

Project Number: 59960

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

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RESEARCH OBJECTIVE

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 after 33 months of a 36-month project. Our work involves several components: (1) structural characterization of the uranyl phases expected to form due to the alteration of spent nuclear fuel, (2) theoretical predictions of incorporation mechanisms of radionuclides into uranyl phases, (3) synthesis of radionuclide-bearing uranyl phases to substantiate theoretical predictions, (4) investigations of ion exchange of radionuclides with uranyl phases. These components, taken together, provide an enhanced understanding of the impact of uranyl phases on the release of radionuclides during the corrosion of spent fuel in a geological repository.

Structural Characterization of Uranyl Phases: Prediction of incorporation mechanisms of radionuclides into uranyl phases that form due to alteration of spent fuel requires a detailed knowledge of the crystal structures of the uranyl phases. At the outset of this project, the structures and chemical details of many of the uranyl phases relevant to repository performance were either unknown or only poorly characterized. We have determined and refined the structures of 19 uranyl phases that are relevant to geologic disposal of spent fuel. We have continued to expand the structural hierarchy for uranyl minerals, with the updated hierarchy examined in detail by Burns (1999a). The structures of the following uranyl phases have been studied successfully: compregnacite, $K_2[(UO_2)_3O_2(OH)_2](H_2O)_7$ (Burns 1998a); boltwoodite, $(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$ (Burns 1998b); weeksite, $K_2(UO_2)_2Si_6O_{15}(H_2O)_4$ (Jackson & Burns 1999); haiweeite, $Ca[(UO_2)_2Si_5O_{12}(OH)_2](H_2O)_3$ (Burns 2000a); synthetic $KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$ (Burns *et al.* (2000a); agrinierite, $K_2(Ca,Sr)[(UO_2)_3O_3(OH)_2] \cdot 2.4H_2O$ (Cahill & Burns 2000); umohoite, $[(UO_2)MoO_4(H_2O)](H_2O)$ (Krivovichev & Burns 2000a); iriginite, $[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$ (Krivovichev & Burns 2000b); wyartite, $CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$ (Burns & Finch 1999); bijvoetite, $[(Y, REE)_8^{3+}(UO_2)_{16}(CO_3)_{16}O_8(OH)_8(H_2O)_{25}](H_2O)_{14}$ (Li & Burns 2000); synthetic $Cs_3[(UO_2)_{12}O_7(OH)_{13}](H_2O)_3$ (Hill & Burns 1999); synthetic $K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$ (Burns & Hill 2000a); synthetic $Sr_{2.84}[(UO_2)_4O_4(OH)_3]_2(H_2O)_2$ (Burns & Hill 2000b), synthetic $Na_6[(UO_2)_2O(MoO_4)_4]$, $Na_6[(UO_2)(MoO_4)_4]$ and $K_6[(UO_2)_2O(MoO_4)_4]$ (Krivovichev & Burns 2000c), synthetic $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ ($M = Cs, NH_4$) (Krivovichev & Burns 2000d) and synthetic $Na_4(UO_2)(CO_3)_3$ (Li *et al.* 2000).

Theoretical Predictions of Radionuclide Incorporation Mechanisms in Uranyl Phases: Fission products such as ^{79}Se ($t^{1/2} = 1.1 \times 10^6$ yrs.) and ^{99}Tc ($t^{1/2} = 2.13 \times 10^5$ yrs.) are of considerable significance to geological disposal of spent fuel owing to their long half lives and their potentially high mobility in natural systems. The geochemical and crystallo-chemical retardation mechanisms for ^{79}Se under conditions similar to those expected in the proposed

repository at Yucca Mountain have been examined and are reported in Chen *et al.* (1999). In brief, $(\text{SeO}_3)^{2-}$ (selenite) and $(\text{SeO}_4)^{2-}$ (selenate) are the dominant aqueous species under repository conditions. Owing to the high solubility of metal selenites and selenates, and the low adsorption of selenite and selenate aqueous species by geological materials under repository conditions, Se may be highly mobile. However, consideration of the crystal chemistry of uranyl phases that form due to the alteration of spent fuel under repository conditions indicates that the Se may be incorporated into some of these phases in small quantities, thereby significantly reducing Se mobility.

