Source-term Reductions by Corrosion Processes and Corrosion Products of Spent Fuel UO_2 with Constituents in Yucca Mountain Repository Geochemistry

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Summary

The onset and rate of release of nuclides from the Yucca Mountain Project (YMP) repository horizon is ultimately determined by the oxidization and dissolution of the U(IV)O_2 fuel pellets after the waste packages degrade in the oxidizing environment in this repository. The source-term that determines times and rates of releases of specific nuclides from this near-field into the far-field migration paths is controlled by the solubility and ad/absorption of these nuclides onto or into the alteration compounds that form on the surface of the high-fired UO_2 fuel pellets.

After the initial decay-heat pulse dissipates, alteration compounds are formed as the UO_2 reacts with the incidental water/brines from adjacent vitreous tuff formation [the Topapah Spring welded unit (Flint 1998)]. This disposal horizon consists of a very thin upper vitrophyre, a thick central zone consisting of several densely welded, devitrified ash-flow sheets, and a thin lower vitrophyre.[a] These incidental brines carry oxygen, hydroxide, silica, alumina, carbonates, and sulfates from the adjacent formation and its unsaturated pore water. These brine constituents can form minerals with low solubilities and high capacities to sequester the nuclides.

This research will

1. Simulate the oxidation and paragenesis of U(IV) to insoluble U(VI) compounds and minerals that form with the incidental brines after the local temperature drops below the boiling point
2. Simulate localized buffering of pH and Eh of incidental brines by UO_2
3. Identify the products of the reaction paths at temperatures that bracket the onset of condensation in the cooling disposal drifts
4. Measure the distributions of key radionuclides that are released during the corrosion of high-fired UO_2 fuel pellets and are then sequestered by the minerals formed during their alteration.

Thermally accelerated static and flow-through exposure experiments will use combinations of fuel pellets and simulated brine to expose tuff, which will then be examined with nano-probes to determine the minerals formed. The leaching or solubility of the U(VI) species will also be measured throughout the alteration processes. Once key alteration products are identified ad/absorption measurements will be made with the principal nuclides that contribute most to the maximum dose at the site boundary.

This study's products will be (1) the identification of key alteration U(VI) products that form under the influence of the oxidizing environment and brines; (2) measurements of the partitioning and distribution of nuclide species on the phases that form during the initial localized reducing environment adjacent to the corroding fuel and incidental brine; and (3) more accurate descriptions of the mechanisms of release/retention of nuclides from the encasing mass of insoluble corrosion products that will form with the oxygen, hydroxides, silica, alumina, sulfates, and carbonates in the incidental brines.

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[a] Vitrophyre is a glassy igneous rock.

Goals and Objectives

This study will determine the scientific basis for a more accurate nuclide source-term for the transfer from the repository near-field, adjacent to the spent fuel pellets, to the far-field migration paths. The retention or sequestration of the key nuclides by the UO_2 alteration products will significantly delay and reduce the rate of release from the near-field repository.

The first step is to identify the alteration products that form under the geochemical conditions that exist after the near-field repository cools enough to allow condensed brines to form. Then measuring their solubility and thermodynamic stability, followed by measuring the ad/absorption capacity of these alteration phases for key nuclides will allow the YMP to take credit for the reduction in off-site doses that will be affected by delaying and lowering the near-field source-terms.

It is estimated, based on ORNL's experience with high-fired UO_2 leaching in high silica brines, that the reduction in dissolution of UO_2 is by factors of 100 to 10,000 (Dole, Mattus 2002) (Dole et al. 2003) (Dole, Mattus 2005). This would result in a significant reduction in the current estimates of the maximum dose at the boundary of the YM site (see Fig. 1). Figure 1 also shows the principal nuclides that contribute most to long-term off-site doses.

