Spent Nuclear Fuel

Radiolytic and Thermal Processes Relevant to Dry Storage of Spent Nuclear Fuels

Project ID: 60392

Dr. Steven C. Marschman, Pacific Northwest National Laboratory

Prof. Theodore E. Madey, Rutgers University
Dr. Peter E. Haustein, Brookhaven National Laboratory
Dr. Thomas M. Orlando, Pacific Northwest National Laboratory
Dr. James P. Cowin, Pacific Northwest National Laboratory

Research Objectives

The purpose of this program is to deliver pertinent information which can be used to make rational decisions concerning the safety and treatment issues associated with dry storage of spent nuclear fuel materials. In particular, we will establish an understanding of: i) water interactions with failed-fuel rods and metal-oxide materials; ii) the role of thermal processes and radiolysis (solid-state and interfacial) in the generation of potentially explosive mixtures of gaseous H_2 and O_2, and iii) the potential role of radiation assisted corrosion during fuel rod storage.

The project meets several major DOE/EMSP science needs for the Spent Nuclear Fuel Focus Area: i)"Stabilization of spent nuclear fuel, including mechanism of pyrophoricity and combustion parameters for various fuel types"; ii)"Characterization of spent nuclear fuel";iii)"Development of methods to remove moisture without damage to fuel elements" iv)"Characterization of corrosion, degradation, and radionuclide release mechanisms, kinetics, and rates for fuel matrices.

Research Progress and Implications

This report summarizes work after 2.5 years of a 3-year project.

- Interaction of water vapor with UO_2(001) was studied by using low energy electron diffraction, X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and electron stimulated desorption (ESD). ESD measurements of clean UO_2 indicate the desorption of H^+ and O^+; the kinetic energy distribution of the latter is peaked at 3.5eV. The O^+ desorption threshold is at 25eV, and is correlated to the ionization of the oxygen 2s level. LEIS, XPS and ESD results indicate that adsorbed water is completely dissociated on UO_2(001) at 300K and that O atoms are incorporated into the surface. The results also suggest diffusion of oxygen into the bulk.
- A high vacuum chamber has been designed for the experiments with K-West Basin fuel samples, conducting in the Radiation Controlled Area of PNNL. The new facility is equipped with a low energy (5-500 eV) electron gun, a high resolution focused ion gun and a secondary electron detector and mass-spectrometer, and allows secondary electron microscopy imaging, secondary ions mass-spectroscopy and ESD of spent fuel samples from the K-West Basin.
- Gamma radiation-induced degradation of water on oxide particle/water interfaces was studied. Thirty powdered ultra-pure (>99.99%) crystal oxides were studied. According to the radiation-chemical yield, the oxides can be generally classified into three groups: i) inhibitors, which lower the H_2 yield, ii) indifferent oxides, and, iii) ZrO_2, and some other oxides which increase the H_2 yield as compared with the radiolysis of pure gas-phase water. A mechanism is proposed for the adsorbed water radiolysis on the ZrO_2 surface, based on the migration of excitons to the surface and their resonant coupling with the H_2O adsorption complex.

- Time- and energy-resolved laser-stimulated luminescence (LSL) measurements were utilized to investigate the dynamics of electronic excitations in ZrO_2. We observe LSL from the decay of three excited states, at 2.70, 2.27 and 2.10 eV. The emission kinetics are hyperbolic for all the luminescence bands, which indicates a recombination mechanism. We suggest recombination primarily involves electrons, trapped at intrinsic and extrinsic defect sites, and mobilized holes.
- The breakdown of zirconia films (important to the integrity of Zr-alloy fuel-rod cladding) under extreme radiation conditions has been systematically studied using low-energy electron and photon bombardment of well-characterized ZrO_2 surfaces. These studies have clarified the mechanism of oxygen removal from such surfaces. This involves ionization of cation core levels, followed by interatomic Auger decay resulting and rapid ejection of O+ ions.

