FINAL REPORT

**U.S. DEPARTMENT OF ENERGY
OFFICE OF SCIENCE
HEAVY ELEMENTS PROGRAM**

CONTRACT NUMBER ER15138

***Actinide Incorporation and Radiation Effects in U(VI) Solids: Thermodynamic and
Mechanistic Study of the Formation of Uranyl-Heavy Element Solid-Solutions***

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Actinide Incorporation and Radiation Effects in U(VI) Solids: Thermodynamic and Mechanistic Study of the Formation of Uranyl-Heavy Element Solid-Solutions

In our first funding cycle, much time was spent developing protocols for characterizing and working with samples containing transuranium isotopes and obtaining preliminary experimental data on non-f-element systems. These studies then provided the basis for our recent work involving the f-elements. To date, we have also focused our efforts on the study of U(VI) silicates, primarily uranophane ($\text{Ca}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_5$), and the substitution of other cations into this phase. Our efforts to date have been on solid phase synthesis, characterization, and radiation effects in these solids. We have not yet completed solubility and detailed phase alteration studies. Our results to date are presented below by first discussing our synthesis and characterization work, followed by our studies of radiation effects.

I. Studies of cation incorporation into uranophane

One of our first studies involved the substitution of Cs^+ and Sr^{2+} into uranophane. We used stable isotopes of these cations to mimic the fission products ^{137}Cs and ^{90}Sr . The U(VI):silicate sheets of uranophane have a net negative charge, which is compensated by the Ca^{2+} and water molecules in the interlayer. We expected that Sr^{2+} should isomorphically substitute for Ca^{2+} , whereas Cs^+ may not be as easily accommodated into the uranophane structure due to the difference in cationic charge. Based on the work of Burns for U(VI) oxide hydrates (e.g., Burns and Li, 2002; Hill and Burns, 1999; and Hoskin and Burns, 2003), we expected both Cs^+ and Sr^{2+} to be incorporated into the uranophane structure by ion exchange with Ca^{2+} in the interlayer. This expectation is also consistent with bond valence calculations for fission product incorporation into uranophane (Burns et al., 1997).

Similar to the work of Vocht et al. (1997) for synthetic boltwoodite and sodium boltwoodite, we prepared a series of U(VI):silicate solids in which we varied the mole ratio of either Ca^{2+} and Sr^{2+} or Ca^{2+} and Cs^+ (in separate experiments). The synthesis method followed was for uranophane (Nguyen et al., 1992), except that the desired mole fraction of Ca^{2+} was replaced by either Cs^+ or Sr^{2+} .

In every case, all of the dissolved Cs^+ or Sr^{2+} was removed from solution and associated with the solid phases formed. Diffractograms for the resulting solids are shown in Figure 1. In both cases, the crystalline solid phase appeared to be primarily uranophane at low mole fractions of either Sr^{2+} or Cs^+ , but other crystalline solids were formed at higher mole fractions of the non-Ca cations. In fact, inspection of all of the solids by SEM demonstrated that mixtures of solids were formed in every case, suggesting that amorphous or very finely divided crystalline materials were also being produced. Interestingly, for the Sr^{2+} studies, the Sr^{2+} cation was incorporated into the bulk solids at ratios expected based on simple ion exchange, as shown in

Table 1, even though the diffraction patterns for the crystalline solids were quite different for 25%, 50%, and 100% substitution. We also observed that aging time was an important factor to consider, as the solids became more crystalline and altered to other solids with time.

Although we were not able to identify all of the various solid phases formed in these assemblages, it was clear that the dissolved concentrations of both Cs^+ and Sr^{2+} were controlled by these solids rather than by discrete Cs or Sr solids. It was also clear that other methods of characterization would be needed to accomplish our objectives for our research. These results were published in *J. Nucl. Sci. Technol.* (Douglas et al. 2002) and is included in the appendix to this proposal. Since the fission products were not the focus of this research effort, we have discontinued these studies (although we have retained the materials that were produced).

