Project ID: **59960**

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

Lead Principal Investigator:

Dr. Peter C. Burns
Associate Professor
Department of Civil Engineering and Geological Sciences
University of Notre Dame
156 Fitzpatrick
Notre Dame, Indiana 46556
Telephone: 219-631-7380
e-mail: Peter.Burns.50@nd.edu

Co Principal Investigators:

Dr. Robert J. Finch
Chemical Technologies Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne Illinois 60439 -4837
Telephone: 630-252-9829
e-mail: Finch@cmt.anl.gov

David J. Wronkiewicz
Assistant Professor
University of Missouri-Rolla
Rolla Missouri 65409

DIRECT INVESTIGATIONS OF THE IMMOBILIZATION OF RADIONUCLIDES IN THE ALTERATION PHASES OF SPENT NUCLEAR FUEL

June 15, 1999

Principal Investigators:

Peter C. Burns (Lead PI), Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick, University of Notre Dame, Notre Dame, IN 46556

Robert J. Finch, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, Illinois 60439.

David J. Wronkiewicz, Department of Geology and Geophysics, University of Missouri-Rolla, Rolla, MO 65409.

Post-Doctoral Workers:

Frances C. Hill, University of Notre Dame.

Christopher L. Cahill, University of Notre Dame.

Graduate Students:

Cheol-Woon Kim, University of Missouri-Rolla.

Jennifer Jackson, University of Notre Dame.

Sarah Scott, University of Notre Dame.

RESEARCH OBJECTIVE

In an oxidizing environment, such as the proposed repository at Yucca Mountain (YM), rapid alteration rates are expected for spent nuclear fuel. Laboratory-scale simulations demonstrate that the dominant alteration products under YM repository conditions will be uranyl phases. There is an inadequate database to relate the effects of alteration products to the release of radionuclides, although this information is essential for providing realistic radionuclide-release estimates. It is likely that many radionuclides contained in spent fuel will be incorporated into alteration products with a potentially profound impact on the future mobility of radionuclides in the repository. Our objective is to characterize the incorporation of radionuclides into U(VI) alteration products by synthesizing uranyl phases doped with radionuclides, appropriate surrogate elements, or non-radioactive isotopes, followed by detailed phase characterization by diffraction and spectroscopic techniques. This research will permit a more realistic estimate of the release rates of radionuclides from the repository's near-field environment.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work after 20 months of a 36-month project. Our work involves several components: (1) structural characterization of the U phases that form due to the alteration of spent nuclear fuel, (2) theoretical predictions of incorporation mechanisms of radionuclides into U phases, (3) synthesis of radionuclide-bearing U phases to substantiate theoretical predictions, (4) investigations of ion exchange of radionuclides with U phases. These components, taken together, provide an enhanced understanding of the impact of U phases on the release of radionuclides during the corrosion of spent nuclear fuel.

1. Structural characterization of U phases

The structures of several of the phases observed during laboratory corrosion of spent nuclear fuel needed to be characterized. We have used a Bruker CCD-based detector mounted on a three-circle goniometer with which to study the structures of U phases. This system facilitates these studies because of

its improved sensitivity to weak reflections, as compared to conventional x-ray diffraction systems, permitting the examination of very small or poorly diffracting crystals.

As part of this project, crystal structure determinations have been done for boltwoodite (Burns 1998a), haiweeite (Burns 1999a), weeksite (in prep.), compreignacite (Burns 1998b), billietite (in prep.), parsonsite (Burns 1999b), and wyartite (Burns and Finch 1999). Of these, boltwoodite, haiweeite and weeksite are U silicates. The structure of boltwoodite contains the alpha-uranophane type sheet, with K and Na in the interlayer. The structure is compatible with a range of cation occupancies within the interlayer, an observation that has implications for the incorporation of radiogenic Cs (^{135}Cs & ^{137}Cs). Haiweeite contains unusually complex uranyl silicate sheets that are connected through interlayer cations. Weeksite contains the same structural sheets as haiweeite, but the sheets are bonded directly to each other, forming a framework structure. Low valence cations and water molecules are located in channels within the framework. Determination of the structure of compreignacite, a K uranyl oxide hydrate that has been observed in spent fuel corrosion studies, demonstrates that it contains a sheet similar to the structure of becquerelite. Refinement of the earlier-determined structure of billietite, a Ba uranyl oxide hydrate, has revealed the positions of the water molecules in the interlayer. The solution of the structure of parsonsite, a Pb uranyl phosphate, has revealed a new type of the uranyl phosphate chain. Finally, our determination of the structure of the mixed-valence U Ca carbonate wyartite demonstrates that it is the first mineral to contain pentavalent U. These structural studies, which help form a basis for our knowledge of uranyl-phase systematics, have significantly expanded our current understanding of radionuclide incorporation into these phases.