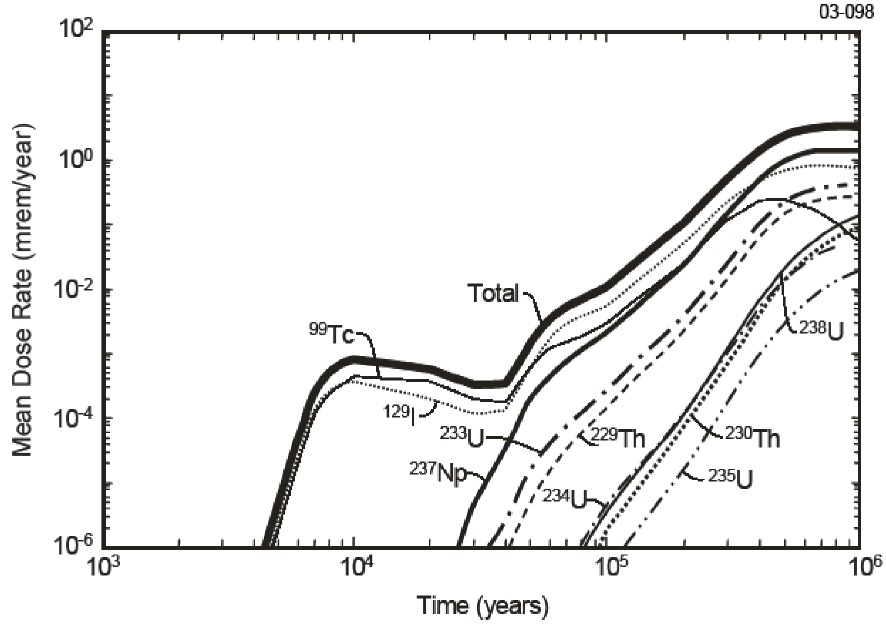
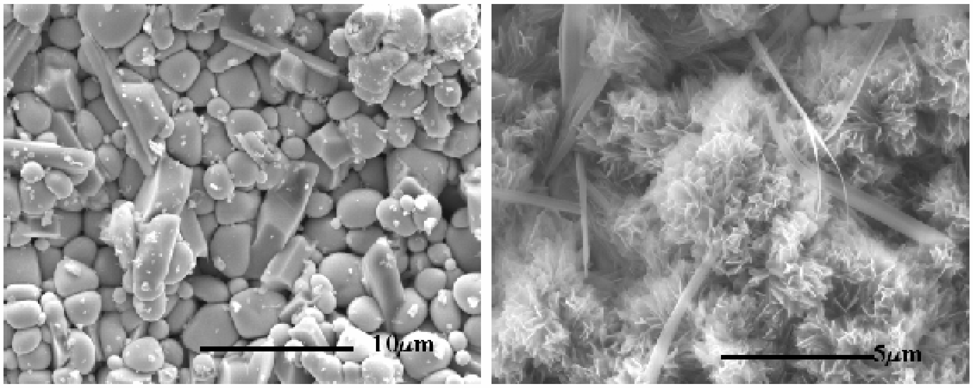


Fig. 1. Current calculations of off-site dose without taking credit for the retention of key nuclides by the UO_2 alteration products.

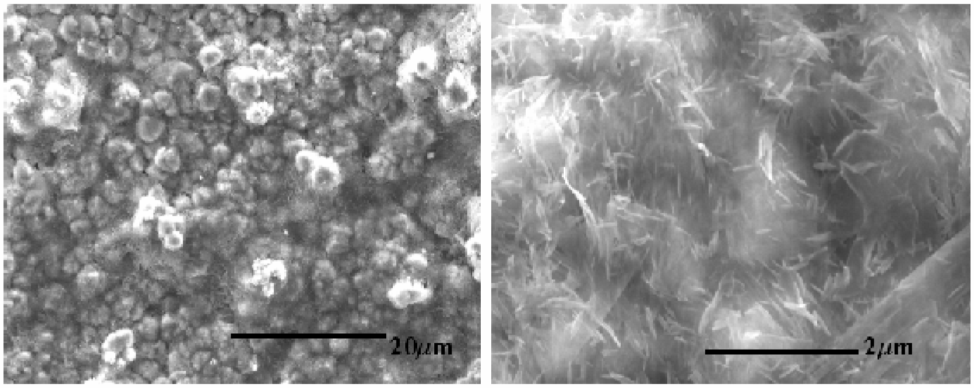
Enabling Elements, Experience, and Background

