THE BEHAVIOR OF ACTINIDE CONTAINING GLASSES DURING GAMMA IRRADIATION IN A SATURATED TUFF ENVIRONMENT

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CONF-841157--15

CONF-841157--15

DE85 002750

ABSTRACT

The influence of gamma irradiation on the reaction of actinide doped SRL 165 and PNL 76-68 glasses in a saturated tuff environment has been studied in a series of tests lasting up to 56 days. The reaction, and subsequent actinide release, of both glasses depends on the dynamic interaction between radiolysis effects which cause the solution pH to become more acidic and glass reaction which drives the pH more basic. The use of large gamma irradiation dose rates to accelerate reactions that would occur in an actual repository radiation field may affect this dynamic balance by unduly influencing the mechanism of the glass-water reaction. Comparisons are made between the present results and data obtained by reacting the same or similar glasses using MCC-1 and NNWSI rock cup procedures.

INTRODUCTION

The Nevada Nuclear Waste Storage Investigations (NNWSI) project is currently evaluating the volcanic tuff beds of Yucca Mountain, Nevada, as a repository for the permanent storage of nuclear waste. The description of this site is continuously being refined [1] and currently, while the repository horizon is described as unsaturated, the potential exists that, for brief interludes, pockets of condensed water may exist. If there were a premature canister failure during the waste containment period (0-300/1000 yrs) there would then be the potential for standing water to contact air and the waste form in the presence of a radiation field.

The probability of this sequence of events occurring is extremely low, especially since the heat generated during this period would likely drive any liquid water away from the waste package. However, since previous studies [2-6] have indicated that increased release from glass waste forms can occur when the air/water/glass system is exposed to a gamma irradiation field, such irradiation tests would provide data that could be used in evaluating repository performance.

Previous studies, done with air present during the reaction, used deionized water, simulated waste glass, and a limited test matrix that restricted the assessment of dynamic interactions that may occur. However, it was determined that increased glass reactivity is mainly attributable to the production of nitric acid which results in the solution becoming more acidic. Typically [2-6] the pH changes ~2 units depending on the total dose, the glass composition, and the ratio of the volume of gas to the volume of liquid (G/L).

The present series of experiments has expanded on this information base by monitoring the behavior of waste package components under unanticipated but possible conditions expected in the potential NNWSI repository site. Components included in the tests are defense and commercial glass formulations that contain both uranium and transuranic elements, 304 L stainless steel (ss), equilibrated J-13 water, and tuff rock. The tests provide information concerning the degradation of the waste form and the

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behavior of important waste elements in the presence of tuff, ss, and a gamma radiation field. The results are compared to similar tests done without the radiation field.

EXPERIMENTAL

Test Matrix

Interactive testing was done to incorporate waste package and repository components into the procedure. Additionally, tests were done using crushed glass to provide data for different SA/V conditions. Three test matrices were used:

(1) Two glass discs in pre-equilibrated J-13 water, SA/V = 0.3 cm^{-1};
(2) Two glass discs in pre-equilibrated J-13 water with crushed tuff, SA/V = 0.3 cm^{-1} with 0.2 gm (<100 mesh) of tuff;
(3) Crushed glass (+40 -80 mesh) in pre-equilibrated J-13 water, SA/V = 1.0 cm^{-1}.

Each matrix was run at 90°C for time periods of 7, 14, 28, and 56 days. Duplicate samples were run for each time period but otherwise MCC-1 protocol [7] was followed. Blanks were run for tests 1 and 3 using only pre-equilibrated J-13 water, and for test 2 using pre-equilibrated J-13 water in tuff.

Test Components

All the tests were done in 304 L stainless steel (ss) Parr reaction vessels. These vessels had a capacity of 22 cm^3 and were sealed with a compression fitting and a silicon rubber gasket. This combination provided a leak-free system where water losses after 56 days were ~0.01 gm. It also used a simple closure system that maintained its integrity for a total dose of up to 5 x 10^8 rad.

During testing, each vessel contained ~16 mL of water and at least 4 cm^3 of air. Calculations indicated that this volume of air would not become depleted in nitrogen due to nitric acid formation throughout the 56 day test period. This was observed, as the amount of NO_3^- and NO_2^- found in solution increased for each test period.

The J-13 water used in these tests had been reacted with tuff for two weeks at 90°C. This period of time is sufficient for most of the changes in water chemistry that result from equilibration of the tuff and J-13 water to occur [8].

The experiments were done in an oven whose temperature was controlled at 90° ± 0.5°C. The gamma irradiation field was produced by a ^{60}Co source and the dose rate, as measured inside the ss vessels was 2 ± 0.2 x 10^5 rads/hr. The entire matrix of 112 tests was completed within one 56 day period.

