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Results from drip tests designed to simulate unsaturated conditions in the proposed Yucca Mountain Repository are reported for an actinide-doped glass (reference glass ATM-10) used as a model waste form. These tests have been ongoing for nearly 7 years, with data collected on solution composition (including transuranics), colloid formation and disposition, glass corrosion layers, and solid secondary phases. This test is unique because of its long elapsed time, high content of thorium and transuranics, use of actual groundwater from the proposed site area, use of contact between the glass and sensitized stainless steel in the test, and the variety of analytical procedures applied to the components. Some tests have been terminated, and scanning electron microscopy (SEM) and analytical transmission electron microscopy (AEM) were used to directly measure glass corrosion and identify secondary phases. Other tests remain ongoing, with periodic sampling of the water that had contacted the glass. The importance of integrated testing has been demonstrated, as complex interactions between the glass, the groundwater, and the sensitized stainless steel have been observed. Secondary phases include smectite clay, iron silicates, and brockite. Actinides, except neptunium, concentrate into stable secondary phases. The release of actinides is then controlled by the behavior of these phases.

Introduction

Actinide-doped West Valley ATM-10 reference glass and sensitized 304L stainless steel have been reacted with liquid groundwater by using the Unsaturated Test Method (drip test) developed at Argonne National Laboratory. These tests, initiated in 1987 and still ongoing for several samples, are designed to evaluate the performance of glass waste forms in the proposed Yucca Mountain Site under potential waste form/water contact modes. While elemental release rates to solution have been reported for these tests, an analysis of reaction products and surface corrosion of the waste form components is important for a more complete understanding of reaction mechanisms and dynamics. Together, these data will provide constraints on long-term geochemical modeling of waste form performance and waste package design in the repository.

The proposed Yucca Mountain repository site is located in a hydrologically unsaturated zone composed of welded and devitrified tuff. Initially, the stainless
steel pour canisters are expected to maintain their integrity, and thus liquid water is not anticipated to make contact with the glass. At later times, when the temperature has cooled to below the boiling point of the groundwater and the canisters have potentially been breached, water vapor and liquid water may contact the waste glass. It is this scenario, where glass, stainless steel, and water (liquid and vapor) interact, that the drip test is designed to simulate.

Experimental Method

Actinide- and technetium-doped glass (ATM-10) was received from the Materials Characterization Center (MCC) at Pacific Northwest Laboratory. The composition of the glass is given in reference 2 and, at the time of test initiation, ATM-10 was the reference glass for the West Valley Demonstration Project (WVDP). While the reference glass for the WVDP has now changed, the composition of ATM-10 is still representative and contains the components (e.g. $P_2O_5$, $ThO_2$) that affect radionuclide release.

The ATM-10 glass was received in the form of cast bars, which were crushed and recast into gently tapered cylinders, approximately 16.0mm diameter at the top and approximately 20mm high. The ATM-10 glass is held in place for the tests by a waste form holder made of two disks of 304L stainless steel, both of which had been perforated with holes to allow free contact with the dripping water. These were held in place on the top and bottom of the glass by two 304L stainless steel pins. The 304L components were sensitized by annealing for 24 hours in a 550°C oven. Their final color was a deep blue. A complete description of the apparatus is given by Woodland et al.3 The ATM-10 glass along with its 304L stainless steel holder is referred to as the waste package assembly (WPA).

Every 3.5 days, approximately 3 drops (0.075 ml) of groundwater from the J-13 well that is pre-equilibrated at 90°C with tuff (EJ-13 water) is injected into the airtight vessel, where it contacts the WPA. The entire apparatus is enclosed in a 90°C furnace except when samples are taken.

Every 26 weeks or upon termination, the water is collected from the vessel for elemental analysis by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) or ICP/mass spectroscopy (MS) and alpha spectroscopy. In the terminated tests, the WPA components were disassembled and weighed, then photographed and stored in labeled containers awaiting analysis. Eight of the tests were terminated in pairs after 12.5, 26, 39, and 52 weeks. Analyses performed on the solid test components include optical microscopy, scanning electron microscopy (SEM), and analytical transmission electron microscopy (AEM). These microscopic techniques allow determination of the size and distribution of reaction products and corrosion damage. Elemental analyses by energy dispersive X-ray fluorescence spectroscopy (EDS) and electron energy loss spectroscopy (EELS); in selected cases, crystal structure was determined by electron diffrac-
tion (ED). The tests, identified as the "N3 Tests," are summarized in Table 1. Tests N3#1 through N3#8 have been terminated, and the solid components from these tests have been analyzed. Tests N3#9 through N3#12 remain ongoing, with solution analyses being performed at each sampling period. N3#11 is a blank (control) test, containing no waste form, and is used to monitor the performance of the groundwater injections into the test vessels.

Table 1. N3 Test Sample Identification.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Description</th>
<th>Date Started</th>
<th>Date terminated</th>
<th>Cumulative Test Period (weeks)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N3#1</td>
<td>Batch</td>
<td>7/6/87</td>
<td>10/1/87</td>
<td>12.5</td>
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<td>Batch</td>
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<td>10/1/87</td>
<td>12.5</td>
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<td>Batch</td>
<td>7/6/87</td>
<td>1/4/88</td>
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</tr>
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<td>N3#5</td>
<td>Batch</td>
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<td>4/4/88</td>
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<td>4/4/88</td>
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<td>7/4/88</td>
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<td>&gt;400</td>
</tr>
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<td>7/6/87</td>
<td>ongoing</td>
<td>&gt;400</td>
</tr>
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<td>N3#11*</td>
<td>Continuous-blank</td>
<td>7/6/87</td>
<td>ongoing</td>
<td>&gt;400</td>
</tr>
<tr>
<td>N3#12</td>
<td>Continuous</td>
<td>10/6/87</td>
<td>ongoing</td>
<td>&gt;400</td>
</tr>
</tbody>
</table>

*N3#11 is a blank test, that is, contains no glass waste form or holder.