ORNL has laboratories that have been certified to meet OCRWM's Quality Assurance Requirements of DOE/RW-0333P REV 16 or later. And for the past four years, ORNL has been conducting long-term exposure experiments on low- and high-fired UO_2 as it forms alteration products with high-silica brines from sintering agents and encapsulating silica-modified cements. During these long-term experiments, ORNL has monitored the formation of secondary minerals on the UO_2 surfaces and the equilibrium concentration of the U, Si, Al, Ti, Zr, and other constituents of these systems. Some examples of ORNL's results are shown in Fig. 2.



A DI Water - 150°C
secondary electrons
The oblong particles contain Ti and some Mg while the rounded ones are made of DU

B NaOH - 150°C
secondary electrons
Alkali-reaction products containing Na, Al, Si, Ca and Ti.



C Cement pore solution - 150°C
secondary electrons
Cement hydration products are covering the DU particles

D Cement pore solution - 150°C
secondary electrons
Cement hydration products contain Ca, Si and Al

Fig. 2 Secondary mineral formation of the surface of the UO_2 particles (Mattus, Dole 2003).

In Fig. 2, panel 2A shows the clean, etched surface of the basalt-sintered UO_2 particles. Panel 2B shows the mineralization on the UO_2 surface of etched basalt components in 1 M NaOH. Panels 2C and 2D show the occlusion of the UO_2 particle surfaces with a calcium aluminosilicate layer that forms from the cement porewater constituents and the leached silicates from the basalt sintering agent (Mattus, Dole 2003).

Therefore, this study's proposed experiments take advantage of previous testing at ORNL that can be extended to apply to the YM repository conditions. So, the likelihood of success is very high because previous work shows conclusively that the formation of alteration products has a profound influence on the release of U(VI) from UO_2 and the nuclides contained within.

For example, evidence shows a dense mat of alteration phases developed on the fuel pellet surface, accompanied by depletion in the alkali and alkaline earth cations and Si in the groundwater brine solution. The nature of these alteration phases and the sequence in which they appear on the fuel are similar to those observed in surficial weathering zones of natural uraninite deposits, which have alkali and alkaline earth uranyl silicates as the long-term solubility limiting phases for uranium. The sequence observed is represented schematically in Fig.3. The formation of this layer of alteration (or corrosion) products prevents further release of UO_2 particles, hence leading to a drop in the U release rate [Shoesmith 2000].

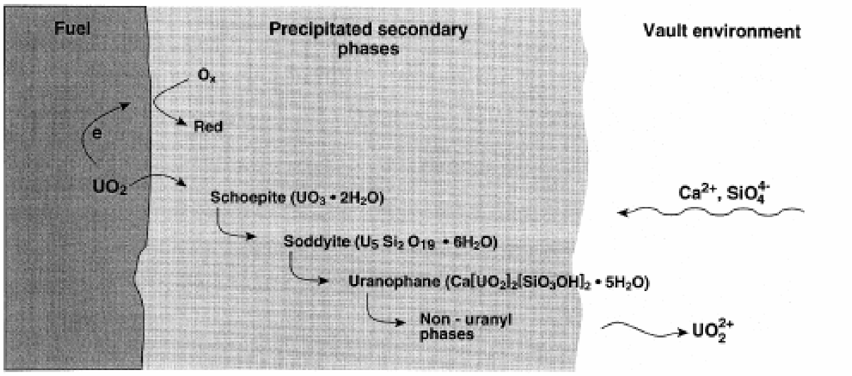


Fig. 3. Reaction sequence showing the alteration of precipitated uranyl phases observed in drip tests with unirradiated UO_2 and expected from observations on surficial weathering zones on natural uraninite deposits.