Sample Description

Each test matrix was done with four different glass types. These were:

(1) Savannah River Laboratory (SRL) 165 black frit to which uranium (1.0%), cesium (0.1%), and strontium (0.1%) had been added;
(2) SRL 165 (glass #1) to which ^{237}Np, ^{239}Pu, and ^{241}Am had been added;
(3) Pacific Northwest Laboratory (PNL) 76-68 glass ATM-1c which contains uranium (3.5%); and

(4) PNL 76-68 glass ATM-8 which contains added ^{237}Np, ^{239}Pu, and ^{99}Tc and some ^{241}Am.

The PNL ATM-8 and ATM-1c glasses have a somewhat different rare earth composition, having not been made from the same base frit. The exact composition and description of these glasses is given elsewhere [9].

The glass discs were core drilled from cast bars and were cut to size. All surfaces of the glass were, therefore, as cut and had a surface finish of ∿250 grit. The glass discs were supported on perforated 304 L ss stands, while the crushed glass and crushed tuff were on the bottom of the vessel.

Analyses

At the completion of each test the solutions were analyzed for pH, cations (inductively coupled plasma spectroscopy), anions (ion chromatography), uranium (atomic fluorescence), cesium (atomic absorption spectroscopy), and radionuclides (γ and α counting). The solid test components were analyzed by weight loss, scanning electron microscopy and associated energy dispersive x-ray analysis, secondary ion mass spectroscopy, and, for the actinide containing samples, ion-microprobe.

RESULTS AND DISCUSSION

These tests have resulted in an extensive collection of data which are presented in detail by Bates [9] and are selectively summarized here. In general, the precision of the solution analytical techniques is 10%, while radioactive counting procedures, which in some instances are affected by near background count rates, produce data of 15% precision.

Some experimental difficulties were encountered due to dissolved gas in the water that made pH and anion measurements more difficult; from the use of silicon rubber gaskets, which had the potential of introducing silicon to the system; and in the tendency of tuff to become distributed on the components due to turbulence when assembling the test. However, none of these effects were judged to significantly bias the results.

The blanks reflected predictable variation between the 7 and 56-day test periods. With additional total dose more nitric acid was generated. This reacted with the test components to give nitrite and nitrate ions in solution. The total amount of fixed nitrogen in solution increased with each time period, going from 7.6 to 19.2 ppm with no tuff present and from 7.6 to 17.3 with tuff present. The other anion concentrations were constant through 28 days and showed an ∿10% increase after 56 days. Cation concentrations were constant except for those that show a significant pH dependence, e.g., alkaline earths and uranium.

A complete interpretation of the reactions that have occurred will combine the results from solution and surface analyses [9]. However, a preliminary discussion, based on solution analyses, can be made as to (1) how much the glass reacted, (2) the magnitude and trend of radionuclide release, and (3) a comparison of these results with the behavior of similar glasses in different test conditions.

Glass Reaction

The reaction of the glass is most easily monitored by two effects, pH and weight change. These effects can then be correlated with the release of specific glass matrix elements. Figure 1 depicts the relationship between pH and time and Δmass and time.