Planned Activities

We are submitting a renewal proposal to:i) characterize major forms of water physically and chemically bonded to major components of the *real SNF samples*; ii)investigate radiation-induced gas generation and surface degradation on real SNF samples, cladding and rubble materials containing residual bounded water; and iii)complete the development of a predictive model for the radiolytic gas release from the surface of SNF and other components during "dry" storage.

Information Access

1. 1997-1998 Progress Report: http://apollo.osti.gov/em52/1998projsum/60392.pdf
2. 1998-1999 Progress Report: http://apollo.osti.gov/em52/1998projsum/60392.pdf
3. EMSP Workshop, July 1998 Projecthttp://apollo.osti.gov/em52/1998projsum/60392.pdf
4. N.G.Petrik, A.B. Alexandrov, T.M. Orlando, A.I. Vall "Radiation-Induced Processes at oxide Surfaces and Interfaces Relevant to Spent Nuclear Fuel Storage..", Trans. ANS 81,101 (1999)
5. W. C. Simpson, W. K. Wang, J. A. Yarmoff and T. M. Orlando, "Photon- and Electron-Stimulated Desorption of O+ from Zirconia", Surf. Sci. 423, 225 (1999).
6. N. G. Petrik, D. P. Taylor, and T. M. Orlando, "Laser-Stimulated Luminescence of Yttria-Stabilized Cubic-Zirconia Crystals", J. Appl. Phys. 85, 6770 (1999).
7. M. N. Hedhili, B. V. Yakshinskiy, and T. E. Madey, "Interaction of water with UO_2 (001)", Surf. Sci. 445 (2000) 512 - 525
8. D.P.Taylor,W.C. Simpson, K. Knutsen, M.A. Henderson, T.M. Orlando "Photon-Stimulated Desorption of Cations from Yttria-Stabilized Cubic ZrO_2", Appl. Surf. Sci. 127 - 129, 101 (1998)
9. N. G. Petrik , A. B. Alexandrov, A. I. Vall, and T. M. Orlando. "Gamma Radiolysis of Water on Oxide Surfaces: Parameters Controlling the Energy Transfer", J. Phys. Chem. B, in prep.
10. S. Thevuthasan, S.I . Yi, Y.J. Kim, T.T. Tran, G.S. Herman, V. Shutthanandan, S.A. Chambers, C.H.F. Peden, and T.M. Orlando "Surface Structure Determination of Y-ZrO_2(001) Using Mass Separated Recoil Spectroscopy and X-Ray Photoelectron Diffraction", Surf. Sci. in preparation.
11. V. Shutthanandan, S. Thevuthasan and T.M. Orlando "Hydrogen-Damage Interactions in Yttrium Stabilized Zirconia", J. Nucl. Mater. (in prep.)
12. P. Haustein, "Nuclear Stimulated Desorption Studies of Oxides Relevant to Spent Fuel Material", J. Nucl. Mater. in prep.

Radionuclide Immobilization in the Phases Formed by Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

Project ID: 59849

Rodney C. Ewing, University of Michigan

Research Objectives

This research program is focused on developing models of the long-term alteration of UO_2 in spent nuclear fuel. The models are based on detailed studies of the long-term corrosion products of naturally occurring UO_{2+x} under oxidizing conditions. The natural samples range in age from a few millions of years (Colorado Plateau in the U.S.A.) to approximately 2 billion years (the Oklo natural reactors in Africa). This research program identifies the phases that form, evaluates their stability and the ability of U^{6+}-phases to incorporate key radionuclides. We have focused on radionuclides (^{237}Np, ^{239}Pu, ^{99}Tc, ^{79}Se and ^{129}I) that make important contributions to exposure dose during geologic disposal.