Assuming the ions are incorporated into U(VI) deposits with very low solubilities, the rapidity of the reduction of the corrosion rate by the addition of Ca/Si indicates that very little of these silica phases is required to suppress corrosion (Shoesmith 2000). This is consistent with electrochemical experiments that show that the incorporation of Ca/Si into U(VI) surface phases is very rapid and that only a few ηm are needed to substantially suppress uranium oxidization. Corrosion experiments in the presence of γ-radiation fields show that the accumulation of secondary phases begins as soon as steady-state corrosion conditions are established. Also, very stable alteration phases are expected to form based on the thermodynamic data in Table 1.

Table 1. Values of $\Delta G^{\circ}_{f,298}$ for some of the U(VI) minerals that are expected to form as UO_2 is oxidized and reacts with the hydroxide, carbonate, and silicate components of the YM brines

Uranyl phases	Formula	kJoule/mol[a]	kJoule/mol[b]
Metaschoepite	$[(UO_2)_8O_2(OH)_{12}]*(H_2O)_{10}$	–13,092.0	–13,092.0
Becquerelite	$Ca[(UO_2)_6O_4(OH)_6]*(H_2O)_8$	–10,324.7	–10,305.8
Rutherfordine	UO_2CO_3	–1,563.0	–1,563.0
Urancalcarite	$Ca_2[(UO_2)_3(CO_3)(OH)_6]*(H_2O)_3$	–6,036.7	–6,037.0
Sharpite	$Ca[(UO_2)_6(CO_3)_5(OH)_4]*(H_2O)_6$	–11,607.6	–11,601.1
Fontanite	$Ca[(UO_2)_3(CO_3)_4]*(H_2O)_3$	–6,524.7	–6,523.1
Liebigite	$Ca_2[(UO_2)(CO_3)_3]*(H_2O)_{11}$	–6,446.4	–6,468.6
Haiweeite	$Ca[(UO_2)_2(Si_2O_5)_3]*(H_2O)_5$	–9,367.2	–9,431.4
Ursilite	$Ca_4[(UO_2)_4(Si_2O_5)_5(OH)_6]*(H_2O)_{15}$	–20,377.4	–20,504.6
Soddyite	$[(UO_2)_2 SiO_4]*(H_2O)_2$	–3,653.0	–3,658.0
Uranophane	$Ca[(UO_2)(SiO_3OH)]_2*(H_2O)_5$	–6,192.3	–6,210.6

[a] Chen 1999
[b] Finch 1997

Furthermore, these stable phases in concert with the locally reducing conditions created by the U(IV)↔U(VI) redox couple have a strong affinity for the key nuclides as has been shown in ORNL's collaborative work with the Russian Academy of Science under ISTC Program #2694, "Interactions Between Depleted Uranium Oxide and Underground Waters and Radionuclide Sorption by Oxides and Hydroxides of Depleted Uranium." While nearly all of the YM sorption work to date has been done with Np(V) and Tc(VII). The reduced species will be much less mobile than Np(IV) and Tc(IV), whose chemical behavior is very different from the oxidized forms.

Beyond the scope of this proposed phase of the near-field retention mechanisms, the corrosion products of waste package components of C-22, 300 series stainless steels, and Zircaloy-4 with the incidental YM brines will certainly contribute to the immobilizations of U and other nuclides. After this proposal's testing protocols have shown to be successful, the study should be expanded to include the waste package constituents.

Experimental Methods

Static Exposures

Static exposures of high-fired UO_2 to incidental brines with and without the presence of Tonopah vitreous tuff will be performed in the vessels that ORNL has used for its other studies of UO_2 alterations.

Synthetic brine and a large number of test specimens will be sealed separately in Teflon-lined pressure-vessels and allowed to equilibrate (see Fig. 4). At intervals, the vessels will be cooled, disassembled, and their contents examined and tested.

