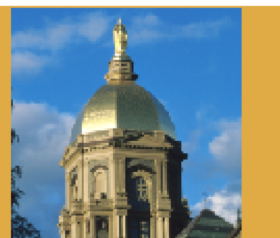
Direct Investigations of the Immobilization of Radionuclides in the Alteration Phases of Spent Nuclear Fuel



PIs: Peter C. Burns[1], Robert J. Finch[2] and David J. Wronkiewicz[3]; Post-Doctoral Researchers: Christopher L. Cahill[1] and Sergey V. Krivovichev[1]

[1]Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick, University of Notre Dame, Notre Dame, Indiana 46556 [2]Argonne National Laboratory, Chemical Technology Division, 9700 South Cass Ave., Argonne, Illinois 60439 [3]Department of Geology and Geophysics, University of Missiouri-Rolla, Rolla, Missouri 65401

Background

Laboratory simulations and studies of natural analogs have shown that spent nuclear fuel is unstable under moist oxidizing conditions, similar to the conditions in the proposed repository at Yucca Mountain. In laboratory simulations alteration rates are appreciable and uranyl (U^{6+}) compounds dominate the alteration products (Fig. 1). The alteration involves matrix dissolution of the spent fuel and thus provides a potential release path for radionuclides contained in the fuel.

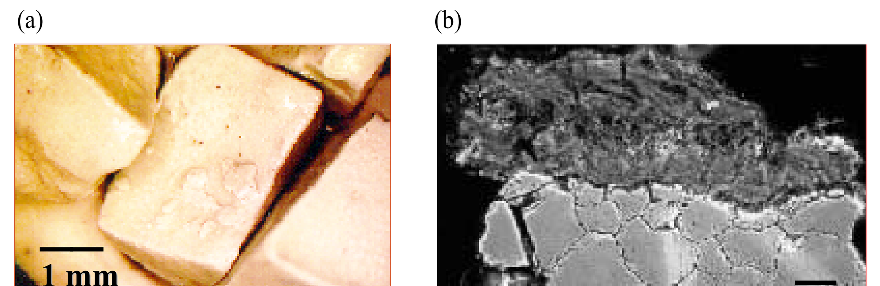


Fig. 1. LWR (UO_2) spent fuel following 4.8 years of treatment in hydrologically unsaturated high-drip-rate tests using EJ-13 water (from Finch *et al.* 1999, MRS Proceedings 556, 431-438). Note the extensive alteration of the fuel. The alteration products are dominated by uranyl compounds, including boltwoodite and uranophane. (a) reflected light, (b) SEM photomicrograph.

Many of the uranyl compounds that are expected to form in the proposed repository are already known as minerals from natural systems. Studies of natural analogs have shown that uranyl minerals persist for thousands of years. As such, these compounds will have a large impact upon repository performance. It is likely that uranyl phases forming due to the alteration of spent fuel will incorporate many of the radionuclides contained in the spent fuel directly into their crystal structures, thus having a profound impact upon the mobility of the radionuclides.

The cumulative releases of various radionuclides from UO_2 spent fuel during hydrologically unsaturated drip tests extending 4.8 years were reported by Finn *et al.* (1999, 7th Int. Conf. on the Chem. and Migration Behavior of Actinides and Fission Products in the Geosphere 7, 17) (data shown in Figure 2). Uranyl compounds form as alteration products by 40 weeks and appear to largely retained the actinide elements (Fig. 2a), whereas the release rates for some fission products are much higher (Fig. 2b).

The objective of our research is to gain a detailed understanding of the crystal chemistry of uranyl compounds, and to use such knowledge to guide experimental studies of incorporation of radionuclides into their structures under repository conditions. The research involves: (1) Structural studies of uranyl compounds, (2) Theoretical prediction of radionuclide incorporation mechanisms, (3) Experimental verification of incorporation of radionuclides, (4) Studies of ion exchange involving uranyl compounds.

