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THE PERFORMANCE OF ACTINIDE-CONTAINING SRL 165 TYPE
GLASS IN UNSATURATED CONDITIONS

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ABSTRACT

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As part of the effort by the Nevada Nuclear Waste Storage Investigations (NNWSI) Project to evaluate the volcanic tuff beds of Yucca Mountain, Nevada, as a repository for the permanent storage of high-level nuclear waste, the interaction of actinide-doped Savannah River Laboratory (SRL) 165 type glass with the unsaturated repository environment has been studied. The NNWSI Unsaturated Test method has been used, and the results from batch and continuous tests completed through 18 months demonstrate that several interactions are important for controlling both the reaction of the glass and the release of radionuclides. These interactions include (1) the reaction between the glass and moist air with interludes of liquid water contact, which results in the release of alkali metals from the glass; and (2) the reaction between standing water, glass, and presensitized 304 L type stainless steel which results in breakdown of the glass matrix and the release of radionuclides from the glass-metal assemblage. A comparison of the results of the Unsaturated Test with those of parametric experiments illustrates the importance of presensitized steel in enhancing the glass reaction, and demonstrates the applicability of the Unsaturated Test to those conditions anticipated to exist in the NNWSI repository horizon.

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INTRODUCTION

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Investigation of the volcanic tuff beds of Yucca Mountain, Nevada, as a potential site for a high-level waste repository is a function of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. As part of this study the NNWSI Unsaturated Test has been developed as a method to obtain data on the release of waste components from the waste package in the NNWSI repository environment under conditions currently envisioned after the 300/1000-year containment period has elapsed. Specifically, the test will provide information to be used by the NNWSI project in licensing the NNWSI repository site. The test method will provide (1) data that describe the release of radionuclides from a specifically designed glass/container assemblage under strictly controlled test conditions, and (2) information concerning synergistic effects that may occur between waste package components. The test results can be used to determine interactions that are important when glass leaching occurs in an environment of air, water vapor, and liquid water.

Previously [1,2] a glass based on Savannah River Laboratory (SRL) frit 165 had been reacted using the Unsaturated Test method (F series tests). These initial results demonstrated that the test method was capable of producing repository-relevant results and that the extent of glass reaction depended strongly on interactions that occurred between waste package components. The greatest degree of reaction occurred when glass, standing water, and weld-affected 304 L stainless steel were in contact. When there was a strong interaction in the weld-affected area, the glass reaction was greater than when there was a weak interaction. The glass reaction was described as occurring via (1) a diffusional process that resulted in a fairly constant release of alkali metals from the entire glass surface, and by (2) matrix breakdown that resulted in the release of all glass components from the weld-affected area.

This first Unsaturated Test matrix served as a trial run of the test method, and several changes were made to the procedure to make the results more consistent and easier to interpret. The change that affected the glass reaction to the greatest extent was that the metal in contact with glass was subjected to a pre-test heat treatment process (24 hours at $550 \pm 10^\circ\text{C}$, followed by slow cooling) with the goal of imparting a uniform degree of sensitization to the stainless steel. Further details of procedural changes are provided elsewhere [3].

In this paper the results of the second Unsaturated Test matrix are presented. This matrix was done using the same SRL 165 type frit as used in the F series of tests, except for the addition of ^{237}Np , ^{239}Pu , and ^{241}Am to the current glass [3]. Batch tests have been completed through 52 weeks while the continuous tests are ongoing having been sampled through 65 weeks. Additionally, to help interpret the effect of varying selected test parameters, parametric experimentation was performed in conjunction with the Unsaturated Test. Discussed here are parametric experiments done to examine the effect of using presensitized metal on the glass reaction. The results of these experiments are compared to those from the Unsaturated Test.

EXPERIMENTAL

The apparatus used in the Unsaturated Test has been described previously [1], and a schematic diagram of the system is shown in Figure 1. The components of the test apparatus are the test vessel, which provides for collection and containment of liquid and support of the waste package; the waste package assemblage (WPA), which consists of the waste form and perforated, presensitized, metallic components representing the pour canister; and a solution feed system to inject test water. The test is performed at 90°C .

