratory simulations and studies of natural analogues demonstrate that the dominant alteration products of spent fuel under repository conditions will be uranyl phases. There is an inadequate database concerning the effects of the alteration products on the release of radionuclides, but this information is essential to provide a radionuclide-release estimate. It is likely that many of the radionuclides contained in the spent fuel will be incorporated into the uranyl phases that form during alteration, potentially with a profound impact on the future mobility of radionuclides in the repository. Our objective is to develop a theoretically founded and experimentally verified understanding of the incorporation of radionuclides into uranyl phases under repository conditions. The research will permit a more realistic estimate of the release rates of the radionuclides from the near-field environment.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work conducted under DOE grant DE-FG07-97ER14820, which has been funded since September, 1997. In addition to significantly improving our understanding of factors impacting the mobility of radionuclides in Yucca Mountain, our research is important for understanding the mobility of actinides in the vadose zone, in altered U mine and mill tailings, and in soils contaminated by U.

Structures and Chemistry of U^{6+} Compounds Relevant to Yucca Mountain

At the beginning of our EMSP research, understanding of the crystal structures, chemistries, stabilities and occurrences of the uranyl compounds relevant to Yucca Mountain performance was entirely insufficient, from the perspective of their impact upon repository performance. In most cases the crystal structures were unknown for these phases, and even their chemical formulae were in doubt. Detailed structural analysis of uranyl phases relevant to repository performance has therefore been a high priority of our ongoing research. Suitable natural crystals have never been found for many of the compounds of interest, so we invested considerable effort in developing synthesis procedures for growth of crystals ~100 µm in dimension. We have now published the detailed structures and chemistries of more than 75 uranyl compounds that are relevant to Yucca Mountain.

Structures we have reported include those of studtite, becquerelite, haiweeite, weeksite, boltwoodite and compreignacite, all of which have been identified as alteration phases on spent fuel and UO_2 in laboratory experiments. Of these, studtite is particularly interesting because studtite and metastudtite are the only peroxide minerals known in nature. Although we had successfully synthesized Np-bearing metastudtite early during this project, we placed renewed emphasis on determining its structure after four presentations at the Fall 2002 Materials Research Society meeting reported identifying studtite or metastudtite on spent fuel in alteration tests conducted with de-ionized water.

Our structure studies have focused on several important chemical classes of U^{6+} compounds, and include detailed structural analysis, chemical characterization, and in many cases, discovery of new phases. New structures can be understood in the context of the hierarchy of structures developed by us, which serves as the basis for prediction of radionuclide incorporation mechanisms.

Uranyl oxide hydrates are usually the first phases to form following the onset of oxidative alteration of spent fuel; we have reported 12 structures. Uranyl silicates are expected to form in the repository, owing to the presence of Si in the groundwater; we have reported 5 structures. Studies indicated that uranyl molybdates may be important alteration phases owing to the presence of Mo in spent fuel; we have undertaken an extensive study of the crystal chemistry of uranyl molybdates, and have reported 28 structures. Uranyl sulfates incorporating S released from corroding steel may form in the repository; we have reported 14 structures, including 3 containing a novel uranyl sulfate cluster that may be an important uranyl sulfate complex in groundwaters or hydrothermal fluids. Uranyl phosphates have very low solubilities, and thus we proposed the possible use of phosphate in backfill to reduce the mobility of actinides; we have reported 12 structures. Our studies of uranyl carbonates have revealed 9 new structures.

XANES and EXAFS Studies of Uranyl Compounds

X-ray absorption spectroscopy (XANES and EXAFS) can provide a wealth of information concerning the oxidation states and coordination environments of U and Np in samples of environmental interest. However, a basic understanding of the relationships between XAS spectra for structures containing actinides has not been fully developed. We have therefore undertaken a systematic study of the U L_{III}-edge XANES and EXAFS spectra for a series of crystalline uranium compounds that have well-refined structures, known valence states and that display a range of coordination environments about U^{6+}. We selected structures that contain the uranyl ion in a variety of coordination environments, as well as structures that have been reported to contain U^{6+} in unusual 6-fold coordination geometry, such as the 4+2 geometry in Li_4UO_5.

Spectra were collected at the BESSRC beam line at the Advanced Photon Source. We studied 13 compounds that included uranyl silicates, uranyl carbonates, uranyl phosphates, uranyl sulfates, and uranyl oxide hydrates, several of which may form in Yucca Mountain once containers are breached. XANES spectra of the 13 compounds are consistent with hexavalent uranium, and posses various features related to the specifics of the U^{6+} coordination geometries.