Possible incorporation mechanisms for Tc into the structures of uranyl phases have been examined, with the results given in Chen *et al.* (2000). Under the conditions of spent fuel alteration to uranyl phases, the dominant oxidation state of Tc will be 7+, with the aqueous species being $(\text{TcO}_4)^{-1}$. The bonds within this tetrahedron are very strong. As a result, the anions have most of their bonding requirements met by the bond to Tc, making it very unlikely that the $(\text{TcO}_4)^{-1}$ group shares anions with other cations of high valence in a crystal structure. As such, it seems unlikely that Tc will be incorporated into the uranyl phases that form due to the alteration of spent fuel.

Synthesis of Radionuclide-Bearing Uranyl Phases: The potential for the incorporation of Pu^{4+} and Am^{3+} into uranyl alteration phases is being evaluated using Ce^{4+} and Nd^{3+} as surrogate elements for the actinides. The crystal-chemical behavior of the lanthanides and actinides are expected to be comparable due to the similarity of their valence charges and ionic radii (e.g., Ce^{4+} 0.94 Å vs. Pu^{4+} 0.93 Å; Nd^{3+} 1.04 Å vs. Am^{3+} 1.07 Å). Crystalline phases were synthesized in these tests by saturating solutions with uranium, plus various combinations of alkali elements, alkaline earths, silicon, cerium and/or neodymium at temperatures between 90 and 185°C. An analysis of the leachant, leachate, and solid phase reaction products (after dissolution in a nitric acid solution) was performed using ICP-MS analysis. Phases were characterized using scanning electron microscopy (SEM) and Analytical Electron Microscope (AEM). Results to date (Kim *et al.* 2000) indicate the incorporation of substantial quantities of Ce^{4+} in dehydrated schoepite, $\text{UO}_3(\text{H}_2\text{O})_{0.8-1.0}$ ($K_d = 5.2$ to 12), and both Ce^{4+} and Nd^{3+} in ianthinite, $[\text{U}_2^{4+}(\text{UO}_2)_4\text{O}_6(\text{OH})_4(\text{H}_2\text{O})_4](\text{H}_2\text{O})_5$ ($\text{Ce } K_d = 146-159$, $\text{Np } K_d = 62$) and becquerelite, $\text{Ca}[(\text{UO}_2)_3\text{O}_2(\text{OH})_3]_2(\text{H}_2\text{O})_8$ ($\text{Ce } K_d = 16$, $\text{Np } K_d = 4.7$). By analogy, it is likely that Pu^{4+} and Am^{3+} behave in a similar fashion. The highest K_d values obtained for both Ce^{4+} and Nd^{3+} are for ianthinite, which is consistent with earlier predictions based upon the structure of ianthinite.

Experiments on the synthesis of a new Ba uranyl molybdate phase found on UO_2 spent fuel from unsaturated drip tests produced small crystals. They were precipitated from aqueous solutions made from the oxides, UO_3 , MoO_3 , and BaO , after two to twenty weeks of reaction at 90°C. However, crystals re-sorbed when reacted for longer times at 90°C. Transmission electron microscopic examinations of the crystals reveal that they are structurally similar to the Cs- and Ba-containing crystals formed during the corrosion of spent nuclear fuels. Subsequent syntheses at 150°C produced larger crystals, for which chemical and structural analyses are in progress. Potassium-bearing crystals have been synthesized at 150°C; chemical and structural analyses of these crystals are currently in progress.

Syntheses of Np-substituted dehydrated schoepite (DS) powders have been successful. X-ray diffraction analyses demonstrated that fine-grained DS synthesized at 90°C is isostructural with pure DS formed under identical conditions, with no difference in unit-cell parameters being apparent. Analyses of the solids by X-ray absorption spectroscopy are currently pending approval for special materials handling.