Research Progress and Implications

As of February, 2000, this report summarizes work that has been completed during the first two-and-half years of a three year program. During this time, a post-doctoral fellow, F. Chen, has focused his efforts on the development of a theoretical basis for predicting the Gibbs free energies, enthalpies and entropies of formation of uranium (VI) phases. A second post-doctoral fellow, Donggao Zhao, completed microchemical analysis of the corrosion products of natural uraninites, UO_{2+x}. Zhao's work has demonstrated that the secondary alteration products can incorporate trace elements into their structures and hence provide for effective retardation. A third post-doctoral fellow, Keld Jensen, has begun a detailed study of samples from the Oklo natural reactors to evaluate the transport and retardation of radionuclides. In collaboration with Professor Peter Burns at Notre Dame, we have continued the evaluation of the capabilities of the uranyl phases to incorporate and retard release of important radionuclides: ^{237}Np, ^{79}Se, ^{99}Tc and ^{129}I.

The Gibbs free energies and enthalpies for uranyl phases have been estimated based on a method that sums polyhedral contributions. The molar contributions of the structural components to ΔG^o_f and ΔH^o_f are derived by multiple regression using the thermodynamic data of phases for which the crystal structures are known. There is good agreement between the predicted mineral stability relations and field occurrences, thus providing confidence in this method for the estimation of ΔG^o_f and ΔH_{of} of the U(VI) phases.

The entropies of uranyl phases used in geochemical calculations are usually based on calorimetric measurements. However, because of the contribution of neglected residual entropy, which cannot be determined by calorimetric measurements, the true third-law entropies for many phases may be quite different from the entropy values derived from thermal data. This may affect calculated solubilities. The ideal site-mixing configurational entropies of uranates, uranyl oxide hydrates, silicates, phosphates, carbonates and sulphates have been calculated based on crystallographic data. Considerable residual entropy may be caused by disorder of hydrogen bonds associated with interstitial H_2O groups. The effect of residual entropy on the solubility of solid phases can be substantial.

^{79}Se is a long-lived (1.1×10^6 year) fission product which is chemically and radiologically toxic. Under Eh-pH conditions typical of oxidative alteration of spent nuclear fuel, selenite, SeO_3^{2-} or $HSeO_{3-}$, or selenate, SeO_4^{2-}, are the dominant aqueous species of selenium. ^{79}Se released from altered fuel may become immobilized by incorporation into secondary uranyl phases as low concentration

impurities, and this may significantly reduce the mobility of selenium. Analysis and comparison of the known structures of uranyl phases indicate that (SeO_3) may substitute for (SiO_3OH) in structures of α-uranophane and boltwoodite that are expected to be the dominant alteration products of UO_2 in Si-rich groundwater.

^{99}Tc is a long-lived radioactive fission product with a half-life of 2.13×10^5 years and a fission yield of 6.13% in nuclear reactors. ^{99}Tc is a prominent contributor to dose in safety assessments of nuclear waste repositories. Under Eh-pH conditions corresponding to the oxidative corrosion of spent nuclear fuel, which is constrained by the stability of uranyl phases relative to that of UO_{2+x} phases, TcO_4^- is the predominant species. TcO_4^- is highly soluble and weakly adsorbed in the near-field. The incorporation of Tc^{7+} into the structure of uranyl phases that are expected to occur as alteration products of spent nuclear fuel will destablize the structure, suggesting that significant substitution of (TcO_4^-) will not occur in uranyl phases.

Planned Activities

During the next year, our program will continue to focus on five areas: **1.** Detailed analysis of natural samples to identify the principal phases and their proportions as a function of geochemical conditions and reaction progress. **2.** Analysis of uranyl phases for their trace element content, that is a determination of the fate of impurity elements that are released during matrix dissolution of the UO_2 **3.** An evaluation of the long-term stability of uranyl phases under oxiding conditions. **4.** Comparison to theoretical calculations of phase stability to actual natural occurrences of these uranyl phases. **5.** An evaluation of ^{129}I incorporation into uranyl phases.

Information Access

Website: http://relw.engin.umich.edu

S.B. Clark, R.C. Ewing and J.C. Schaumloffel (1998) A method to predict free energies of formation of mineral phases in the U(VI)-SiO_2-H_2O system. Journal of Alloys and Compounds, 271, 189-193.