The WPA is contacted intermittently by small measured amounts (drops) of repository water that has been preequilibrated with tuff at 90°C . The nature and degree of radionuclide release from the assemblage are determined by collection and analysis of the water that has contacted the

1. Body
2. Nut
3. Cap
4. Retainer Top
5. Retainer
6. Teflon Gasket
7. Swagelok Tubing

Figure 1. Schematic Diagram of Unsaturated Test Apparatus

package and by surface analysis of the assemblage components. Materials interactions are noted, and secondary alteration products which influence the nuclide release from the assemblage, are identified.

The test schedule incorporates batch and continuous testing. In the batch mode, tests are terminated at 13-week time intervals up to 52 weeks. The test apparatus is disassembled, and analyses of both the solution and components are performed. In the continuous mode, the WPA (including liquid associated with the assemblage) is transferred to a new test vessel at 6.5 week intervals, and the test is continued. Analyses are done on the solution in the old vessel. With the continuous-testing matrix, replication of solution analysis can be achieved. In addition, investigation of the test components is possible at the termination points, and yet the test can continue for an unspecified number of test periods or until information most useful to repository evaluation is obtained.

The parametric experiments [4] are done using an experimental design similar to that used in the Unsaturated Test, but the sampling periods are 13 weeks. The glass used in the parametric experiments does not contain the transuranic elements but otherwise is identical to that used in the Unsaturated Test.

RESULTS

The N2 Unsaturated Test series has been in progress over 65 weeks, and results of both batch and continuous tests are presented.

General Observations

Unlike the F Test series [1], where there was a marked disparity in the post-reaction appearance of the components from individual tests, the components from the N2 Tests were quite similar in appearance. The as-cut sections were uniform in appearance and the sides were reflective and smooth. After testing the top and bottom surfaces were noticeably reacted as shown in Figure 2. Reaction products accumulated in the regions of

Figure 2. Micrograph of (a) Top Section of Glass Showing Circular Regions of Iron Oxide and Hydroxide Formation, Mag. = 19x; and (b) Associated Retainer Section, Mag. = 1200x

non-glass metal contact. The majority of the reaction products were found surrounding the circumference of the holes in the retainer top. This is where standing water was observed to exist in some of the tests upon opening the vessels. The regions of glass/metal contact showed little evidence of coverage by alteration products except in some localized cases where channels appeared to exist between open areas (Figure 2a). The extent of coverage by the rust-colored alteration products appeared to increase between the 13- and 26-week samples, but was fairly constant thereafter.

The side surfaces of the glass retained their reflective appearance, but were covered with random watermarks. This appearance suggests that some water flowed over the sides, but that the strong interactions present on the top and bottom surfaces did not occur on the sides. During the sampling and termination periods water was observed standing on the bottom canister section at the interface between the glass and the metal. Only in a few samples was water observed on the top section of the waste form holder. It is believed that water collects in this area during the test but evaporates during the cool down period before the vessels are opened. Condensed water is always observed on the inner sides and tops of the vessels.

The pre-test appearance of the top and bottom waste form holders ranged from a uniform deep blue coverage to a mix of blue and gold. No measure of the extent of sensitization was made on the actual test specimens prior to testing. Such studies were done only after the test periods were complete.

After testing the top and bottom holders were discolored in the glass contact region, attaining a dark brown to rust-colored appearance. The interface where the glass contact ended was clearly marked by a buildup of precipitates (Figure 2b). However, the extent of precipitate coverage did not visually increase during the 52-week testing period. This observation agrees with the measured weight gains of the top and bottom canister sections which are constant throughout the 52-week test period.

Solution Analysis

The test solutions were analyzed either at the end of a test period or, for the continuous tests, during the sampling period. At the termination of a test the WPA was rinsed with 10 mL of high purity water, while for the continuous tests, only the water collected in the bottom of the vessel was analyzed. Thus, the terminated tests contained a rinsed component that was not present in the continuous tests. A blank test was also run in the continuous mode. The purpose of this test was to evaluate whether any cross-contamination of radionuclides had occurred during sample handling and to serve as a check of the EJ-13 water composition collected during a test period. The solutions were analyzed for components of the glass frit, the EJ-13 water, and for radionuclides.

The raw solution results can be used in two ways: (1) after correction for components present in the EJ-13 water the extent of glass reaction can be monitored, and (2) for the continuous tests an estimate of the composition of the water in contact with the WPA can be made. This water compositional information, in combination with the identification of alteration products formed on the test components, can be used to model the interactions that occurred during the test.