Thermochemistry of U^{6+} Compounds

Recent advances in the understanding of the crystal chemistry and structures of U^{6+} compounds important for repository performance provide the foundation for studies of their thermodynamics. We have conducted preliminary high temperature oxide melt drop-solution calorimetry to measure drop-solution enthalpies (ΔH_{ds}) of select U^{6+} carbonate, oxyhydrate, and phosphate phases. Experiments were done, with the assistance of Prof. Alexandra Navrotsky, using a Calvet-type high temperature custom-built calorimeter located at the University of California-Davis.

Prediction of Radionuclide Incorporation into Uranyl Compounds

The structural hierarchy of uranyl compounds we developed has been continuously extended by our studies. The hierarchy is provides a broad conceptual basis for understanding structural relations among various uranyl compounds, many of which posses complex structures, as well as providing the basis for predicting and explaining compositional variations and mechanisms for radionuclide substitutions. Likely sites for incorporation of radionuclides such as ^{135}Cs, ^{90}Sr, Np and Pu have been established.

Ion Exchange of Cs and Sr into Uranyl Compounds

We have demonstrated exchange of Cs into boltwoodite and compreignacite, and Sr into becquerelite. Our studies indicate that uranyl compounds can exchange lower-valence radionuclides with solutions after they grow, and that they can incorporate such radionuclides during growth. These phases may either sequester radionuclides or release them, depending upon the relative activities of different ions in the solution.

Experimental Studies of Np^{5+} Incorporation into Uranyl Compounds

The long half-life of Np-237 (2.14 x 10^6 years), radiotoxicity and potentially high mobility of Np^{5+} in chemically oxidizing groundwater make it a major dose contributor in current performance-assessment models for the potential repository at Yucca Mountain, Nevada, and therefore one of the most important radionuclides for the long-term performance of the repository. One of our major objectives is to determine if incorporation of Np^{5+} into selected uranyl compounds can occur.

Our initial studies of Np^{5+} incorporation into uranyl compounds focused on four phases: the Ca uranyl silicate uranophane, $Ca[(UO_2)_2(SiO_3OH)_2](H_2O)_5$, and the uranyl oxide hydrates meta-schoepite, $UO_3.2H_2O$, Na-compreignacite, $Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$, and β-$UO_2(OH)_2$. Our intent to study incorporation of Np^{5+} into structures mandated that we develop one-step synthesis techniques for each. We conducted >100 synthesis experiments to optimize our synthesis approaches, which included a double-containment method because of the radiological hazards of Np-237. We then synthesized each compound at either 70°C or 100°C from solutions containing from 10 to ~450 ppm Np. Products were recovered and washed with boiling water, and aliquots of the mother solutions were taken before and after the synthesis experiments. Portions of each powder were also washed in acetic acid to strip any Np that may have been sorbed to the surface of the crystals. Products were confirmed by X-ray powder diffraction, and products and solutions were analyzed using ICP-AES for U, Na and Ca, and ICP-MS for Np.

Neither meta-schoepite or β-$(UO_2)(OH)_2$ incorporated more than a few ppm Np. In contrast, Na-compreignacite and uranophane appears to have incorporated Np^{5+} into their crystal structures in proportion to the Np concentration in the mother solution, with crystals of each containing more than 400 ppm Np (of total Np + U). The Np concentration in the crystals was not significantly reduced by washing in acid, thereby demonstrating incorporation, rather than sorption onto the mineral grains. This study indicates that incorporation of Np^{5+} into uranyl compounds that form in Yucca Mountain is possible, and that this incorporation may have a significant impact upon the mobility of Np.

Development of a bent-Laue X-ray analyzer for measuring XAFS of trace transuranium actinide in U solids

We have been developing a special detector for XAFS data collection at the MRCAT beam line at the Advanced Photon Source. This detector, which uses a bent-Laue configuration, allows us to collect high-quality X-ray absorption spectra from low levels of Np in U compounds. Because the Np-Lα fluorescence (Lα_1 = 13.944 keV, Lα_2 = 13.760 keV) is very close in energy to the U-Lα fluorescence (Lα_1 = 13.615 keV, Lα_2 = 13.439 keV) and occurs at higher energy, the use of standard fluorescence detectors is precluded. Employing a bent Laue analyzer, which provides superior energy discrimination, isolates the signal of the relatively small amount of Np in our samples. Several published reports and one paper (submitted) have resulted from this work.