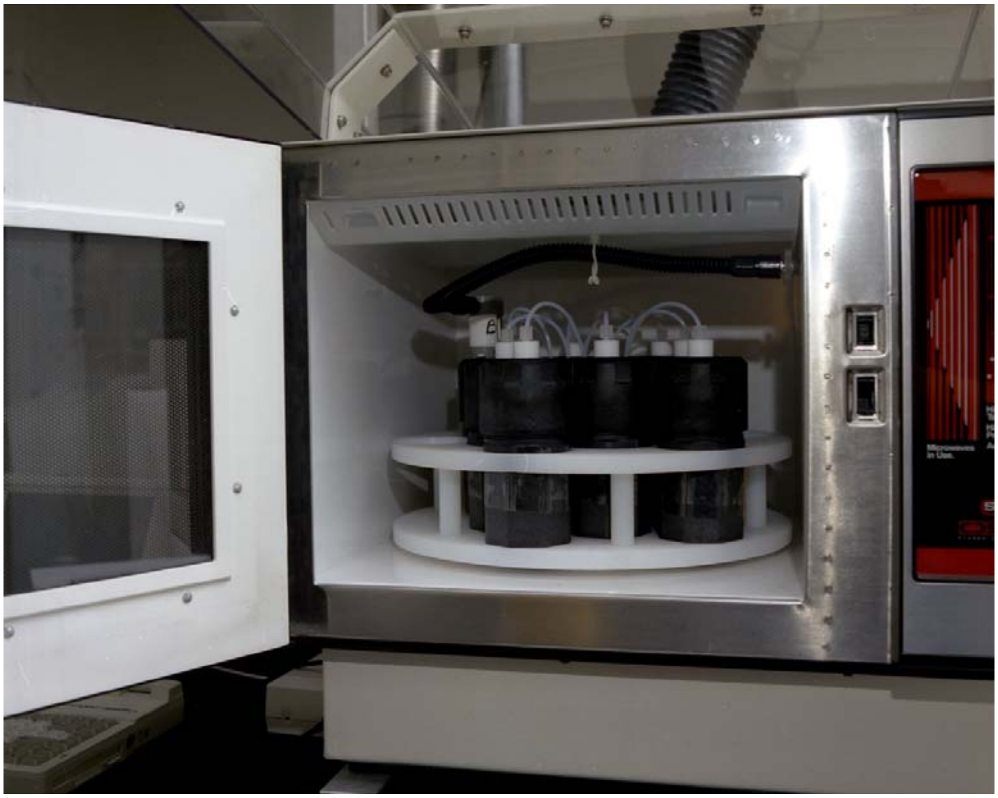


Fig. 4. Example of ORNL's previous exposure studies of high-fired UO_2 in sealed Teflon-lined Parr vessels capable of testing combinations of UO_2, incidental YM brines, and tuff to temperatures of 160ºC.

The chemical compositions of input solutions will be established. Candidate brines in the system Ca^{2+}-Mg^{2+}-Na^{+}-K^{+}-Al^{3+}-Si^{4+}-Cl^{-}-NO_3^{-}, F^{-}, and -SO_4^{2-} include those identified in YMP Technical Basis Document No. 5: *In-Drift Chemical Environment, Revision 1* (November 2003), Appendix G, Table G-3, as being those most likely to enter the drift environment from the geological formation. The final composition of this solution will be established by consultation with other members of the OCRWM S&T project research group and program managers.

Static Test at 90ºC

For this temperature, the high-fired UO_2 fuel pellet will be immersed synthetic brine in Teflon containers stored in an oven at 90ºC. Both the solution and pellet will be tested and analyzed. The solution will be tested for pH and chemical composition and the pellets' surfaces will be examined, as described below.

Static Test at 120ºC

This test will be conducted in commercially available pressure vessels in an air oven at 120ºC. The vapor pressure at this temperature is less than five atmospheres (gauge), so thin-walled, Teflon-lined vessels can be used. These vessels will be fitted with titanium sampling capillary lines and valves which will allow periodic sampling of the solutions without removal from the oven.