R.J. Finch, F.C. Hawthorne and R.C. Ewing (1998) Structural relations among schoepite, metaschoepite and "dehydrated schoepite". Canadian Mineralogist, 36, 831-845.

F. Chen, R.C. Ewing and S.B. Clark (1999) The Gibbs free energies and enthalpies of formation of uranium (VI) phases: An empirical method of prediction. American Mineralogist 84(4), 650-654.

I. Casas, J. De Pablo, J. Giménez, M.E. Torrero, J. Bruno, E. Cera, R.J. Finch and R.C. Ewing (1998) The role of pe, pH, and carbonate on the solubility of UO_2 and uraninite under nominally reducing conditions. Geochimica et Cosmochimica Acta 62(13), 2223-2231.

R.C. Ewing (1999) Nuclear waste forms for actinides. Proceedings of the National Academy of Sciences, 96(7) 3432-3439.

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

R.C. Ewing (1999) Less Geology in the Geological Disposal of Nuclear Waste. Science 286, 415-416.

R.C. Ewing, M.S. Tierney, L.F. Konikow and R.P. Rechard (1999) Performance assessments of nuclear waste repositories: A dialogue on their value and limitations. Risk Analysis 19(5), 933-958.

Fanrong Chen and R.C. Ewing (1999) Structural contributions to the third-law entropy of uranyl phases. Symposium Proceedings of the Materials Research Society, vol. 556, 1017-1024.

Fanrong Chen, P.C. Burns and R.C. Ewing (1999) ^{79}Se: Geochemical and crystallo-chemical retardation mechanisms. Symposium Proceedings of the Materials Research Society, vol. 556, 1115-1122.

M. Fayek, Peter Burns, Young-Xiang Guo and R.C. Ewing (2000) Micro-structures associated with uraninite alteration. Journal of Nuclear Materials 277, 204-210.

R.J. Finch, M.A. Cooper, F.C. Hawthorne and R.C. Ewing (1999) Refinement of the crystal structure of rutherfordine. Canadian Mineralogist 37, 929-938.

F. Chen, P.C. Burns and R.C. Ewing (in press) Near-field behavior of ^{99}Tc during the oxidative alteration of spent nuclear fuel. Journal of Nuclear Materials.

D. Zhao and R.C. Ewing (in press) Alteration products of uraninite from the Colorado Plateau. Radiochimica Acta.

K.A. Jensen* and R.C. Ewing (in press) The Okélobondo natural fission reactor, southeast Gabon: Geology, mineralogy and retardation of nuclear reaction products. Geological Society of America Bulletin.

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

Project ID: 59960

Peter C. Burns, University of Notre Dame

Robert J. Finch, Argonne National Laboratory
David J. Wronkiewicz, University of Missouri-Rolla

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 28 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 13 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: compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$ (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, $K_2(Ca,Sr)[(UO_2)_3O_3(OH)_2]\ 2.4H_2O$ (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).

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, $(SeO_3)^{2-}$ (selenite) and $(SeO_4)^{2-}$ (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 $(TcO_4)^{-1}$. 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.