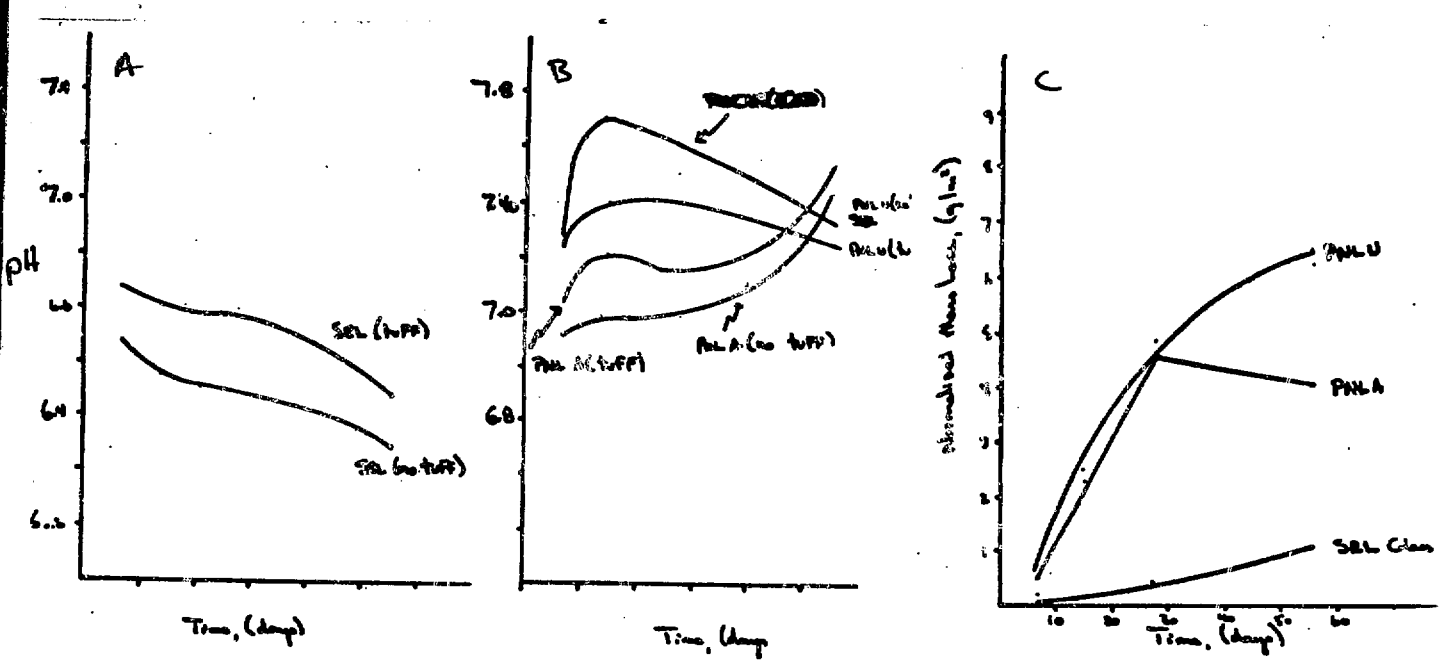

Fig. 1. The Relationship Between a) pH and Time for SRL Glass, b) pH and Time for PNL Glass, and c) $(NL)_{wt}$ and Time for SRL and PNL Glasses.

The SRL glass compositions are the same except for the actinide elements and, as expected, values for pH and Δmass for each glass were within experimental error and the data for each glass type were combined. However, the PNL glass compositions were different and the data for each glass type are presented separately.

Typically, when borosilicate nuclear waste glasses react with water, the pH of the leachate becomes more basic due to the diffusional release of elements, notably Na, into solution. As the pH becomes more basic the glass network begins to dissolve more rapidly. It is generally noted that in a neutral pH range of 6-8 glasses react very little.

In the present experiments the solution pH is affected not only by glass dissolution, but by irradiation induced nitric acid formation which drives the pH more acidic. The final solution pH is a dynamic balance between the two effects. For SRL glass the initial reaction of the glass with the water is small, and as the pH changes from 8.1 to 6.5, the mass loss increases directly proportional to the reaction time.

For both PNL glasses there is a greater initial reaction than for SRL glass, which drives the pH more basic after 14 days. However, for the 28 and 56 day periods PNL U and PNL A glasses produce different results. For PNL U glass the pH levels off then becomes more acidic and the mass loss continues to increase. For PNL A glass the pH levels off then becomes more basic, while between 28 and 56 days there is no additional net mass loss.

The same reactivity trends that were noted for pH and Δmass are corroborated by the releases for the more leachable elements. For SRL glass these are B, Li, and Na, while for the PNL glasses they are B, Mo, and Na. The normalized mass losses $(NL)_i$ for these elements are shown in Figure 2. For SRL glass the release for these elements is increasing almost linearly after 56 days, as was observed for $(NL)_{wt}$.