Table 1. Uranyl phases found as alteration products on UO_2 and spent nuclear fuel

Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$
Becquerelite	$Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$
Billietite	$Ba[(UO_2)_3O_2(OH)_3]_2(H_2O)_4$
Soddyite	$(UO_2)_2(SiO_4)(H_2O)_2$
Na-boltwoodite	$(Na,K)[(UO_2)(SiO_3OH)](H_2O)_{1.5}$
Sklodowskite	$Mg[(UO_2)(SiO_3OH)]_2(H_2O)_6$
Uranophane	$Ca[(UO_2)(SiO_3OH)]_2(H_2O)_5$
Weeksite	$K_2(UO_2)_2Si_6O_{15}(H_2O)_4$
Dehydrated schoepite	$UO_3(H_2O)_{0.8-1.0}$
Compreignacite	$K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$
Na-compreignacite	$Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$
Haiweeite	$Ca(UO_2)_2Si_6O_{15}(H_2O)_5$

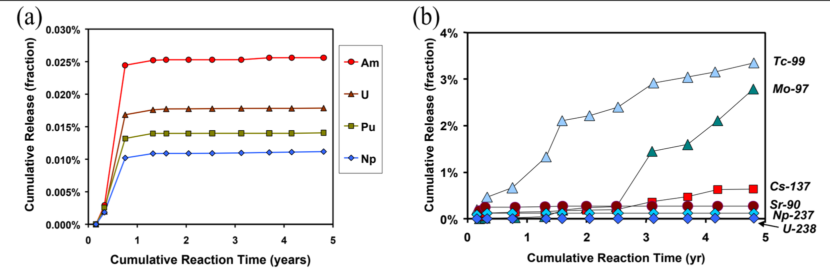


Fig. 2. Cumulative release fractions of actinides (a) and fission products (b) from UO_2 (LWR) spent fuel in hydrologically unsaturated drip tests (plotted using data from Finn *et al.* 1999)

Structures of Uranyl Phases

A major focus of our research has been studies of the structures of uranyl compounds, including minerals, that are predicted to form under repository conditions. Structures have been examined using a single-crystal diffraction system equipped with a CCD-based detector (Fig. 3). The CCD-based detector provides much enhanced sensitivity, resolution and efficiency as compared to a scintillation detector mounted on a serial diffractometer. The structures of numerous uranyl compounds relevant to geological disposal of nuclear waste have been successfully studied (Table 2).

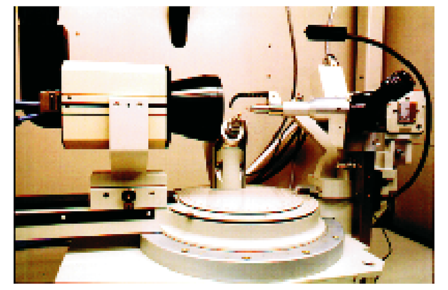


Fig. 3. Bruker SMART CCD single-crystal X-ray diffraction system.

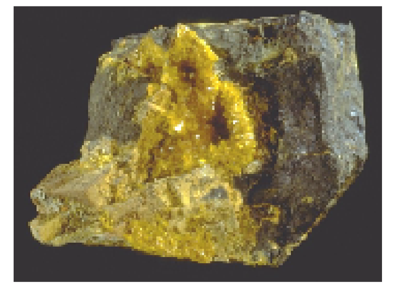


Fig. 4. Natural specimen of UO_2 (the analog of LWR spent fuel) with extensive alteration to uranyl minerals.