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, $UO_3(H_2O)_{0.8\text{-}1.0}$ (K_d = 5.2 to 12), and both Ce^{4+} and Nd^{3+} in ianthinite, $[U_2^{4+}(UO_2)_4O_6(OH)_4(H_2O)_4](H_2O)_5$ (Ce K_d = 146-159, Np K_d = 62) and becquerelite, $Ca[(UO_2)_3O_2(OH)_3]_2(H_2O)_8$ (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. 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, in press): $KNa_3(UO_2)_2(Si_4O_{10})_2(H_2O)_4$, a new compound formed during vapor hydration of an actinide-bearing borosilicate waste glass. *Journal of Nuclear Materials*.
11. Burns, P.C. (in press): A new uranyl phosphate chain in the structure of parsonsite. *American Mineralogist*.
12. Burns, P.C. & Hill, F.C. (2000a, in press): 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*.
13. Burns, P.C. & Hill, F.C. (2000b, in press): Implications of the synthesis and structure of the Sr analogue of curite. *Canadian Mineralogist*.
14. Chen, Fanrong, Burns, P.C. & Ewing, R.C. (2000, in press): Near-field behavior of ^{99}Tc during the oxidative alteration of spent nuclear fuel. *Journal of Nuclear Materials*.
15. Fayek, M., Burns, P.C., Guo, Y.X. & Ewing, R.C. (2000, in press): Micro-structures associated with uraninite alteration. *Journal of Nuclear Materials*.
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, accepted): The structure of agrinierite: A Sr-containing uranyl oxide hydrate mineral. *American Mineralogist*.
18. Li, Y. & Burns, P.C. (2000, accepted): A new rare-earth element uranyl carbonate sheet in the structure of bijvoetite-(Y). *Canadian Mineralogist*.
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, submitted): Crystal chemistry of uranyl molybdates. I. The structure and formula of umohoite. *Canadian Mineralogist*.
21. Krivovichev, S.V. & Burns, P.C. (2000b, submitted): Crystal chemistry of uranyl molybdates. II. The crystal structure of iriginite. *Canadian Mineralogist*.

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): ^{79}Se: 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 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.
9. Cahill, C.L. & Burns, P.C. (1999): The structure of agrinierite: a K-Ca-Sr uranyl oxide hydrate sheet of the α-U_3O_8 type. *GSA* (Denver).
10. Finch, R.J., & Buck, E.C. (1998): Synthesis and characterization of $Ba[(UO_2)_5MoO_6(OH)_6]\cdot nH_2O$. 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 Ce^{4+} and Nd^{3+}-bearing ianthinite: Implications for the incorporation of Pu^{4+} and Am^{3+} 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.

Flow Visualization of Forced and Natural Convection in Internal Cavities

Project ID: 60144

Dr. John C. Crepeau, University of Idaho

Research Objective

The general goal of this program is to develop innovative flow visualization methods and reliable predictive techniques for the energy, mass, and momentum transfer in the presence of surface reactions for the passivation treatment operations of SNF elements.

Research Progress and Implications

This report summarizes the work accomplished after about two and a half years of a three-year collaborative project. The University of Idaho developed a flow visualization technique to simulate a passivation reaction between oxygen gas and uranium hydride found on corroded, wet-stored SNF elements. An apparatus was constructed whereby a mixture of hexanoic acid and mineral oil flowed down a long channel. The hexanoic acid and mineral oil represented the oxygen and helium, respectively in the passivating gas. In the channel we placed a thin, flat aluminum plate with a small cavity filled with sodium metal. The sodium represented an exposed, corroded area on an SNF element. As the solution flowed over the plate, the acid in the solution reacted with the sodium, releasing hydrogen bubbles into the flow.

Based on observations of the generic SNF canister, our experiments were performed along a flat plate, at a Reynolds number of around 350. Figure 1 shows a typical flow pattern as viewed from the side. The fluid moves from left to right, and one observes the bubbles floating up and being convected downstream. The rising bubbles stretch and thin the dye filaments, and compress the streamlines toward the air-fluid interface. As the flow progresses downstream, nonlinear interactions between the bubbles and the dye cause further mixing. It is clear from the photograph and subsequent observations that the chemical reaction along the solid surface and subsequent release of the hydrogen bubbles convect the fluid away from the reaction, and introduce velocity fluctuations into an otherwise laminar flow. The bubble entrainment enhances mixing, and may serve to break flow symmetries and uneven flow distribution that have been observed in previous experiments. These flow symmetries, which may be circumferentially periodic, prevent a complete and thorough mixing throughout the canister, and decrease the likelihood that all of the possible corroded areas will be properly treated.