We have also studied the incorporation of a series of divalent cations into uranophane. In this work, we varied the mole fraction of Ca^{2+} with either Mg^{2+} , Sr^{2+} , Ba^{2+} , or Cd^{2+} . We also investigated the application of high resolution TEM and SAED for characterization of these solids. In the case of Mg^{2+} incorporation into uranophane, it should be noted that sklodowskite, $\text{Mg}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})_6$, is a 1:1 U(VI):silicate that is often considered the Mg^{2+} analog for uranophane. We had hypothesized that partial replacement of Ca^{2+} with Mg^{2+} would lead to the formation of a solid solution series between uranophane and sklodowskite, much like the solid solutions between boltwoodite and sodium boltwoodite reported by Vochten et al., 1997. However, the diffractograms shown in Figure 2.a indicate that the crystalline solids formed when 25% of the Ca^{2+} is replaced with Mg^{2+} are similar to uranophane, with no reflections expected for sklodowskite observed. With TEM, it is clear that needle-like crystals consistent with uranophane are present in the 25% substituted system (Figure 2.b), along with another solid that is very finely divided. SAED analysis of these two different materials indicate the diffraction pattern for the needles is consistent with uranophane, whereas the spacings of the rings observed for the polycrystalline material excludes uranophane. Unfortunately, the SAED pattern does not allow us to conclude that the material is sklodowskite. Identification of this material will require additional study.

For the case of incorporation of Sr^{2+} , Ba^{2+} , or Cd^{2+} , the polycrystalline material was found to be very important for the partitioning of the non-Ca simple divalent cations. TEM images of these materials were similar to that shown in Figure 2.b for Mg^{2+} , in that uranophane-like needles were observed along with a very finely divided, poorly ordered material. Elemental analysis of these different materials by EDAX demonstrated that the non-Ca simple divalent cations were partitioned preferentially into the polycrystalline material, which is also a U(VI):silicate (data not shown) although small quantities of the non-Ca simple divalent cations could be detected in the uranophane needles. Although we were not able to identify the polycrystalline phase, it is clearly important for controlling the dissolved concentration of the non-Ca simple divalent cations. We do not plan to continue this work in the future, since it is not the focus of this research.

From the experiments defined above, we gained the experience needed to proceed to working with radioactive materials. Therefore, we initiated study of the partitioning of f-elements into U(VI):silicate phases using Eu^{3+} and NpO_2^+ . Figure 3 shows the results obtained when Eu^{3+} is included in the synthesis of uranophane. At low mole fractions of Eu^{3+} ($\leq 10\%$; Figure 3.a), Eu^{3+} appears to be accommodated into the uranophane structure, with little evidence for additional polycrystalline phases. When greater quantities of the Ca^{2+} are replaced with Eu^{3+} , the polycrystalline material is observed in addition to uranophane needles. Eu^{3+} is found in both materials with most of it occurring in the polycrystalline U(VI):silicate.

For experiments involving the incorporation of NpO_2^+ , much smaller quantities of Np were used in the synthesis. Also, we expected that Np would replace U in the structure, so Np:U

mole ratios of 0.02, 0.01, and 0.005 were used. In all cases, the NpO_2^+ was removed from solution and associated with the solid phase. Bulk x-ray diffraction indicated that the material produced was uranophane (Figure 4.a), and EDAX analysis of the solid indicates that the Np is uniformly distributed throughout the solid. No separate polycrystalline phases were observed. For this work, we completed EELS on various crystallites, and found that Np was associated with the solid and was present as NpO_2^+ (Figure 4.b). This data has been submitted for publication in *Radiochimica Acta*, and a copy of that manuscript is included in the Appendix for this proposal.

II. Radiation effects in substituted uranophane materials

Here, we have been studying the effect of ionizing radiation on synthetic α -uranophane, and the non- Ca^{2+} analogues of α -uranophane synthesized and described in the previous section. Using the materials prepared above for the incorporation studies, the solids were subjected to varying doses of electron irradiations. Irradiations are designed to mimic alpha-recoil effects. Selected area electron diffraction (SAED) and high-resolution TEM (HRTEM) were used to study loss of crystallinity in the solids with increasing irradiation. To date, most of our work has involved α -uranophane, the Mg^{2+} analog of α -uranophane (e.g., sklowdowskite), and the Sr^{2+} and Eu^{3+} analogs of α -uranophane. For the analog materials in these studies, all of the Ca^{2+} was replaced with the non- Ca^{2+} cation.

Radiation effects for our synthetic uranophane are shown in Figure 5, A and B. In this case, an electron fluence of $6.3 \times 10^{19} \text{ e}^- \text{cm}^{-2}$ was needed to amorphize the α -uranophane. We observed an increase in amorphization dose with increasing atomic mass for the non- Ca^{2+} cations (Figure 6). This means that when cations of higher mass are used to replace Ca^{2+} , higher doses of electron irradiation are required to achieve equivalent amounts of amorphization. Temperature is also an important parameter, with the temperature dependence of amorphization dose for α -uranophane indicating two stages: one occurring at temperatures $\leq 413 \text{ K}$ and the other occurring at temperatures above 413 K . Interestingly, the loss of structural periodicity was not simply proportional to dose. Similar to electron-irradiated zeolites, the crystalline-to-amorphous transition required lower doses as the amorphous regions became larger. These results also suggest that water and OH⁻ may accelerate the formation of point defects in the solid during irradiation.