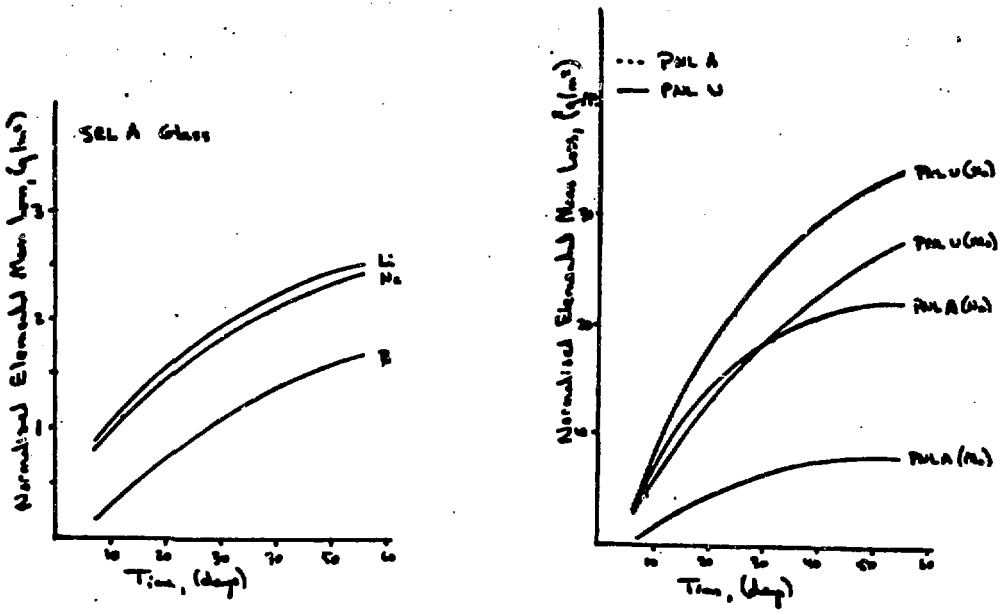

Fig. 2. Normalized Elemental Release of Frit Elements from a) SRL A Glass and b) PNL Glasses During NNWSI Gamma Irradiation Tests. Data plotted are for matrix #1, glass disk and no tuff.

For PNL U glass the release of these elements continues to rise at only a slightly reduced rate after 56 days, while for PNL A glass the glass degradation has nearly ceased.

When tuff is included in the system, the same pH trends and reactions are evident. The pH and mass changes are very sensitive to the glass composition as evidenced by the different reactions of PNL A and PNL U glasses. Hopefully surface analysis of the reacted glass will provide additional indication as to what process is controlling the reaction.

Radionuclide Release

In these experiments the behavior of both the short half-life radionuclides and the actinide elements are of interest because the release being examined would occur during the containment period. Radionuclide release for selected elements is presented in Figure 3. The values are based on the total amount of each element detected in solution, including that which is stripped from the stainless steel test components. The amount associated with the tuff is not included.

For SRL glass the normalized release of Am and Pu is the lowest of the measured elements and is approximately ten times less than that of Li, the element with the largest normalized release. The trend for Am and Pu release is toward a markedly decreasing rate, while that for the major frit elements Li, B, and Na is only decreasing slightly. Total U in solution is also still increasing although its total normalized release is about three times less than that of the frit elements. It is likely the Am and Pu release is being affected by saturation constraints, which are, in part, controlled by the solution pH. The pH has decreased only slightly through the test.

For PNL A glass the release of all elements has been drastically affected between the 28 and 56 day periods. After 28 days the total release of all elements (Figure 3) is increasing, but after 56 days, there is actually less Pu, Am, Np, and U in solution than after 28 days, while the total release of Cs and the major frit elements has only slightly increased. This behavior may correlate with the pH reversal toward a more basic solution that occurred after 28 days and would indicate that back precipitation of insoluable components may impede the further degradation of the glass. Elemental profiling may help explain this observation.

Comparison with Other Tests

Bazan and Rego [10] have investigated the leaching behavior of SRL 165 frit simulated waste glass in J-13 water. The water was pre-equilibrated with tuff for 30 days at 90°C prior to use. Their studies showed similar results for release of lithium for three systems: J-13 water, J-13 water plus tuff, and J-13 water plus tuff plus stainless steel. Data for (SA/V) = 0.3 cm^{-1} and 90°C reported by them will be directly comparable to data in this paper, except for minor differences in glass compositions. Normalized mass loss based on Li was 0.6 g/m^2 at 28 days and 0.9 g/m^2 at 56 days, which is about two to three times lower than the value found in our experiments in the presence of gamma radiation.

Bibler et al. [11] measured release rates from SRL 165 frit glass in J-13 water at 90°C at SA/V = 1.0 cm^{-1}. They did not pre-equilibrate the