Table 2. Uranyl structures determined using a CCD-based detector system that are relevant to geologic disposal of spent fuel

Mineral name	Formula	Reference
Compreignacite	$K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$	Burns (1998)
Boltwoodite	$(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$	Burns (1998)
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 (2000)
	$KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$	Burns *et al.* (2000)
Agrinierite	$K_2(Ca,Sr)[(UO_2)_3O_3(OH)_2]\ 2.4H_2O$	Cahill & Burns (2000)
Umohoite	$[(UO_2)MoO_4(H_2O)](H_2O)$	Krivovichev & Burns (2000)
Iriginite	$[(UO_2)Mo_2O_7(H_2O)_2](H_2O)$	Krivovichev & Burns (2000)
Wyartite	$CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$	Burns & Finch (1999)
Bijvoetite	$[(Y, REE)^{3+}_8(UO_2)_{16}(CO_3)_{16}O_8(OH)_8(H_2O)_{25}](H_2O)_{14}$	Li & Burns (2000)
	$Cs_3[(UO_2)_{12}O_7(OH)_{13}](H_2O)_3$	Hill & Burns (1999)
	$K_5[(UO_2)_{10}O_8(OH)_9](H_2O)$	Burns & Hill (2000)
	$Sr_{2.84}[(UO_2)_4O_4(OH)_3]_2(H_2O)_2$	Burns & Hill (2000)

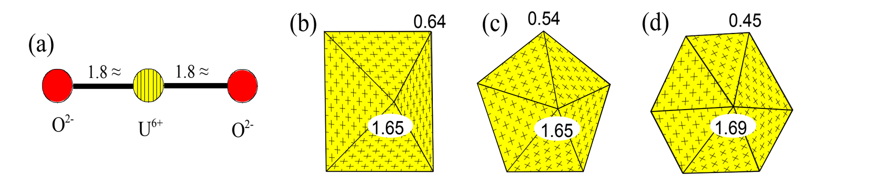


Fig. 5. Uranyl polyhedra observed in inorganic structures. (a) uranyl ion (*Ur*), (b) UrO_4 square bipyramid, (c) UrO_5 pentagonal bipyramid, (d) UrO_6 hexagonal bipyramid. Bond-valences incident upon polyhedral vertices due to the bond to the U^{6+} cation at the center of the polyhedron are given (Burns *et al.* 1997, Can. Mineral. 35, 1551-1570).

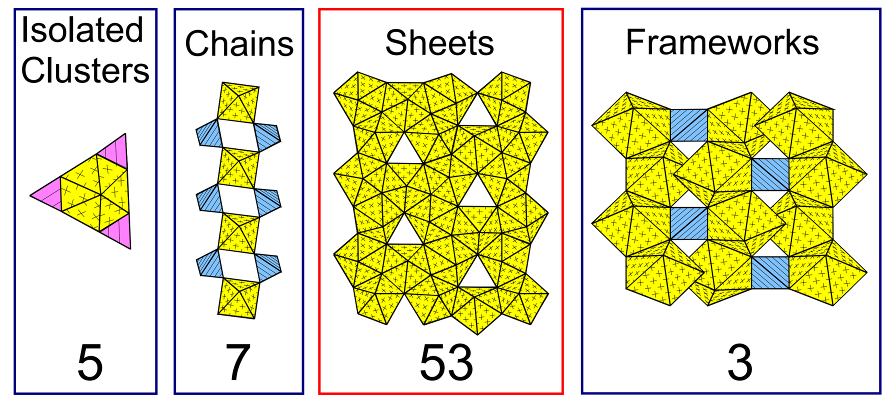
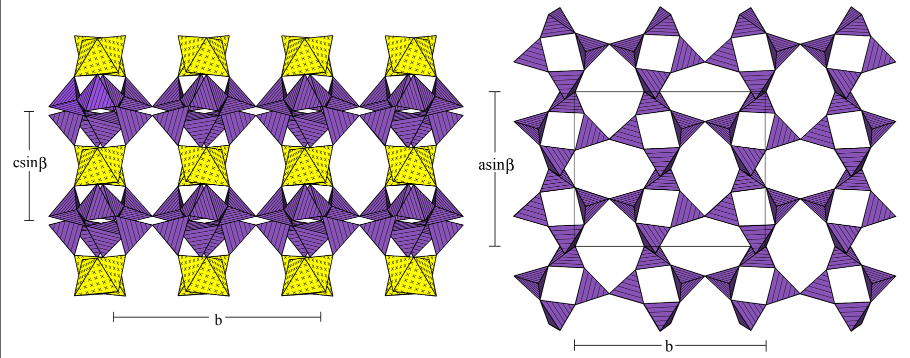


Fig. 6. Structural hierarchy of uranyl phases based upon the polymerization of the cation polyhedra of higher bond-valence (From Burns, 1999, Reviews in Mineralogy 38, 23-90). The hierarchy is dominated by structures based upon sheets of polyhedra of higher bond-valence owing to the uneven distribution of bond strengths in uranyl polyhedra (see Fig. 5).