Mineralogical Evaluation

The specimens will be examined to identify alteration products that were formed during exposures. The following evaluations will be performed:

- Mineralogy of the alteration phases
- Elemental analysis of the phases' compositions by GFAA, IC, ICP-MS, ICP-AES
- SEM-EDX for selected samples
- Nanoprobe determination of nuclide ad/absorption

The exposure tests will study the solubility and rates of dissolution of UO_2 using a series of experiments with and without tuff to characterize the alteration products, and understand the mechanisms involved during element mobility between the solid and the liquid phases. In addition, we intend to employ techniques such as secondary ion microscope (SIMS) imaging coupled with HRTEM analysis of the solid phase to characterize the nanotextures that develop during the alteration process. ICP-MS, ICP-AES, and pH analysis of the liquid phase will allow us to monitor changes in chemistry of the fluid during the alteration process and the inclusion of nuclides into the alteration phases.

For example, we have initiated preliminary studies on coupled reaction/diffusive exchange during the alteration of silicate phases such as alkali feldspar by placing grains of Amelia albite and Madagascar sanidine in 1 *m* and 2 *m* NaCl and KCl solutions, respectively, with a solvent of composition $HD^{18}O_{0.5}{}^{16}O_{0.5}$. Samples were heated to 600°C at a pressure of 200 MPa for periods of 4–6 days (see Fig.5). The resulting exchanged rims were up to ~25% of the original grain diameter. We determined the elemental composition of the feldspar grains by electron microprobe analysis, the width of the rims by scanning X-ray and back-scattered electron images, and the distribution of ^{18}O, H, and D by scanning ion images using secondary ion mass spectrometry (equivalent to ORNL's Cameca 4f and/or Washington University's Cameca NanoSIMS).

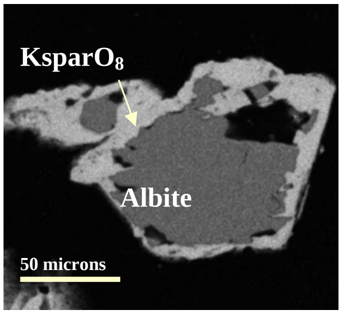


Fig. 5a. Electron backscatter image of K-spar replacing albite at 600°C.

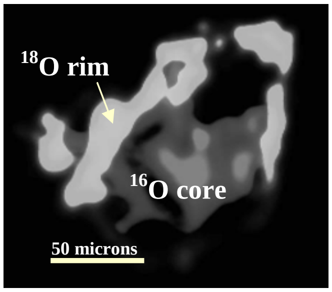


Fig. 5b. ^{18}O enriched zones (light) coincident with K-Na exchange.

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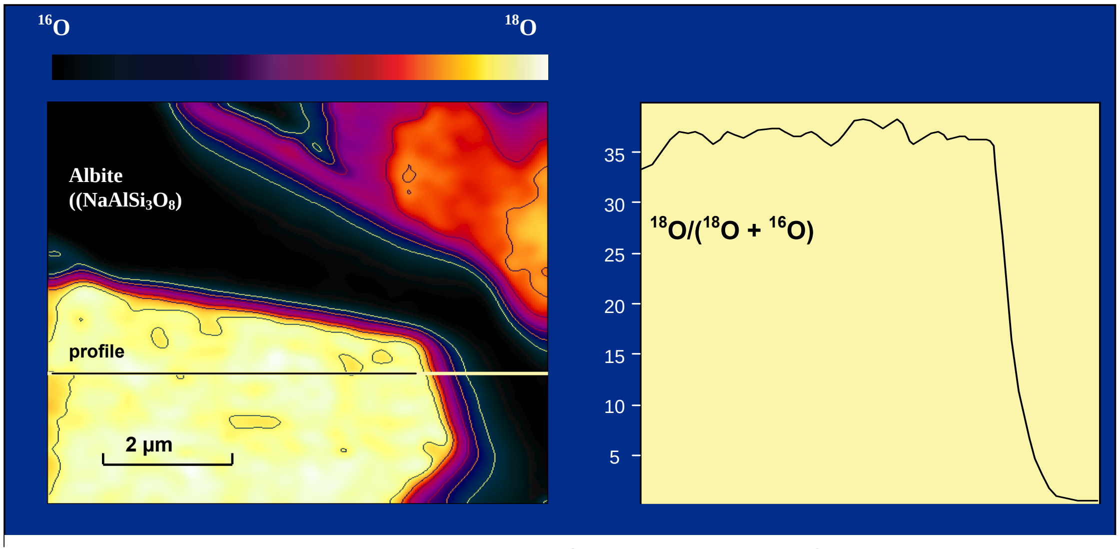