Investigations of Ion Exchange of Radionuclides with Uranyl Phases: Using single crystals of natural boltwoodite, Burns (1999b) demonstrated the exchange of Cs into the interlayer. This is the first demonstrating ion exchange in single crystals of a uranyl phase, and has significant implications for the mobility of Cs under repository conditions. Additional experiments performed using synthetic boltwoodite demonstrated ion exchange of Cs into the structure where Cs was present in solution at concentrations of ~100 ppm (Hill & Burns 1999c). We have recently obtained similar results for Cs exchange into compreignacite. These results indicate that minerals such as boltwoodite are likely to incorporate ^{135}Cs into their structures as they grow under repository conditions. Such phases are also likely to exchange ions with solutions that contact them after they grow, and may either sequester Cs or release it, depending upon the relative concentrations of different ions in the solution.

PLANNED ACTIVITIES

During the final months of the project, we will continue to research the structures of uranyl phases relevant to repository performance, in some cases utilizing synchrotron radiation in an attempt to solve structures that have been intractable using in-house X-radiation sources. Characterization of the synthesized Cs uranyl molybdate and

Np-bearing phases will be completed, with crystal-structure studies being a high priority. Studies of ion exchange in uranyl phases will also continue, with the focus broadened to several uranyl phases that possess sheet structures.

INFORMATION ACCESS

Archival Journal Publications concerning this project

1. Burns, P.C. (1999a): The crystal chemistry of uranium. *Reviews in Mineralogy* 38, 23-90.
2. Burns, P.C. (1999b): Cs boltwoodite obtained by ion exchange from single crystals: Implications for radionuclide release in a nuclear repository. *Journal of Nuclear Materials* 265, 218-223.
3. Burns, P.C. & Finch, R.J. (1999): Wyartite: crystallographic evidence for the first pentavalent-uranium mineral. *American Mineralogist* 84, 1456-1460.
4. Burns, P.C. (1998b): The structure of boltwoodite and implications of solid-solution towards sodium boltwoodite. *Canadian Mineralogist* 36, 1069-1075.
5. Burns, P.C. (1998a): The structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$. *Canadian Mineralogist* 36, 1061-1067.
6. Chen, Fanrong, Burns, P.C. & Ewing, R.C. (1999): ^{79}Se : Geochemical and crystallo-chemical retardation mechanisms. *Journal of Nuclear Materials* 275, 81-94.
7. Finch, R.J. & Murakami, T. (1999): Systematic mineralogy and paragenesis of uranium minerals. *Reviews in Mineralogy* 38, 91-179.
8. Hill, F.C. & Burns, P.C. (1999): Structure of a synthetic Cs uranyl oxide hydrate and its relationship to compreignacite. *Canadian Mineralogist* 37, 1283-1288.