Selected Structures of Uranyl Compounds

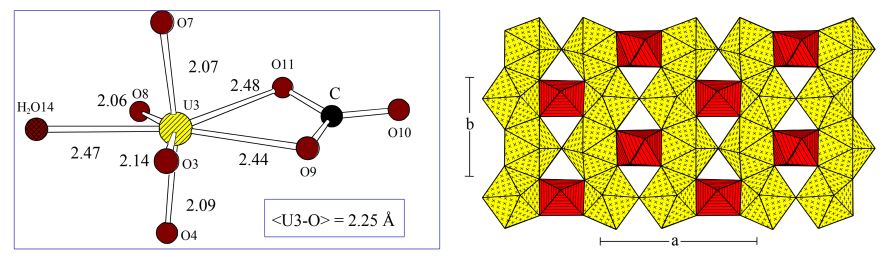
$KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$

The title phase was found growing on actinide-bearing borosilicate waste glass subjected to vapor hydration experiments at 200°C. The structure is based upon sheets of silicate tetrahedra that are cross-linked by sharing vertices with uranyl square bipyramids. There is potential for transuranic and fission product incorporation in the channels running through the structure (Burns *et al.* 2000, J. Nuclear Materials 278, 290-300).

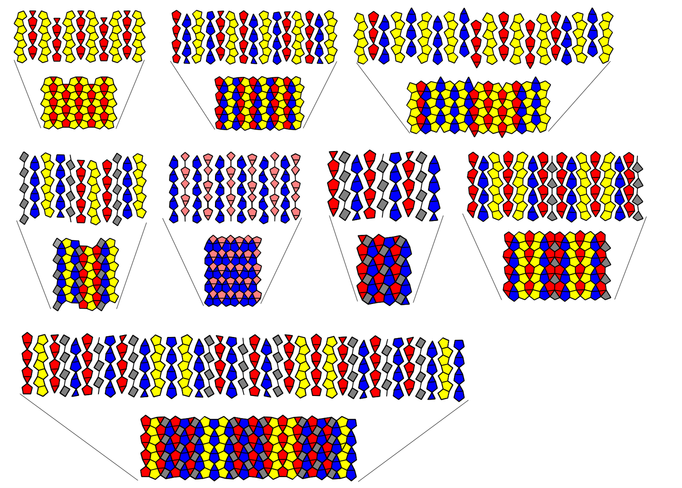


Wyartite: $CaU^{5+}(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$

Structure determination demonstrated that wyartite contains structurally essential U^{5+}, making it the first pentavalent-uranium mineral. This discovery has important implications for geochemical modeling of uranium in natural systems, as well as under conditions relevant to a geological repository.



The sheet anion-topology approach has been developed as a means to investigate the underlying relationships between different structural sheets that dominate uranyl compounds. Description of sheet anion-topologies as stacking sequences of chains of polygons reveals the modular structures of complex sheets (Burns 1999, Reviews in Mineralogy 38, 23-90). Each topology shown here corresponds to a sheet of uranyl polyhedra in a mineral or synthetic compound.