The objective of the INEEL and OSU effort is to develop an innovative measuring system and obtain fundamental measurements of the basic velocity and turbulence fields in generic idealizations of flow processes in SNF canisters. A water-flow experiment with a 3/4-scale model of the generic

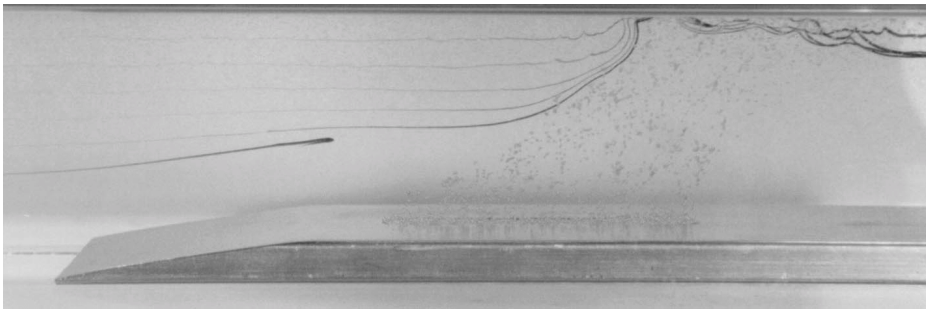

Figure 1. Side view of bubble-dye interaction

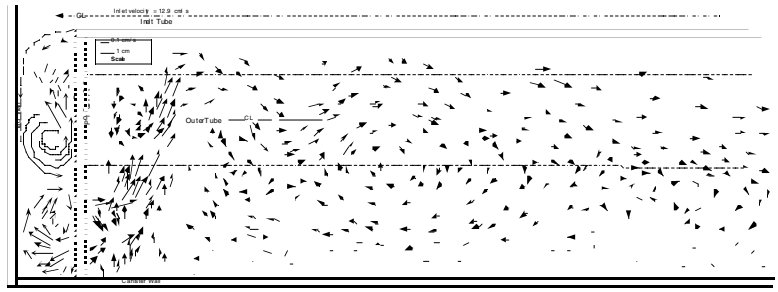

Figure 2. Velocity measurements in a plane midway between two simulated fuel elements

SNF canister was used for overall flow visualization and velocity measurements, with and without an array of simulated fuel elements. The flow is approximately circumferentially periodic and symmetrical about cross-sections through the four outer tubes for experiments using each of the three perforated plates. Figure 2 shows complicated, non-uniform flow patterns with a wide range of velocities in the simulated region of the fuel element array. Local velocities differed by more than an order-of-magnitude from the bulk mean velocity used in simple analyses. These data demonstrate clearly that the flow in a typical basket would not be co-axial with its elements. Flows were both across, inducing turbulence, and along the elements at a low Reynolds number, encouraging laminarization. The expected effects on local mass transfer to support chemical reactions at the surface would be highly non-uniform.

The INEEL used its Matched-Index-of-Refraction flow system to measure flow in and around complex geometries, employing optical techniques without disturbing the flow. A 0.6-scale model has been installed in this unique facility to obtain detailed pointwise data for the three-dimensional flow field by laser Doppler velocimetry. New velocity and turbulence measurements to date have concentrated on low Reynolds number turbulent flow in the entry tube and the semi-confined, submerged impinging jet. Other experiments were performed to determine the turbulence and velocity fields of the flow approaching the perforated plate, and the inflow turbulence of the impinging jet. The examination of these questions requires fundamental measurements of the decay of turbulence and velocity in the low Reynolds number impinging jet and its surroundings and of the low Reynolds number turbulent flow in the inlet tube. Initial measurements of U, V, u´, v´ and $\overline{uv}$ have been obtained in the tube, about a diameter upstream from the exit, and at 0.07 diameters along the jet axis for Re $\approx$2510. These data provide the initial conditions for the impinging jet and permit assessment of the turbulence models employed in the numerical predictions.