More recently, this work has been repeated using natural U(VI) mineral samples. It appears that the alpha recoil events induce localized reduction of the U(VI) to U(IV) dioxide, which can oxidize back to U(VI) with time. During this cycle, any non-U cations that were present in the natural mineral sample are excluded from the U(VI) solid phase. This continuous zone refinement in the presence of ionizing radiation tends to prevent incorporation of the non-U cations into the U(VI) solid phases.

III. Summary of accomplishments during this grant

Publications Resulting from This Grant

"Neptunium(V) Partitioning to Uranium(VI) Oxide and Peroxide Solids," M. Douglas[†], S. B. Clark, J. I. Friese[†], B. W. Arey, E. C. Buck, and B. D. Hanson, *Environmental Science & Technology* (in press).

- "Microscale characterization of U(VI) silicate solids and associated Np(V)", *Radiochimica Acta*, Matthew Douglas, Sue B. Clark, Judah I. Friese, Bruce W. Arey, Edgar C. Buck, Brady D. Hanson, Satoshi Utsunomiya and Rodney C. Ewing, 2005, 93, 265-272.
- "Cesium and Strontium Incorporation into Uranophane, $[\text{Ca}(\text{UO}_2)(\text{SiO}_3\text{OH})]_2 \cdot 5\text{H}_2\text{O}$ ", *Journal of Nuclear Science and Technology*, M. Douglas, S. Clark, S. Utsunomiya, and R. Ewing, 2002, vol. 3, 504-507.
- "An Empirical Method for Calculating Thermodynamic Parameters for U(VI) Phases: Applications to Performance Assessment Calculations", in *The Use of Thermodynamic Databases in Performance Assessment*, Nuclear Energy Agency, R. C. Ewing, F. Chen, and S. B. Clark, 2002, pp. 93-103.
- "Stability of U(VI) Solid Phases in the U(VI)-Ca²⁺-SiO₂-OH System", *Radiochimica Acta*, B. Ritherdon, C. Phelps, H. Neff, A. G. Sowder, and S. B. Clark, 2003, vol.91, 93-96.
- "The effect of ionizing radiation on uranophane", *American Mineralogist*, S. Utsunomiya, L. Wang, M. Douglas, S. Clark, R. Ewing, 2003, vol. 88, 159-166.
- "Structure-configurational entropy and its effect on the thermodynamic stability of uranyl phases: With special application for the geological disposal of nuclear waste" *Science (China, Series D)*, F. Chen and R.C. Ewing, 2003, vol. 46(1), 39-49.

Students and Post-doctoral Associates Supported with this Grant

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Figure 1 Partial replacement of Ca^{2+} by either Sr^{2+} or Cs^+ in the synthesis of uranophane. (a) Diffractograms obtained when Sr^{2+} is substituted for Ca^{2+} in varying amounts. (b) Diffractograms obtained when Cs^+ is substituted for Ca^{2+} in varying amounts.

Table 1 Ratios of U, Ca, and Sr in for the solid phases obtained with partial replacement of Ca^{2+} by Sr^{2+} . Solids were digested in nitric acid and concentrations were determined by ICP-AES analysis.

Mole % Substitution For Ca^{2+}	Mole U: Mole Sr Measured	Mole Ca: Mole Sr Measured	Mole Ca: Mole Sr Ideal
3	86.1 (± 2.4)	34.8 (± 0.8)	32.3
10	33.6 (± 0.9)	13.8 (± 0.3)	9
25	9.5 (± 0.4)	2.5 (± 0.1)	3
50	5.0 (± 0.1)	0.7 (± 0.0)	1
100	1.4 (± 0.1)	NA	NA

Figure 4.a X-ray powder diffraction patterns for uranophane synthesized in the presence (top) and absence (bottom) of Np. The reference pattern for uranophane is shown at the bottom of the series.

Figure 4.b Electron energy-loss spectrum collected in second difference mode showing the presence of two different concentration levels of neptunium in two samples from the sodium boltwoodite/uranophane series. Data shown for the solid synthesized with 2 mol% Np (6300 ppm measured in the bulk) and 1 mol% Np (3000 ppm Np measured in the bulk). The two spectra have been overlaid and the peaks due to uranium overlap perfectly. The energy difference between the two the edges labeled 'Np' are clearly separated by more than 176 eV. Indeed, the separation is consistent with the Np-M₅ to Np-M₄ splitting (184 eV). If plural scattering dominated under these conditions, we would not expect to see variation in the intensity of the Np-M₅ feature.