Fig. 5c. NanoSIMS ion imaging (contour map on left; line scan on right) of O isotopes in a reaction zone in which albite reacted with ^{18}O-enriched 2 molal KCl at 600°C, 200 MPa for 6 days.

Flow-Through Exposure Testing

ORNL researchers with extensive experience in the use of high-pressure, high-temperature, chemically inert reaction systems will measure the solubility of the highly insoluble alteration minerals (Palmer et al. 2002, Bénézeth et al. 2002, Palmer et al. 2004). Existing systems are described in detail by Palmer et al. (2002) and Bénézeth et al. (2002). The system will have all wetted parts composed of titanium, gold, platinum, and PEEK, so as to ensure chemical nonreactivity of the vessel materials. The system will also include provision for injection of strong base solutions (NaOH) into the output stream, downstream from the reaction zone within the high-temperature, high-pressure portion of the circulation system to prevent plugging of capillary tubing and valves by precipitating silica and other species.

Samples of high-fired UO_2 will be crushed and sized, exposed in the high-temperature flow cell, then characterized for mineralogical and textural properties. The methods will include SEM, XRD, optical thin section examination, and trace element determinations using SIMS, EPM, and other techniques. One of these samples will then be loaded into the high-temperature and pressure-flow system, and a series of reaction studies will be conducted at temperatures of 90, 100, and 120°C.

Research Team

The following are examples of this team's recent collaborations:

C.H. Mattus and L.R. Dole, ORNLTM-2005/xx, "Durability of Depleted Uranium Aggregates in DUCRETE Shielding Applications," Oak Ridge National Laboratory, UT-Battelle, LLC, Oak Ridge, TN, in editing 2005.

L.R. Dole, C.H. Mattus, M. Fayek, L.M. Anovitz, J.J. Ferrada, D.J. Wesolowski, D. Olander, D.A. Palmer, L.R. Riciputi, L. Delmau, S. Ermichev and V.I. Shapovalov, **ORNL/TM-2004/296**, *Cost-Effective Cementitious Material Compatible with Yucca Mountain Repository Geochemistry*, Oak Ridge National Laboratory, UT-Battelle, LLC, Oak Ridge, TN, December 2004.

C.H. Mattus. and L.R. Dole, *Testing the Durability of Shielding Concrete Containing Uranium Dioxide Aggregate*, Waste Management 03, Tucson, AZ USA, Waste Management Society, Waste Management Society, Tucson, AZ, USA, 02/23/2003-02/26/2003.

C.W. Forsberg and L.R. Dole, *An Integrated Once-Through Fuel Cycle with Depleted Uranium Dioxide SNF Multifunction Casks*, Proceedings of the Advances in Nuclear Fuel Cycle Management III Conference, Hilton Head Island, South Carolina, October 5-8, 2003, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6179, October 2003.

C.W. Forsberg and L.R. Dole, *Maintaining Chemically Reducing Waste Package Conditions in an Oxidizing Geochemical Environment*, Symposium II: Scientific Basis for Nuclear Waste Management XXVI, Boston, MA USA, Materials Research Society, 12/02/2002-12/06/2002.