2. Theoretical predictions of incorporation mechanisms of radionuclides into U phases

Our increased understanding of the crystal chemistry of U phases is being applied to further predict radionuclide incorporation into uranyl phases. Our efforts have focused on ^{79}Se (Chen et al. 1999a) and ^{99}Tc (Chen et al. 1999b), both of which have very long half-lives and are potentially mobile under YM repository conditions. We predict that several U phases may incorporate substantial ^{79}Se . However, it appears unlikely that ^{99}Tc will be immobilized to a significant degree by U phases that formed during corrosion of spent nuclear fuel. Experiments to test these hypotheses are now underway.

3. Synthesis of radionuclide-bearing U phases

A major thrust of our research to date has been the development of techniques for the synthesis of uranyl phases, with emphasis on obtaining crystals of sufficient size for complete characterization, including crystal structure determinations. Hydrothermal synthesis techniques usually result in fine-grained material, although the crystallinity of the products is dependent upon pH, temperature, degree of saturation, and crystallization time. In most cases, crystals with sizes suitable for structural analyses cannot be obtained by these methods. This requires the development of a new technique for the growth of larger crystals. We are developing a novel technique that utilizes an intermediate glass phase for the synthesis of crystals by hydrothermal alteration. Preliminary studies have shown that this technique results in crystals with maximum dimensions of 100 micrometers.

A series of precipitation tests were conducted at 90°C to determine the potential incorporation of Ce^{4+} and Nd^{3+} (surrogates for Pu^{4+} and Am^{3+} , respectively) into uranyl phases. An analysis of the leachant, leachate, and solid phase reaction products (after dissolution in a nitric acid solution) was performed by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). A Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Spectrometer (EDS) and an Analytical Electron Microscope (AEM) with an Energy Electron Loss Spectrometer (EELS) were used to characterize the morphology, composition, and structure of the solid phases.

Dehydrated schoepite ($\text{UO}_3 \cdot 0.8\text{--}1.0\text{H}_2\text{O}$) was produced by dissolving uranyl acetate into a solution containing either 2.10 ppm cerium or 286 ppm neodymium. The particles of dehydrated schoepite possessing the characteristic boat-shape were observed during TEM examination. With x-ray energy dispersive spectroscopy it was not possible to see any element other than uranium. Electron energy-loss spectroscopy (EELS) was performed on particles that were sufficiently thin. However, the Ce

concentration in subsequently formed dehydrated schoepite was below the detection limit of the AEM/EELS technique. ICP-MS results indicate a concentration that decreased from 26, to 20, and finally 11 ppm for crystals produced in 7, 35, and 190 day tests, respectively. This pattern suggests a lowering of the potential for Ce substitution in dehydrated schoepite as the crystals progressively become coarser over time. ICP-MS results indicate an overall composition of 1240 ppm Nd in the seven-day test, and 920 ppm after 35 days. However, a heterogeneous distribution of Nd was noted during the AEM/EELS examination of these samples. This evidence suggests that a separate Nd-rich solid phase must have precipitated.

Ianthinite ($\text{U}^{4+}\text{U}^{6+}_5\text{O}_{17}\cdot 10\text{H}_2\text{O}$) was produced by dissolving uranyl acetate in a solution containing copper acetate as a reductant. The leachant solution used in these tests was doped with cerium or Nd at the same levels as the tests with dehydrated schoepite. Ianthinite is of interest with respect to potential transuranic element retention due to the presence of both U^{4+} and U^{6+} ions in its structure. The ICP-MS results indicate that about 306 ppm Ce was present in the ianthinite after seven days, while Nd contents were much higher, being approximately 24,800 ppm. Solid phase examinations using SEM/EDS indicate a uniform distribution of Nd while Ce contents were too low to be detected. The relatively large thickness of the particles may have impacted the AEM-EELS technique; therefore we will try to produce thinner samples in the future to see whether we can characterize the Ce distribution.