Prediction of Incorporation Mechanisms

On the basis of the structural hierarchy for uranyl compounds and knowledge of the crystal chemistry of various radionuclides, we have predicted incorporation mechanisms for various radionuclides in uranyl compounds that are likely to form under repository conditions. Results for transuranic elements are given in Burns *et al.* (1997, J. Nucl. Mater. 249, 1-9). We have also considered ^{79}Se ($t^{1/2} = 1.1 \times 10^6$ yrs.) and ^{99}Tc ($t^{1/2} = 2.13 \times 10^5$ yrs.) because of their long half lives and their potentially high mobility in natural systems. Our results for ^{79}Se are reported in Chen *et al.* (1999). 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 (Fig. 7).

Under the conditions under which spent fuel is altered to uranyl phases, the dominant oxidation state of Tc will be 7+, with the aqueous species being $(TcO_4)^{-1}$. 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 $(TcO_4)^{-1}$ 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 (Chen *et al.* 2000).

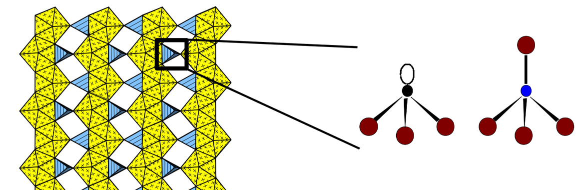


Fig. 7. Incorporation mechanism for selenite into a uranyl silicate sheet in place of a silicate tetrahedron. The lone pair of electrons on the selenite group replaces the apical (non-sheet) anion of the silicate tetrahedron.

Experimental Verification of Incorporation of Radionuclides

The potential for 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 (e.g., ionic radii: Ce^{4+} 0.94 Å vs. Pu^{4+} 0.93 Å; Nd^{3+} 1.04 Å vs. Am^{3+} 1.07 Å). Uranyl compounds 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 (Fig. 8). An analysis of the leachant, leachate, and solid phase reaction products was performed using ICP-MS analysis. Results indicate the incorporation of substantial quantities of Ce^{4+} in dehydrated schoepite (K_d = 5.2 to 12), and both Ce^{4+} and Nd^{3+} in ianthinite, (Ce K_d = 146-159, Np K_d = 62) and becquerelite (Ce K_d = 16, Np K_d = 4.7). By analogy, it is likely that Pu^{4+} and Am^{3+} behave in a similar fashion.

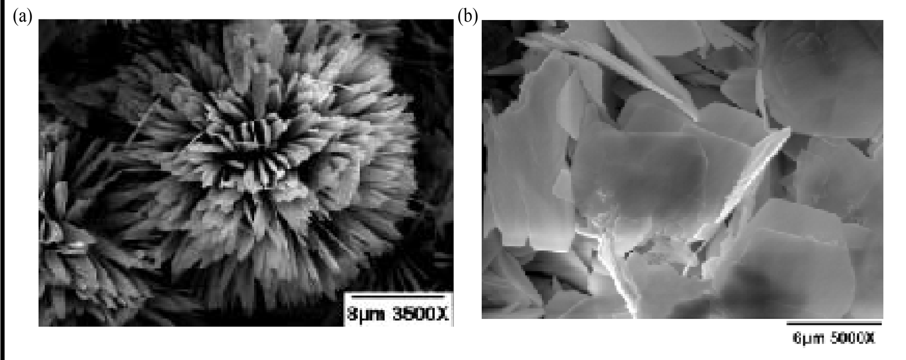


Fig. 8. SEM photomicrographs of (a) ianthinite and (b) becquerelite containing Ce and Nd as surrogate elements for actinides.

Ion Exchange

Using single crystals of boltwoodite and compreignacite, both of which have sheet structures, we have demonstrated exchange of Cs into the interlayer. This is the first demonstration of ion exchange in single crystals of a uranyl phase, and has 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. Compounds such as boltwoodite and compreignacite are likely to incorporate ^{135}Cs ($t^{1/2} = 3 \times 10^6$ yrs.) into their structures as they grow under repository conditions. They 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.