The objective of the computer modeling effort is to qualitatively assess the flow patterns in support of the experimental effort and to work towards validation of the modeling approach. Various turbulence models were utilized to model the pipe flow, and the computational results compare favorably with previously published experimental data. Several standard turbulence models were used to analyze the flow out of the pipe onto the lower plate. It was also necessary to examine the sensitivity of the jet spreading to the type of numerical model used (turbulence model and upwinding scheme). Results show a large variation in the different models and numerical schemes. It is readily apparent that the type of model and numerical scheme selected will impact the predicted flow field.

Planned Activities

The research group is continuing the experiments and analysis stated above in order to complete our tasks before the end of the project. A renewal proposal is being prepared to finalize the work accomplished so far, and to assist the SNF clean-up mission.

Information Access

Updated information is available at: http://teton.if.uidaho.edu/emsp/index.html

Gamma Ray Imaging for Environmental Remediation (GRIER)

Project ID: 60141

W. N. Johnson, Naval Research Laboratory

R. A. Kroeger, Naval Research Laboratory
J. D. Kurfess, Naval Research Laboratory
G. Phillips, Naval Research Laboratory
B. F. Phlips, George Mason University
P. N. Luke, Lawrence Berkeley National Laboratory

Research Objective

The objective of the GRIER project is to apply germanium detector systems with both high spectral resolution and good imaging capabilities to the problems of environmental remediation.

Research Progress and Implications

Over the last year, much progress has been made. We have

1. developed and built amorphous-contact germanium detectors of increasing sophistication,
2. built and tested an array of four position-sensitive germanium detectors, and
3. demonstrated spectroscopy and imaging uses with ^{235}U.

Results from this research were presented at the EMSP's first workshop in Chicago in 1998, at the SPIE Session in July 1999, and at the IEEE Nuclear Science Symposium in November 1998 and 1999.

Amorphous Contacts

The goal of the amorphous contact effort was to extend the single element (pixel) amorphous technology developed by Luke et al. to double-sided orthogonal strip detectors. Amorphous contact provides multiple advantages over the current lithium contact technology.

We have fabricated the first orthogonal strip detector with dimensions appropriate for field use. The detector has an active volume of 50 mm $\times$ 50 mm $\times$ 10 mm and has 25 $\times$ 25 strips (see Figure 1). It is currently undergoing tests. The resolution is ~12 keV FWHM, which is dominated by electronic noise. The noise was high because of the large capacitance and the non-optimal electronics used with the test cryostat.

Detector Array

We acquired a 2 $\times$ 2 array of germanium strip detectors with conventional contact technology to build a prototype array. The individual detectors have an active volume of 50 mm $\times$ 50 mm $\times$ 10 mm and have 25 strips on each side. The full array in its cryostat is shown in Figure 2. For the first time, this array tested the possibility of daisy-chaining strips while still achieving excellent spectroscopy. The energy resolution is ~ 2 keV FWHM on individual strips as expected, proving the possibility of daisy-chaining.

We designed and manufactured a collimator to use in conjunction with the detector array. The collimator is a parallel hole collimator. It has a two-dimensional pattern of 400 micron square holes, with a pitch of 500 micron. Since the pitch is much smaller than the strip pitch on the detector, the collimator does not have to be aligned accurately with respect to the detector.

The image of a medical phantom with a circular pattern filled with Technetium-99 is shown in Figure 3. The protrusions on the top right and bottom left of the circle are real. They are created by notches in the phantom cavity that were also filled with the radioactive Technetium. The vertical strip of low flux in the image at ~45 mm is caused by a structural support in the cryostat that blocks two of the strips.