9. Wronkiewicz, D.J. & Buck, E.C. (1999): Uranium mineralogy and the geologic disposal of spent nuclear fuel. *Reviews in Mineralogy* 38, 475-498.
10. Burns, P.C., Olson, R.A., Finch, R.J., Hanchar, J.M. and Thibault, Y. (2000): $KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$, a new compound formed during vapor hydration of an actinide-bearing borosilicate waste glass. *Journal of Nuclear Materials* 278, 290-300.
11. Burns, P.C. (2000): A new uranyl phosphate chain in the structure of parsonsite. *American Mineralogist* 85, 801-805.
12. Burns, P.C. & Hill, F.C. (2000a): A new uranyl sheet in $K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$: New insights into sheet anion-topologies. *Canadian Mineralogist* 38, 163-174.
13. Burns, P.C. & Hill, F.C. (2000b): Implications of the synthesis and structure of the Sr analogue of curite. *Canadian Mineralogist* 38, 175-182.
14. Chen, Fanrong, Burns, P.C. & Ewing, R.C. (2000): Near-field behavior of ^{99}Tc during the oxidative alteration of spent nuclear fuel. *Journal of Nuclear Materials* 278, 225-232.
15. Fayek, M., Burns, P.C., Guo, Y.X. & Ewing, R.C. (2000): Micro-structures associated with uraninite alteration. *Journal of Nuclear Materials* 277, 204-210.
16. Burns, P.C. (2000a, accepted): A new uranyl silicate sheet in the structure of haiweeite and comparison to other uranyl silicates. *Canadian Mineralogist*.
17. Cahill, C.L. & Burns, P.C. (2000, in press): The structure of agrinierite: A Sr-containing uranyl oxide hydrate mineral. *American Mineralogist*.
18. Li, Y. & Burns, P.C. (2000): A new rare-earth element uranyl carbonate sheet in the structure of bijvoetite-(Y). *Canadian Mineralogist* 38, 153-162.
19. Kim, C.W., Wronkiewicz, D.J. & Buck, E.C. (2000, submitted): Incorporation of radionuclides in the alteration phases of spent nuclear fuel. *Radiochimica Acta*.
20. Krivovichev, S.V. & Burns, P.C. (2000a, in press): Crystal chemistry of uranyl molybdates. I. The structure and formula of umohoite. *Canadian Mineralogist*.
21. Krivovichev, S.V. & Burns, P.C. (2000b, in press): Crystal chemistry of uranyl molybdates. II. The crystal structure of iriginite. *Canadian Mineralogist*.
22. Krivovichev, S.V. & Burns, P.C. (2000c, submitted): Crystal chemistry of uranyl molybdates. III. New structural themes in $Na_6[(UO_2)_2O(MoO_4)_4]$, $Na_6[(UO_2)(MoO_4)_4]$ and $K_6[(UO_2)_2O(MoO_4)_4]$. *Canadian Mineralogist*.
23. Li, Y., Krivovichev, S.V. & Burns, P.C. (2000): The crystal structure of $Na_4(UO_2)(CO_3)_3$ and its relationship to schröckingerite. *Mineralogical Magazine* (submitted).
24. Krivovichev, S.V. & Burns, P.C. (2000): Crystal chemistry of uranyl molybdates. IV. The structures of $M_2[(UO_2)_6(MoO_4)_7(H_2O)_2]$ ($M = Cs, NH_4$). *Canadian Mineralogist* (submitted).