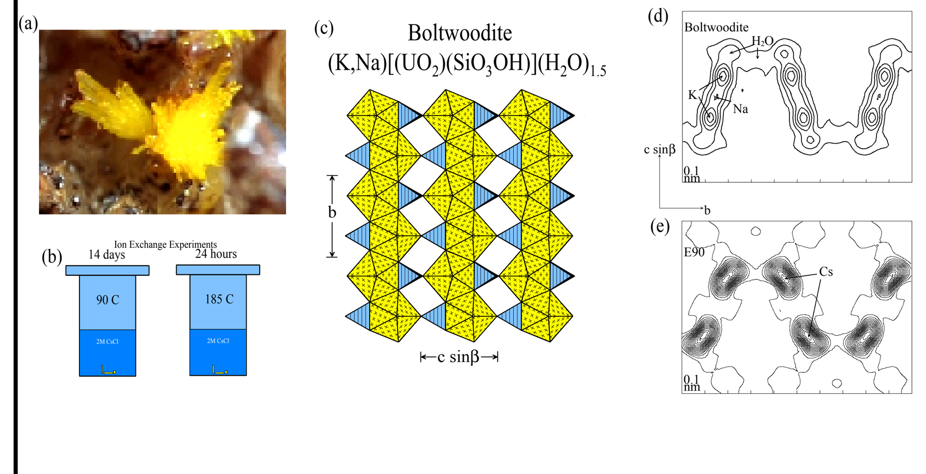


Fig. 9. Ion exchange of Cs for K and Na in boltwoodite using a 2M CsCl solution. (a) crystals of boltwoodite, (b) experiment design, (c) uranyl silicate sheet in boltwoodite, (d) electron density in the interlayer of an untreated crystal obtained from X-ray diffraction, (e) electron density in the interlayer of the crystal treated at 90°C obtained from X-ray diffraction. The contour intervals are identical in (d) and (e).

Microporous Uranyl Phases

Microporous uranyl phases are important for repository performance because they may form under repository conditions and incorporate radionuclides, and they show promise as alternative nuclear waste forms that will permit the exchange of radionuclides such as ^{137}Cs and ^{90}Sr. We have synthesized several microporous uranyl phases, including UND-1 and UND-2 (Fig. 10), both of which are uranyl molybdates.

The topology of UND-1 ($Cs_2(UO_2)_2(MoO_4)_3$) is that of an open structured material consisting of MoO_4 tetrahedral and $(UO_2)O_5$ pentagonal bipyramidal building units. These polyhedra define an anionic framework containing large channels and voids, within which reside charge balancing Cs cations. The arrangement of these building units is analogous to a previously described aluminosilicate zeolite structure type, ABW.

The formation of a zeolite topology within UND-1 suggests that an entire family of related compounds may exist with structures resembling those of the aluminosilicates. Noting the ion-exchange capabilities of many zeolite type materials, it is plausible that the formation of UND type phases will impact the release of radionuclides if formed under repository conditions. The formation of Cs-U-Mo-O phases on spent nuclear fuel has been noted previously (Buck *et al.* 1997, J. Nucl. Mater. 249, 70-76), therefore a variety of structure types may form under the range of hydrothermal conditions present under repository conditions. Experiments are in progress to synthesize these and other framework materials in the presence of Na and K (abundant elements in YM groundwater), followed by exchange of the cations for Cs and Sr.

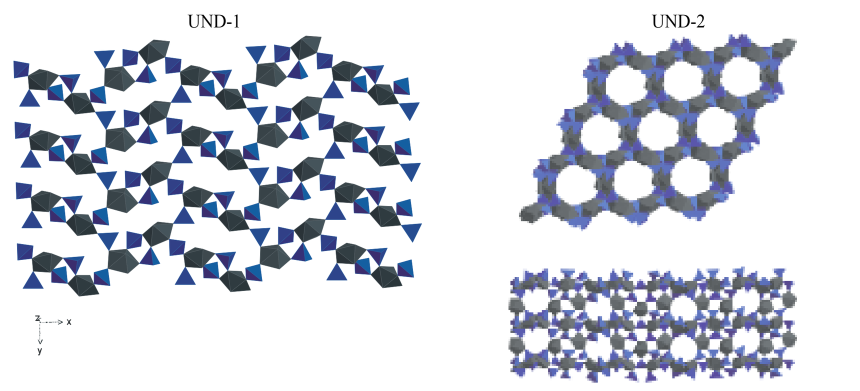


Fig. 10. Microporous uranyl molybdates with Cs (UND-1), K (UND-2) and NH_4 (UND-2) in the pores.