Glass Reaction

The extent of glass reaction is best measured by monitoring elements whose presence in solution can be associated mainly with the glass, as

opposed to the EJ-13 water or the metal components of the system. Such elements include Li, U, ^{237}Np , ^{239}Pu , ^{241}Am , and B.

Blank corrected solution results demonstrate several things:

- (1) All elements except Si show a net release from the glass. Silicon shows a net release in both 26-week batch tests and one 39-week batch test, but is abstracted from solution in the remaining tests.
- (2) An intercomparison of the batch test results indicates an apparent trend of increasing reaction for the 13- to 26-week tests. However, in the 39- and 52-week tests, the release value for Li and Na are comparable with the 26-week values, while the glass reaction as measured by B release and weight loss is actually less than for the 26-week results (Figure 3).
- (3) Normalized release values, calculated to compare the release behavior of different elements, indicates the alkali elements Li and Na are released from the glass at nearly equivalent rates which are larger than that calculated for B or the actinide elements (Figure 3 and Table I). These plotted releases are calculated based on the total surface area of the glass and on the measured amount of each element released from the WPA after rinsing. However, if the amount of Pu, Am, and U remaining with the metal components of the WPA is measured via complete stripping (Table I) of the metal and it is assumed that the release of these elements is associated mainly with the end sections of glass that contacts metal, then a modified $(\text{NL})_{\text{Pu,Am,U}}$ can be calculated (Table I).

In the continuous tests, where the components have not been rinsed before the solution is analyzed, several elements, including Ca, Mg, Na, and Si, are depleted in the analyzed solution compared to the starting EJ-13 water. Normalized release values for Li in the continuous tests are plotted in Figure 4. While these values will be slightly lower than the batch tests due to the lack of a rinse component, it is seen that there is continuous release from the glass through the 65-week time period.

Solution Composition

The composition of the solution that is in contact with the WPA can be estimated from the results of the continuous tests (Figure 5). This solution composition is important because it is the interaction between this solution and the waste package components that results in the formation of alteration products that are more stable than the glass and may over the course of the repository time period dictate the reactions that occur. After 65 weeks the concentration of Li is still decreasing while the concentrations of Na, Si, Ca, and B have leveled off.

Analysis of Test Components

To characterize the interactions that have occurred during testing, the components of the batch tests have been examined using SEM/EDS and XRD. The purpose of such characterization is to (1) in combination with the solution results, provide a description of the reaction progress; and (2) to catalog and identify, if possible, alteration products that form during the course of the reaction. Both of these issues need to be addressed to provide input to be used in projecting the performance of the waste form to repository time frame.

Figure 3. Normalized Release of (Δ) Li, (□) Na, (○) B, and (◇) wt loss for the N2 Batch Tests

Figure 4. Normalized Release of Li for Three Continuous Tests in the N2 Test Series

TABLE I
Normalized Release^a of Actinides from Unsaturated Test

Test Period (Weeks)	Solution Only				Solution + Acid Strip	
	(NL) _{Np}	(NL) _{Pu}	(NL) _{Am}	(NL) _U	(NL) _{Pu}	(NL) _{Am}
13	0.2	0.008	0.008	0.01		
13	0.4	0.015	0.018	0.06	0.3	0.4
26	1.3	0.024	0.022	0.21		
26	2.0	0.028	0.028	0.19	0.7	1.1
39	1.3	0.024	0.020	0.42		
39	0.4	0.008	0.008	0.04	0.5	0.7
52	0.6	0.014	0.012	0.18		
52	0.8	0.026	0.015	0.12	0.6	0.7

^aThe entire surface area of the glass was used to calculate (NL)_i for the solution only results, while only the surface area of the end sections of the glass were used in the Solution + Acid Strip calculations.

Figure 5. Log of the Concentrations of (□) Na, (◇) Si, (▽) Ca, (Δ) Li, and (○) B in the Test Solutions for the Three Continuous Tests in the N₂ Unsaturated Test Series

Glass

The major accumulation of reaction products occurred in the regions of standing water around the circumference of the punched holes (Figure 1). These products were identified by XRD as FeOOH and ferrihydrate ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$). Silicate phases rich in either Fe, Cr, Ni, or Mn were also observed (Figure 6a) but were not as prevalent as the iron oxide phases. Other phases identified on the surface by XRD and SEM/EDS included gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, SiO_2 cristobalite, orthoclase (KAlSi_3O_8), and possibly a sodium feldspar ($\text{NaAlSi}_3\text{O}_8$). Many other accumulations of reaction products were identified often with non-uniform compositions. These groups were amorphous to XRD and consisted of Si, Ti, Ca, Mg, Cl, and S in varying amounts. Other phases had unique compositions, but were either too small to analyze with XRD or gave amorphous patterns. Such phases with unique EDS spectra are showed in Figure 6a-c.