Becquerelite ($\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6]\cdot 8\text{H}_2\text{O}$) was produced by dissolving uranyl acetate in a solution containing Ca. The leachant solutions in these tests were doped with either 4.6 ppm Ce or 277 ppm Nd. The Ce concentration in the solid phase from the 190-day test was 103 ppm, whereas Nd contents were 1310 ppm after seven days and 680 ppm after 35 days. Both the Ce and Nd contents in the solid were below the limits of detection using SEM/EDS. The more sensitive AEM-EELS technique will also be used to examine for becquerelite phase heterogeneities in the future.

Synthesis of Cs and Sr bearing U phases has demonstrated that ^{137}Cs , ^{135}Cs , and ^{90}Sr may be incorporated into alteration products of corroded spent fuel. Our synthesis of a new Cs uranyl oxide hydrate, and determination of its crystal structure, showed that it contains the compregnacite-type sheet (Hill and Burns 1998), suggesting that substantial Cs may be incorporated into the structure of compregnacite, a phase that is expected to form under repository conditions. Sr-substituted boltwoodite has been synthesized, as confirmed by a crystal structure determination (in prep.). Sr substitutes for K in the interlayer of the structure, with two K cations being replaced by one Sr cation. Synthesis of the Sr analogue of curite, a Pb uranyl oxide hydrate, again demonstrates that Sr may be incorporated into the structures of uranyl oxide hydrate phases (Burns and Hill 1998). Synthesis of a new K uranyl oxide hydrate, followed by structure determination, has revealed a novel uranyl oxide hydrate sheet that demonstrates additional complexity in uranyl sheet anion topologies (Burns and Hill 1999).

4. Ion exchange of radionuclides with U phases

Boltwoodite, a K-Na uranyl silicate, is expected to be an abundant alteration product of spent nuclear fuel under YM repository conditions. Attempts to synthesize the Cs analogue of boltwoodite, thereby demonstrating the potential for incorporation of Cs into the structure, failed to result in crystals of a size suitable for detailed structural analysis. Using natural boltwoodite crystals, we demonstrated that Cs ions exchange with Na and K in the interlayer of the boltwoodite structure very rapidly at 90 degrees Celsius when crystals are contacted by Cs-bearing solutions. Full structure determinations of ion-exchanged crystals clearly demonstrate that Cs entered stable structural sites in the interlayer of boltwoodite (Burns 1999c). This is a significant demonstration that boltwoodite can incorporate substantial Cs under YM repository conditions, thereby reducing Cs mobility.

Other work

In collaboration with Rudolph Olson of Argonne National Laboratory, we solved the crystal structure of a novel uranyl silicate formed during the corrosion of an actinide-bearing waste glass (Burns et al. 1999). The structure contains sheets of eight- and four-membered silicate tetrahedral rings, linked together by uranyl square bipyramids. Channels within the uranyl silicate framework are occupied by low-

valence cations including K and Na, as well as water molecules. We expect this phase to form under YM repository conditions.

PLANNED ACTIVITIES

Owing to the significance of ^{79}Se and ^{99}Tc for the disposal of spent nuclear fuel (Chen et al. 1999a,b), synthesis experiments are planned to test theoretical predictions of incorporation mechanisms for these radionuclides into U phases. Re will be used as a surrogate for Tc in these experiments.

The potential for uranyl phases to ion exchange with solutions under repository conditions was demonstrated by Burns (1999c). A series of experiments will be conducted to further investigate the possibility of ion exchange of Cs and Sr into various uranyl phases. This work is significant because solutions bearing radionuclides released from spent fuel are likely to contact earlier-formed uranyl phases.

Incorporation of Np into uranyl phases may have a substantial impact on the mobility of ^{137}Np within the repository. Initial attempts to synthesize Np-doped dehydrated schoepite (DS) are underway and will be continued. X-ray diffraction analyses demonstrate that fine-grained, Np-doped DS synthesized at 90°C is isostructural with pure DS formed under identical conditions; no difference in unit-cell parameters is evident. Syntheses of Np-doped Na-boltwoodite, $\text{Na}(\text{UO}_2)(\text{SiO}_3\text{OH})(\text{H}_2\text{O})_{1.5}$, has been undertaken and these experiments will continue. Experiments are underway that expose uranyl oxy-hydroxides and uranyl silicates to simulated groundwaters that are saturated with U and have low concentrations of dissolved Np. The uranium(VI) solids from these experiments will be examined by transmission electron microscopy to discern whether Np and U precipitate together on existing uranyl oxy-hydroxides and uranyl silicates.