Results and Discussion

Elemental release into solution from the continuous N3 Tests was reported through 345 weeks by Bates et al. 1; selected data are reproduced in Figure 1. Lithium, boron, and neptunium serve as benchmarks for monitoring glass reaction, as they are not expected to form secondary phases. Normalizing their release to elemental concentrations and glass surface area gives remarkably similar values, consistent with this expectation. The relative release of uranium measured in this manner, however, is an order of magnitude lower, indicating the formation of uranium-bearing secondary phases. Importantly, Bates et al. reported complex release behavior for elements such as Si, Ca, Na, and K which could only be explained by taking into account their concentrations in the EJ-13 groundwater; in many cases, these elements were actually sorbed onto the waste package components, giving a negative net release. 1

Examination of the solid components from the terminated tests revealed evidence of interaction both with the groundwater and with the stainless steel holder. Visually, clay formation was apparent on the glass surfaces, as were rust-colored markings that matched areas where the stainless steel holder had experienced the greatest corrosion. The SEM observations revealed easily detectable amounts of a thorium-calcium-phosphate phase, later identified as brockite by
AEM. The brockite not only was found on the glass, but also on the bottom components of the stainless steel holder. Its appearance increased both in particle number and size with increasing test duration. Brockite is known to entrain actinides and can be transported within clay colloids when the particles are sufficiently small. Brockite has been observed in colloids from solution material taken from the continuous N3 tests.

Figure 1. Cumulative mass releases of lithium, boron, uranium, and neptunium from the continuous tests through 345 weeks, from Bates et al.

Analytical transmission electron microscopy was performed on micron-sized samples removed from the surfaces of the glass. Samples included chips of the glass surface, which often held an intact clay layer and secondary phases. These particles were imbedded in epoxy and thin-sectioned by ultramicrotomy for AEM work.

Figure 2 shows AEM micrographs of iron-silicate layers on the glass surface from regions where the glass was in contact with the 304L stainless steel. After 12.5 weeks, a very thin (<50 nm) layer of reaction had formed. By 54 weeks, the layer had grown to over 100 nm and was covered by an extended layer.
Figure 2. Iron-silicate layer formations on the surfaces of the N3 Test glass that had contacted the sensitized 304L stainless steel holder; (a) after 12.5 weeks (N3#1) and (b) after 52 weeks (N3#8).

(>200 nm) of smectite-type clay. The glass appears “chattered,” having fractured periodically as it was thin-sectioned. The surface layers, being softer, frequently remain intact and are representative of the original surface.

The AEM micrograph in Figure 3 illustrates the development of the dominant actinide-bearing phase, brockite. The appearance of this phase after only 12.5 weeks is followed by rapid growth to particles as large as 3 μm across by 52 weeks. The large particles were observed by SEM. Careful examination by EELS revealed that the brockite concentrates rare earth elements by nearly 100-fold, most likely as +3 cations. The EELS technique provides increased sensitivity to heavy elements (to approximately 50 ppm) and ability to resolve spectra of rare earth elements better than EDS. Although brockite is known to entrain transuranics (as mentioned previously), Pu and Am are not observed by EELS. While Pu and Am are present in the glass at concentrations about ten times less than the rare earth elements, their absence in the EELS spectrum suggests that they are not concentrated as effectively in the brockite as are the rare earths. This could be due to oxidation state differences and suggests that care should be taken in using rare earths as surrogates for specific actinide elements.
Figure 3. Brockite particles from the N3 Tests after 39 weeks (N3#5). The brockite is attached to the top surface of the clay layer (the glass separated from the clay in the area shown, but had been on the opposite side of the clay from the brockite particle). Above are EELS spectra; note presence of Ce, La, and Nd.
In Figure 4, the formation of smectite-type clay is depicted in an AEM micrographs after 39 weeks. As the layer grows, it begins to develop a “backbone” structure, seen previously in other glass tests. This is believed to occur when the original clay layer starts to separate from the glass, allowing new clay to form in the void left as the glass continues to etch. The clay has a much simpler elemental composition than the glass, being depleted in alkalis and actinides (Th, U, and Am) and somewhat enriched in Fe, Al, and Mg. Also note that an unusual thorium-titanium-silicate secondary phase, distinct from the clay, appears between the glass and the clay in the micrograph of the 39-week test. This thorium-titanium-silicate phase appears to be completely amorphous, giving no crystalline diffraction pattern whenever it is observed, and is probably related to
the metamict mineral davidite. It also is devoid of rare earths, further distin-
guishing it from the brockite. The davidite has been observed within cracks or
near-surface voids in the glass. This observation suggests that it either forms
colloidally, collecting where the flow of liquid is restricted, or that it forms in situ,
where liquid water concentrates dissolved cations. The key observation in
these studies is that during reaction the actinide elements migrate through the re-
acted layer and, except for neptunium, concentrate in stable secondary phases.
The release of these elements is then controlled by the behavior of these phases.

Conclusions

Long-term integrated tests of an actinide-doped reference waste glass under un-
saturated post-containment conditions have revealed complex interactions
among the groundwater, sensitized stainless steel waste form holder, and the
glass. Secondary phases consist mainly of smectite clay, iron silicates, brockite,
and davidite, the latter two incorporating Th, U, and possibly transuranic ele-
ments into their structure. The importance of using a realistic test procedure and
components is revealed by the resulting products and disposition of transuranics
during glass corrosion.

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