Characterization of Np-doped U_3O_8

Np-doped U_3O_8 was examined at the MRCAT beam line at the Advanced Photon Source using the bent-Laue detector that we helped develop. Analyses of XANES spectra indicate that Np occupies distorted U sites in U_3O_8 and most likely occurs as Np(IV). As Np(IV) replaces U in U_3O_8, the ratio of U(VI) to U(V) must increase until all U is hexavalent in $Np_xU_{3-x}O_8$. Charge balance, therefore, requires that the value of *x* not exceed one in $Np_xU_{3-x}O_8$. Powder X-ray diffraction analyses of Np-doped U_3O_8 indicates that it forms a homogeneous solid solution from approximately 0.1 wt.% Np up to 9.5 wt. % Np, and that the dependence of the lattice parameters on Np concentration suggests that a complete solid solution is possible for values of *x* in $Np_xU_{3-x}O_8$ from zero to one; that is, between end-member compositions U_3O_8 and NpU_2O_8. The substitution of Np(IV) for U in U_3O_8 impacts significant strain to the sheets, although the distortion to the sheets quickly reaches a maximum for *x* of 0.3 and above; in fact, the distortion is nearly isovolumetric, with the *a* and *b* cell parameters changing in a complementary fashion, such that the area defined by the *a-b* plane remains nearly constant (the *c* cell dimension changes only slightly). As noted, Np(IV) occupies six-coordinated U sites in $Np_xU_{3-x}O_8$, such as occur in beta-U_3O_8, and we suggest that NpU_2O_8 is isostructural, or nearly so, with beta-U_3O_8.

Synthesis of uranyl oxyhydroxides from Np-bearing U_3O_8

Exposure of Np-bearing U_3O_8 to humid air (100% relative humidity) at 90° and 150°C under nominally oxidizing conditions produces a variety of U(VI), Np(V) and Np(IV) solids. The primary sink for Np during corrosion of $Np_{0.33}U_{2.67}O_8$ at 150° C is crystalline NpO_2; corrosion of $Np_{0.33}U_{2.67}O_8$ at 90° C produces approximately equal proportions of crystalline NpO_2 and Np_2O_5. Dehydrated schoepite, $(UO_2)O_{0.25-z}(OH)_{1.5+2z}$ ($0 \leq z \leq 0.15$), is the predominant U(VI) compound formed in these experiments and does not incorporate measurable amounts of Np (earlier reports of Np in this solid were the result of an interference inherent to the analytical technique used – the same technique used to “discover” Np in dehydrated schoepite formed from spent fuel [Buck et al. 1997]). Results have been presented at several conferences.

XAFS examinations of spent fuel and its corrosion products

Detailed understanding of the structural roles that Np, Pu and Am play in spent fuel and the uranyl compounds formed as corrosion products is an important part of understanding the crystal-chemical and potential geochemical behaviors of these actinides. As part of this effort, we have conducted the first-ever EXAFS examinations of fully radioactive spent nuclear fuel. Owing to our development of the bent-Laue detector for XAFS (see above), we have been able to obtain high-quality EXAFS spectra from Pu, and Np in unaltered spent fuel at concentrations of 1.3 and 0.08 wt.%, respectively. Preliminary analyses indicate that both Np and Pu are tetravalent and substitute for U in the UO_2 fuel. Similar high-precision EXAFS analyses of uranyl oxyhydroxides (dehydrated schoepite) formed during the oxidative alteration of spent fuel after more than eight years (104 months) in humid air have demonstrated that Np is not incorporated into these solids, a result consistent with other studies we have conducted, which also found no incorporation of Np into schoepite (see above).

EXAFS of lanthanide-bearing silicates and effects of lanthanide substitutions on physical properties

Lanthanides are useful, non-radioactive chemical analogues of many actinides of environmental concern, so we have also been examining solid-state structural effects of lanthanide substitutions in synthetic crystals of zircon ($ZrSiO_4$). A major part of this effort is aimed at developing our capabilities for collecting EXAFS data from compounds with elements that may experience absorption-edge interferences from neighboring elements, as is the case for many actinides and lanthanides. Furthermore, non-radioactive lanthanides provide useful surrogates for examining structural changes induced by substitutions into crystalline materials, such as $ZrSiO_4$. Recent efforts at Argonne have focused on examining REE substitutions by XRD and XAS. Results of these studies indicate that coupled substitutions of REE and P into zircon induces substantial strain at the *Si* site, limiting the degree of solid solution between zircon and xenotime (YPO_4). EXAFS analyses indicate that REE occupy Zr sites rather than interstitial sites, as has been proposed. A recent compressibility study of REE- and P-doped zircon is "softer" (lower compressibility), delaying the onset of the high-pressure phase transformation to riedite. Such changes to the physical properties of zircon (a notably durable mineral) suggests that substitutions of actinides and lanthanides into waste forms and uranyl alteration products may impact the long-term durability of substituted solids.

INFORMATION ACCESS

Bold = PI, PD = Post-Doc, GS = Graduate Student, US = Undergraduate Student

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