INFORMATION ACCESS

Archival Journal Publications concerning this project

- Burns, P.C. (1998a): The structure of boltwoodite and implications of solid-solution towards sodium boltwoodite. *Canadian Mineralogist* 36, 1069-1075.
- Burns, P.C. (1998b): The structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$. *Canadian Mineralogist* 36, 1061-1067.
- Burns, P.C. & Hill, F.C. (1998): Implications of the synthesis and structure of the Sr analogue of curite. *Canadian Mineralogist* (accepted).
- Burns, P.C. (1999a): A new uranyl silicate sheet in the structure of haiweeite and comparison to other uranyl silicates. *Canadian Mineralogist* (submitted).
- Burns, P.C. (1999b): A new uranyl phosphate chain in the structure of parsonsite. *American Mineralogist* (submitted).
- Burns, P.C. (1999c): Cs boltwoodite obtained by ion exchange from single crystals: Implications for radionuclide release in a nuclear repository. *Journal of Nuclear Materials* 265, 218-223.
- Burns, P.C. (1999d): The crystal chemistry of uranium. *Mineralogical Society of America Reviews in Mineralogy* (accepted).
- Burns, P.C., Olson, R.A., Finch, R.J., Hanchar, J.M. and Thibault, Y. (1999): $KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$, a new compound formed during vapor hydration of an actinide-bearing borosilicate waste glass. *Journal of Nuclear Material* (submitted).
- Burns, P.C. & Finch, R.J. (1999): Wyartite: crystallographic evidence for the first pentavalent-uranium mineral. *American Mineralogist* (in press).
- Burns, P.C. & Hill, F.C. (1999): A new uranyl sheet in $K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$: Implications for understanding sheet anion-topologies. *Canadian Mineralogist* (submitted).
- Chen, Fanrong, Burns, P.C. & Ewing, R.C. (1999a): ^{79}Se : Geochemical and crystallo-chemical retardation mechanisms. *Journal of Nuclear Materials* (in press).
- Chen, Fanrong, Burns, P.C. & Ewing, R.C. (1999b): Near-field behavior of ^{99}Tc during the oxidative alteration of spent nuclear fuel. *Journal of Nuclear Materials* (submitted).
- Hill, F.C. & Burns, P.C. (1999): Structure of a synthetic Cs uranyl oxide hydrate and its relationship to compreignacite. *Canadian Mineralogist* (accepted).
- Finch, R.J. & Murakami, T. (1999): Systematic mineralogy and paragenesis of uranium minerals. *Mineralogical Society of America Reviews in Mineralogy* (submitted).
- Wronkiewicz, D. & Buck, E. (1999): Uranium mineralogy and the geologic disposal of spent fuel. *Mineralogical Society of America Reviews in Mineralogy* (submitted).

Refereed Conference Abstracts and Symposium Proceedings concerning this project

- Chen, F., Burns, P.C., & Ewing, R.C. (1998): ^{79}Se : Geochemical and crystallo-chemical retardation mechanisms. *The Scientific Basis for Nuclear Waste Management XX*. MRS Proceedings (in press).
- Burns, P.C. & Finch, R.J. (1999): The structure of wyartite: Crystallographic evidence for the first pentavalent-uranium mineral. *GAC-MAC* (Sudbury).
- Hill, F.C. & Burns, P.C. (1999): The importance of uranyl silicates for the disposal of nuclear waste. *GAC-MAC* (Sudbury).
- Burns, P.C. (1998): Topological aspects of uranyl mineral structures. *IMA* (Toronto).
- Burns, P.C., Finch, R.C. & Wronkiewicz, D.J. (1998): Direct investigations of the immobilization of radionuclides in the alteration products of spent nuclear fuel. *EMSP Workshop* (Chicago).
- Hill, F.C. & Burns, P.C. (1998): Investigations of the crystal chemistry of uranyl oxide hydrates. *IMA* (Toronto).
- Hill, F.C. & Burns, P.C. (1998): Chemical and structural diversity in the uranyl oxide hydrate system. *GSA* (Toronto).
- Kim, C.W. & Wronkiewicz, D.J. (1998): Alteration phases of spent nuclear fuel. Missouri Academy of Sciences, 1998 Annual Meeting (abst.).