Symposium Proceedings and Conference Abstracts

1. Burns, P.C. & Finch, R.J. (1999): The structure of wyartite: Crystallographic evidence for the first pentavalent-uranium mineral. *GAC-MAC* (Sudbury).
2. Burns, P.C., Hill, F.C., Finch, R.J. & Olson, R.A. (1999): Radionuclide retardation in uranyl silicate forming in a geological repository for nuclear waste. *GSA* (Denver).
3. Burns, P.C. (1998): Topological aspects of uranyl mineral structures. *IMA* (Toronto).
4. Burns, P.C. (1999): Corrosion of Spent Nuclear Fuel in a Geological Repository and the Impact of Alteration Phases on the Release of Radionuclides. Russian Academy of Sciences - U.S. Department of Energy Joint Seminar "Science Behind Safe Geological Disposition of Radioactive Waste", October 19-21, Moscow, Russia.
5. 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).
6. Chen, F., Burns, P.C., & Ewing, R.C. (1998): ⁷⁹Se: Geochemical and crystallo-chemical retardation mechanisms. *The Scientific Basis for Nuclear Waste Management XX*. MRS Proceedings (in press).
7. Kim, C.W., Wronkiewicz, D.J., & Buck, E.C. (accepted): Potential incorporation of transuranics into uranium alteration phases", in: Scientific Basis For Nuclear Waste Management XXIII. Material Res. Soc., Symp. Proc. (D.W. Shoesmith and R.W. Smith, eds.).
8. Wronkiewicz, D.J., Bates, J.K., & Buck, E.C., (1997): Grain boundary corrosion and alteration phase formation during the oxidative dissolution of UO₂ pellets. in: Scientific Basis For Nuclear Waste Management XX. Material Res. Soc., Symp. Proc. (W.J. Gray & I.R. Triay eds.) Vol. 465, pp. 519-526.
9. Cahill, C.L. & Burns, P.C. (1999): The structure of agrinierite: a K-Ca-Sr uranyl oxide hydrate sheet of the α-U₃O₈ type. *GSA* (Denver).
10. Finch, R.J., & Buck, E.C. (1998): Synthesis and characterization of Ba[(UO₂)₅MoO₆(OH)₆]· nH₂O. Materials Research Society, Boston, MA, November 30 - December 4, 1998. MRS 1998 Fall Meeting Abstracts volume 25, 723 (abstract)
11. Finch, R.J., Hanchar, J.M., Hoskin, P.W.O. & Burns, P.C. (1998): Rare earth elements in synthetic zircon: the roles of P and Li. *GSA* (Toronto).
12. Hill, F.C. & Burns, P.C. (1999c): Cs ion exchange in boltwoodite. *GSA* (Denver).
13. Hill, F.C. & Burns, P.C. (1999): The importance of uranyl silicates for the disposal of nuclear waste. *GAC-MAC* (Sudbury).
14. Hill, F.C. & Burns, P.C. (1998): Investigations of the crystal chemistry of uranyl oxide hydrates. *IMA* (Toronto).
15. Hill, F.C. & Burns, P.C. (1998): Chemical and structural diversity in the uranyl oxide hydrate system. *GSA* (Toronto).
16. Jackson, J.M. & Burns, P.C. (1999): The structure of weeksite: a potassium uranyl silicate hydrate. *GSA* (Denver).
17. Kaszuba, J., Burns, P.C., Runde, W. & Janecky, D. (1999): Radionuclide Capture by Uranium Minerals. EMSP Actinide Chemistry Workshop, November 9-10, Albuquerque, NM.
18. Kim, C.W., Wronkiewicz, D.J., & Buck, E.C. (1999): Synthesis of Ce⁴⁺ and Nd³⁺-bearing ianthinite: Implications for the incorporation of Pu⁴⁺ and Am³⁺ into the alteration phases of spent nuclear fuel. Geological Society of America 1999 annual fall meeting, p. A-135.
19. Kim, C.W. & Wronkiewicz, D.J. (1999): Incorporation of radionuclides in the alteration phases of spent nuclear fuel. Migration '99, 7th International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, p. 20.
20. Kim, C.W. & Wronkiewicz, D.J. (1999): Incorporation of radionuclides in the alteration phases of spent nuclear fuel. Missouri Academy of Sciences, 1999 Spring Meeting.
21. Kim, C.W. and Wronkiewicz, D.J. (1998): Alteration phases of spent nuclear fuel. Missouri Academy of Sciences, 1998 Spring Meeting.
22. Li, Yaping & Burns, P.C. (1999): A new REE-bearing uranyl carbonate sheet in the structure of bijvoetite. *GSA* (Denver).
23. Wronkiewicz, D.J. (1999): Uranium mineralogy and the geologic disposal of spent nuclear fuel. Geological Society of America 1999 annual fall meeting, p. A-135 (1999).
24. Wronkiewicz, D.J. (1999): The role of natural analogues in evaluating the long-term corrosion behavior of nuclear waste forms. Missouri Academy of Sciences, 1999 Spring Meeting.
25. Li, Y., Krivovichev, S.V. & Burns, P.C. (2000): The structure of Na₄(UO₂)(CO₃)₃ and the environmental importance of uranyl carbonates. *AGU* (Washington).

26. Scott, S.M. & Burns, P.C. (2000): A single-crystal study of ion exchange in compreignacite. *AGU* (Washington).
27. Krivovichev, S.V. & Burns, P.C. (2000): Crystal chemistry of uranyl molybdates: review of new structures studied using CCD detector. *AGU* (Washington).