Metal

The metal in contact with glass was covered with an amorphous mat rich in Al and Si. Few distinct phases were observed in the glass/metal interface region. Most of the alteration products accumulated in areas of standing water and were identified as iron oxides. Several unique phases were observed on the metal including a solid solution of the calcite-type structure $\text{Ca}_{0.74}(\text{Mn}, \text{Mg})_{0.26}\text{CO}_3$ (Figure 6b). Other alteration products were too small to identify using XRD analyses. A SEM/EDS spectrum of a uranium-rich phase is shown in Figure 6e.

After surface analyses the metal samples were acid stripped to remove actinides, cross-sectioned, epoxy mounted polished, and subjected to an oxalic acid etch to determine the extent of sensitization that had been imparted during heat treatment (Figure 7a,b). It can be seen that two distinct levels of sensitization were imparted to the metal. In all the N series samples studied, carbide precipitation at the grain boundaries is evident in the interior of the sample. However, in the 13- and 26-week retainers the sensitization proceeds to within $10\text{ }\mu\text{m}$ of the surface of the steel, while in the 39- and 52-week tests the sensitization is to within only $40\text{ }\mu\text{m}$ of the surface. Note that the extent of B and wt loss reaction (Figure 3) measured in the 39- and 52-week results was less than noted in the 13- and 26-week tests.

Figure 6. Reaction Products that Form during Unsaturated Testing. (a) Glass surface, 39 weeks, 3000x; (b) glass surface, 52 weeks, 1500x; (c) glass surface, 52 weeks, 700x; and (d) metal surface, 52 weeks, 500x (e) metal surface, 13 weeks, 2500x

Figure 7. Micrographs of Polished Cross-Sections of Etched Stainless Steel Retainers for Unsaturated Testing. (a) 26-week bottom retainer, (b) 52-week top retainer, and (c) analog/parametric retainer. Magnification 750x

Parametric Experiments

Parametric experiments were done to study the effect of sensitization on the reaction process. In these experiments the 304 L ss was treated at $535 \pm 10^\circ\text{C}$ for 24 hours and cooled slowly. The ss used in these experiments was from a different heat than of that used in the N2 Tests, being richer in N (0.082/0.036 ppm) and depleted in C (0.016/0.022), both factors that increase resistance to sensitization [5]. The solution results for these experiments are shown in Figure 8. The batch experiments, which consisted of single experiments which terminated at 13, 26, 39, and 52 weeks, showed strong interaction with the metal only in the 52-week sample. Note that the releases of B and U for the 52-week sample are about ten times greater than would be estimated based on the earlier sampling periods; whereas the Li release is about 30% higher than would be predicted. In the continuous experiments there is not strong interaction, and the release of Li and B is not much different from what was observed in the F series continuous glass tests where there was also no strong interaction between the glass and metal.

DISCUSSION

The focus of this discussion will be interactions that affect the glass reaction and the behavior of the actinide elements. Further application of the data are described elsewhere [3]. The results of the several sets of Unsaturated Tests (F and N series) and the parametric experiments are consistent and indicate that there is a correlation between the degree of sensitization of the retainer sections, the extent of visually observed interaction, and the measured SRL 165 glass reaction.

In the N Unsaturated Test series, all the metal retainers showed some degree of sensitization accompanied by a strong interaction in the glass/metal interface region. The 13- and 26-week batch tests showed a slightly greater degree of sensitization than the 39- and 52-week batch tests and larger $(\text{NL})_i$ values were observed in the shorter tests.

In the 52-week parametric experiment, a strong interaction was also observed and the $(\text{NL})_i$ values closely matched those of the N series Unsaturated Tests. However, the remaining parametric experiments showed no sensitization, no strong interaction, and the $(\text{NL})_i$ values were near to those observed in the continuous F series Unsaturated Test for which no strong interaction was observed.

