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

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Research Objective

In an oxidizing environment, such as in the proposed repository at Yucca Mountain, rapid alteration rates are expected for spent nuclear fuel. Laboratory-scale simulations have repeatedly shown that the dominant alteration products under repository conditions will be uranyl phases. There is an inadequate database that relates to 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 fuel will be incorporated into the alteration products that form, potentially with a profound impact on the future mobility of radionuclides in the repository. Our objective is to characterize the incorporation of radionuclides into alteration products by synthesis of uranyl phases doped with radionuclides, appropriate surrogate elements, or non-radioactive isotopes, followed by detailed phase characterization by diffraction and spectroscopic techniques. 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 after 8 months of a 3-year project. Our objective of investigating radionuclide incorporation in uranyl phases has required the development of synthesis techniques for various uranyl phases that are expected to form under repository conditions. We have synthesized and determined the structures of several uranyl phases that are new to science and that may be important alteration products under repository conditions. We have also undertaken the determination and refinement of the crystal structures of various uranyl phases that are likely to form under repository conditions. Other experiments include the investigation of the ion-exchange properties of uranyl phases under repository conditions.

Development of synthesis techniques

A major thrust of our research to date has been the development of synthesis techniques, with emphasis on obtaining crystals of sufficient size for complete characterization, including crystal structure determinations. Three basic synthesis techniques are being developed: (1) hydrothermal synthesis in Teflon-lined reaction vessels, (2) crystal nucleation and growth by diffusion in Si gels at room temperature, and (3) batch crystallization at room temperature. Efforts to date have provided the uranyl phases dehydrated schoepite $\text{UO}_3(\text{H}_2\text{O})_{0.8-1.0}$, uranophane $\text{Ca}[(\text{UO}_2)(\text{SiO}_3\text{OH})]_2(\text{H}_2\text{O})^5$, boltwoodite $(\text{K},\text{Na})[(\text{UO}_2)(\text{SiO}_3\text{OH})](\text{H}_2\text{O})_{1.5}$, becquerelite $\text{Ca}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_8$, ianthinite $[\text{U}_4+(\text{UO}_2)_4\text{O}_6(\text{OH})^4(\text{H}_2\text{O})^4](\text{H}_2\text{O})^5$, and compreignacite $\text{K}_2[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})^7$, all of which are expected to form under repository conditions. Our experiments have shown that the crystallinity of the products is dependent upon pH, temperature, degree of saturation, and time. We have made significant progress in identifying the optimal conditions for the synthesis of each phase of interest. Our efforts to synthesize the Sr analogues of uranophane and becquerelite, and the Cs analogues of boltwoodite and compreignacite have provided a variety of uranyl phases, although crystals of a size

suitable for structure characterization have not yet been obtained. Characterization of the run products is continuing using X-ray powder diffraction.

We have attempted to synthesize a Cs-Ba-Mo phase that has been found as a corrosion product on spent nuclear fuel in laboratory tests. This phase has proven to be difficult to synthesize, but recently we have obtained a Cs-Ba-Mo uranate phase that may be the same as the phase found on the spent fuel. Characterization of this phase is continuing.

Synthesis and structures of new uranyl phases

Our synthesis efforts have resulted in several uranyl phases that are new to science. These include the Sr analogue of the Pb uranyl oxide hydrate mineral curite, a Cs uranyl oxide hydrate, and a new polymorph of uranophane composition. Each of these phases are possible alteration products under repository conditions. We obtained excellent crystals of each of these phases, and have determined and refined the crystal structures of each, providing considerable new insight into the crystal-chemistry of uranyl phases in general, and especially those that contain Cs and Sr.

Determination of the structures of compreignacite and boltwoodite

Compreignacite has been identified as an alteration product in experiments on spent fuel. We have determined the crystal structure of compreignacite using natural crystals. This structure, which was previously unknown, contains sheets of uranyl polyhedra with K and H₂O in interlayer positions. Knowledge of the structure facilitates the prediction of radionuclide incorporation mechanisms in this phase. We have also determined the structure of a crystal of boltwoodite with Na-K solid-solution, and demonstrated the compatibility of the structure for radionuclide incorporation.

Discovery of ion-exchange properties of uranyl minerals

We have demonstrated for the first time ion exchange in single crystals of a uranyl mineral by replacing K⁺ and Na⁺ with Cs⁺ in the interlayer sites of boltwoodite, a common alteration product of spent fuel under laboratory conditions. These experiments were done with single crystals of natural boltwoodite, and ion exchange was demonstrated by crystal-structure determination. The ease of Cs exchange into boltwoodite has implications for the mobility of Cs in a repository containing spent nuclear fuel. Boltwoodite will likely form in close proximity to corroded spent oxide fuel, and is likely to be abundant. If Cs is in the water from which boltwoodite crystals nucleate and grow, boltwoodite will incorporate Cs directly into its structure, thereby inhibiting the release of radioactive Cs from the repository. In addition, contact of Cs-rich solutions with pre-existing boltwoodite may result in Cs exchange into the boltwoodite crystals, also reducing Cs mobility. However, subsequent interaction of Cs-poor solutions that contain other alkali metals with Cs-containing boltwoodite could liberate Cs by ion exchange and increase its mobility. Our work has also shown that it is likely that additional radionuclides can be exchanged into uranyl minerals, and this has important implications for the long-term evolution of a geological repository containing spent nuclear fuel.

Planned Activities

Synthesis of uranyl phases doped with radionuclides

During the next several months we plan to continue the development of optimal techniques for the synthesis of uranyl phases that are likely to form under repository conditions. During the second year of the project, and following complete characterization of these phases, we will investigate the incorporation of radionuclides into their structures by synthesizing radionuclide-doped phases. One phase that we consider to be a high-priority is dehydrated schoepite because it incorporates minor amounts of Np into its structure based upon corrosion experiments conducted on spent fuel. We will attempt to synthesize Np-doped dehydrated schoepite, and demonstrate this by XAS.

Ion exchange in uranyl phases

Our discovery of the ion-exchange properties of boltwoodite implies that ion exchange may be possible in many of the alteration phases that will form under repository conditions. We are continuing our investigations of ion exchange in several uranyl phases expected to form under repository conditions, with early emphasis on Cs, and with later work to include actinide elements. This will permit us to delineate the phases for which ion exchange is potentially important, and will aid in assessing the significance of ion exchange for estimating radionuclide mobility under repository conditions.

Other Access To Information

- Burns, P.C. (sub.): The crystal structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3] \cdot 2(H_2O)$. Canadian Mineralogist.
- Burns, P.C. (sub.): Implications of solid-solution in the structure of boltwoodite. Canadian Mineralogist.
- Burns, P.C. & Hill, F.C. (sub.): Implications of the synthesis and structure of the Sr analogue of curite. Canadian Mineralogist.
- Hill, F.C. & Burns, P.C. (sub.): Investigations of the crystal chemistry of uranyl oxide hydrates. IMA, Toronto (1998) (abst.).
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- Kim, C.W. & Wronkiewicz, D.J. (1998): Alteration phases of spent nuclear fuel. Missouri Academy of Sciences, 1998 Annual Meeting (abst.).