Information Access

Buck, E.C., Wronkiewicz, D.J., Finn, P.A., & Bates, J.K. (1997): A new uranyl oxide hydrate phase derived from spent fuel alteration. Journal of Nuclear Materials 249, 70-76 (1997).

Burns, P.C. (accepted): A new uranyl silicate sheet in the structure of haiweeite and comparison to other uranyl silicates. Canadian Mineralogist.

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.

Burns, P.C. (in press): A new uranyl phosphate chain in the structure of parsonsite. American Mineralogist.

Burns, P.C. & Hill, F.C. (2000): 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.

Burns, P.C. & Hill, F.C. (2000): Implications of the synthesis and structure of the Sr analogue of curite. Canadian Mineralogist 38, 175-182.

Burns, P.C. (1999): The crystal chemistry of uranium. In: Uranium: Mineralogy, Geochemistry and the Environment, by P.C. Burns and R.J. Finch Eds. Reviews in Mineralogy 38, 23-90 (Mineralogical Society of America, Washington, D.C.).

Burns, P.C. (1999): 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. & Finch, R.J. (1999): Wyartite: crystallographic evidence for the first pentavalent-uranium mineral. American Mineralogist 84, 1456-1460.

Burns, P.C. (1998): The structure of boltwoodite and implications of solid-solution towards sodium boltwoodite. Canadian Mineralogist 36, 1069-1075.

Burns, P.C. (1998): The structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$. Canadian Mineralogist 36, 1061-1067.

Cahill, C.L. & Burns, P.C. (in press): The structure of agrinierite: A Sr-containing uranyl oxide hydrate mineral. American Mineralogist.

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.

Chen, Fanrong, Burns, P.C. & Ewing, R.C. (1999): ^{79}Se: Geochemical and crystallo-chemical retardation mechanisms. Journal of Nuclear Materials 275, 81-94.

Chen, Fanrong, Burns, P.C., & Ewing, R.C. (1999): ^{79}Se: Geochemical and crystallo-chemical retardation mechanisms. The Scientific Basis for Nuclear Waste Management XX. MRS Proceedings 556, 1115-1122.

Finch, R.J. & Murakami, T. (1999): Systematic mineralogy and paragenesis of uranium minerals. In: Uranium: Mineralogy, Geochemistry and the Environment, by P.C. Burns and R.J. Finch Eds. Reviews in Mineralogy 38, 91-179 (Mineralogical Society of America, Washington, D.C.).

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.

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.

Kim, C.W., Wronkiewicz, D.J., & Buck, E.C. (submitted): Incorporation of radionuclides in the alteration phases of spent nuclear fuel. Radiochimica Acta.

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.).

Krivovichev, S.V. & Burns, P.C. (in press): Crystal chemistry of uranyl molybdates. I. The structure and formula of umohoite. Canadian Mineralogist 38.

Krivovichev, S.V. & Burns, P.C. (submitted): Crystal chemistry of uranyl molybdates. II. The crystal structure of iriginite. Canadian Mineralogist.

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.

Wronkiewicz, D.J. & Buck, E.C. (1999): Uranium mineralogy and the geologic disposal of spent nuclear fuel. In: Uranium: Mineralogy, Geochemistry and the Environment, by P.C. Burns and R.J. Finch Eds. Reviews in Mineralogy 38, 475-498 (Mineralogical Society of America, Washington, D.C.).

Wronkiewicz, D.J., Bates, J.K., & Buck, E.C., (1997): Grain boundary corrosion and alteration phase formation during the oxidative dissolution of UO_2 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.