The sensitization process results in the precipitation of chromium carbides in the grain boundary regions and is dependent on the processing conditions and composition of the metal, and on the time and temperature

Figure 8. $(NL)_i$ Values from the Parametric Experiments (○) B Continuous, (●) B Batch, (□) Li Continuous, (■) Li Batch, (△) U Continuous, (+) U Batch, (X) is for Li from the continuous F1 Unsaturated Test Series

of the heat treatment process. No one time-temperature-transformation diagram has been constructed which encompasses all 304 L ss compositions. The conditions used in the present experiments were chosen to impart only a partial degree of sensitization to the metal. The observation that nearly identical heat treatment conditions resulted in radically different degrees of sensitization demonstrated the variability in sensitization that may be expected in the actual pour canisters.

After sensitization, the remaining chromium depleted metal is no longer resistant to oxidative processes, and metal (iron) oxides and silicates form where there is close contact between the glass and metal with a limited supply of water. These conditions apparently enhance the reaction of both the glass and the metal. As Si is released from the glass, the glass matrix breaks down releasing all the components of the glass nearly equally. Thus, those elements that are released mainly by breakdown of the glass matrix will have lower normalized release values in the tests that show a greater extent of metal sensitization. For example, B in the 13- and 26-week N2 batch tests is released to a greater extent than in the 39- and 52-week tests because of the slightly greater sensitization observed in those tests.

Note that this interaction process occurs only in the glass/metal contact region. The glass sides show no evidence of strong interaction and $(NL)_{Li}$, which should be controlled via an exchange process with water over the entire glass surface, is only moderately enhanced due to the matrix breakdown.

A strong interaction between glass and metal has been noted previously when ductile iron and glass were present in the same leaching container as the glass [6]. However, previous studies involving stainless steel and glass using standard leaching conditions showed no enhanced reaction due to the metal [6-8]. The exact nature of the increased interaction is being investigated further, but it is interesting to note that in several regions of strong interaction chloride containing precipitates are observed (Figures 6b and 6d).

The release of the actinide elements from the WPA follow the trend $Np > U > Pu \approx Am$. A similar trend has been observed in leaching studies of SRL 165 type glass under saturated NNWSI conditions [8]. Neptunium released to only a slightly less extent than Li, and showed little interaction with the metal components of the test. Uranium release to solution, although somewhat variable, was about five times less than that

of Np. Uranium was the only actinide for which a unique phase was detected using SEM/EDS (Figure 6e); although the U phase was not identified on all samples, which may explain some of the variability in U release. Plutonium and Am were found only sparingly in solution. Previous studies [9,10] indicate that these elements can sorb strongly to metal surfaces or can either sorb or be incorporated into metal oxide and hydroxide phases. The acid stripping process accounts for all the Pu and Am associated with the metal components (metal plus precipitates), and the total Pu and Am release is only slightly less than expected from matrix breakdown of the glass. The remaining Pu and Am is likely associated with the reaction products that remain on the glass surface.

There is no evidence that the sorption capacity of the metal components and alteration phases formed during the reaction process decreases with time, and the enhanced glass reaction that occurs due to metal sensitization may adequately generate new reaction phases that will incorporate Pu and Am as they are released from the glass.

CONCLUSIONS

Unsaturated testing with associated parametric experimentation of SRL 165 type glass has been completed for up to 65 weeks. These tests, which are specific to the NNWSI repository site, result in the formation of several identifiable reaction phases and reasonably constant elemental concentrations in solution. The data presented, in combination with pH and anion analyses (not presented), should be amenable to modeling using geochemical codes to project the long-term repository performance of glass waste.

Other data presented suggests that sensitized 304 L ss interacts strongly with glass in the presence of small volumes of repository water. This strong interaction results in matrix breakdown of the glass, thereby increasing elemental release up to ten times the amount observed without the interaction. However, the matrix breakdown does not necessarily result in equal release to solution of all the actinide elements. Neptunium is released to solution without interacting significantly with either alteration phase or metal components. However, U interacts moderately with the reaction products and forms unique stable phases which decreases its release to solution. The release of Pu and Am to solution is even more greatly reduced as these elements strongly interact with reaction products.

The Tests reported here are still in progress and will be continued to gain additional information regarding glass/metal/water interactions under unsaturated conditions.

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