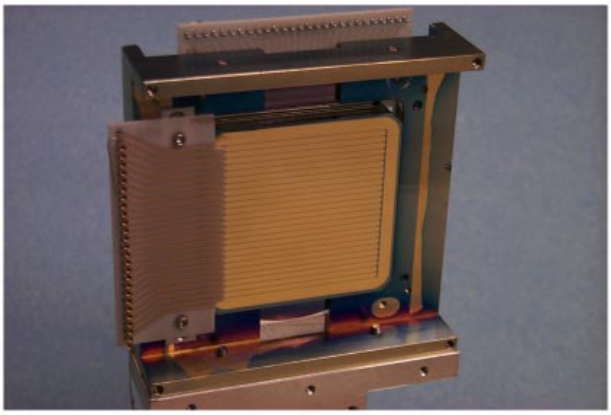

Figure 1. Full sized Ge detector with amorphous contacts. Each side has 25 strips with 2 mm pitch.

Figure 2. Array of 4 Ge detectors in cryostat. The 2 x 2 array has 2 mm position resolution.

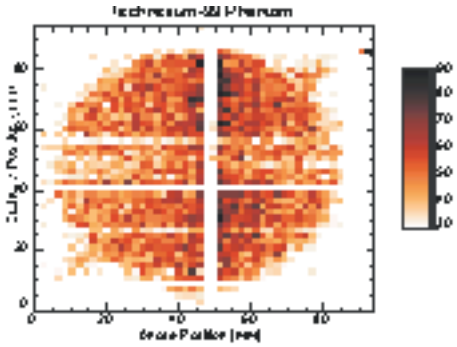

Figure 3. Image of ^{99}Tc phantom measured at 140 keV. Uniform disk of 8 cm diameter. Fill tubes are seen in upper right and lower left corners.

Laboratory Demonstrations

We have started testing the 2×2 germanium array in the laboratory and have demonstrated good spectroscopy and imaging with various isotopes. As an initial test of the system with isotopes of interest to the end users, we imaged a piece of uranium (U-235). The piece, shown in Figure 4, was roughly rectangular, with dimensions of ~2 by 3 cm.

The image shown in Figure 5 was obtained using the collimator and detectors described previously and selecting a narrow energy window around the 185 keV line in the measured spectrum (Figure 6). The shape of the imaged object is clearly reconstructed, as expected. This energy windowing capability is essential for isolating a particular element, especially in a high background environment. A similar demonstration is also planned with a ~1 cm cube of plutonium (Pu-239). The plutonium measurements will be done with a thicker version of the collimator.

Planned Activities

The remaining months of the program shall be devoted to improvements to the data acquisition and imaging systems in preparation for field test demonstrations.

Figure 4. Photograph of ^{235}U sample for imaging test. Its dimensions are ~ 2 x 3 cm.

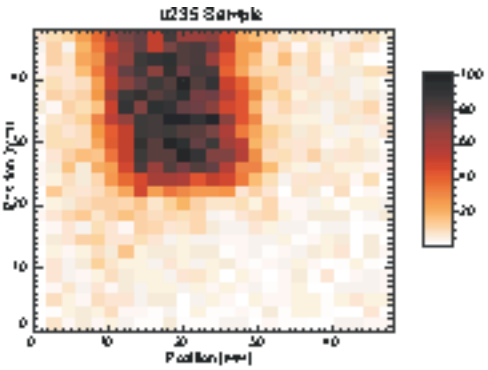

Figure 5. Image of ^{235}U sample measured in 185 keV gamma rays. Image pixels are 2 x 2 mm.

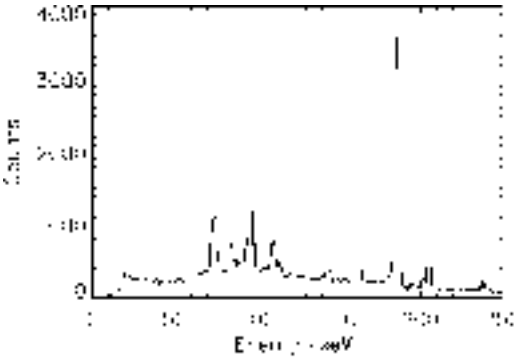

Figure 6. Complete ^{235}U spectrum measured while collecting the image in Figure. The image is in the gamma ray line at 185 keV.