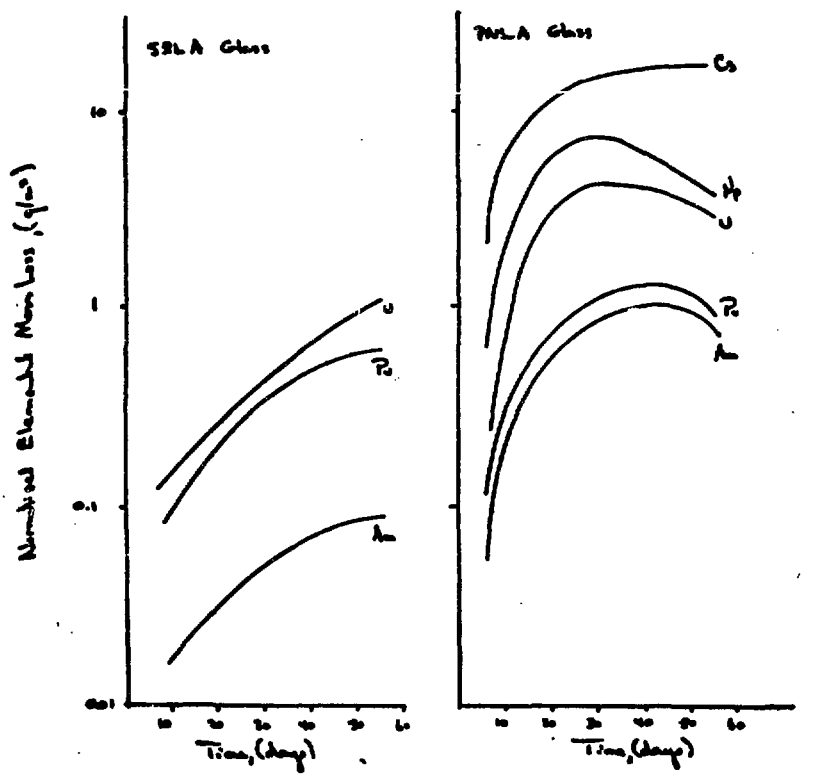

Fig. 3. Normalized Elemental Release of Important Radionuclides from a) SRL A Glass and b) PNL A Glass During NNWSI Gamma Irradiation Tests.

water with tuff. This would be expected to cause somewhat higher initial dissolution rates for the glass because the leachate would have a lower initial silica concentration. Data for Li release from a radioactive "sludge-only" glass showed normalized mass loss of 0.8 g/m^2 after 7 days and 1.8 g/m^2 after 14 days. Both non-radioactive and radioactive glass samples had similar release rates at 28 days with mass loss based on Li being approximately 2 g/m^2. In order to compare these data to the results reported here we must scale the reaction time to adjust for differences in SA/V. Using the (SA/V)(time) scaling parameter, 8.4 days at 1 cm^{-1} should correspond to 28 days at 0.3 cm^{-1}, and 16.8 days at 1 cm^{-1} to 56 days at 0.3 cm^{-1}. This suggests that direct comparison of the 7 and 14 day Bibler et al. [11] data with the 28 and 56 day gamma radiation results should be reasonable. The Bibler et al. [11] data are lower than the results reported here, which suggests that the gamma radiation of 2×10^5 rad/hr may have increased the glass dissolution. The results of Bibler et al. [11] showed similar leaching behavior for two SRL 165 frit glasses that had fairly large differences in composition. This suggests that the lower release rates found by them are probably not due to minor differences in composition of the glass used in our work in comparison to theirs.

The three sets of data, with the 1.0 cm^{-1} data scaled to the equivalent SA/V = 0.3 cm^{-1} reaction times, show a range from 0.6 g/m^2 to 1.6 g/m^2 at 28 days, and 0.9 g/m^2 to 2.3 g/m^2 at 56 days. The gamma radiation may increase the glass dissolution rate somewhat, but the differences between the Bazan and Rego [10] and Bibler et al. [11] nonradioactive glass data are at least as large as any differences that might be attributed to radiolysis effects.

CONCLUSIONS

It is apparent that in the present tests, the parameters that control the reaction of glass with water are dependent on the dynamically occurring processes of glass dissolution and nitric acid generation. Anything that artificially upsets this balance will unnaturally affect the degree of reaction. Thus, if a gamma field, larger than expected in the repository, is used to "accelerate" the reaction, the actual effect may be to alter the mechanisms by which the glass reacts. Nitric acid generation would be accelerated by the larger dose rate, and this may overcome the glasses' buffering action and cause dissolution of selected glass constituents that might not occur with lower dose rates. Alternatively, gamma-irradiation tests done using deionized water as the starting solution begin with an initial pH of ~5.8 and quickly become more acidic. This may introduce pH conditions that would not be attained using actual repository dose rates and repository waters, thereby artificially influencing glass leaching.

In the present experiments, a dose rate of 2×10^5 rad/hr was used. This is the rate expected for freshly generated commercial waste, but is ~5 to 10 times larger than expected for SRL glass. Of course, the actual dose rate would depend on when the waste package was prematurally breached, and the nature of the glass/water/air interaction would depend on that dose rate. The present experiments indicate that a generic prediction of the repository behavior would be difficult. Perhaps, using expected NNWSI conditions, the effect of gamma-irradiation would be to moderate the reaction between glass and water by exerting an influence toward keeping the system at a neutral pH. The effect of dose rate on the bufering action of the system will be investigated in future experiments. These will provide an indication of the limits on accelerated testing conditions that will preserve relevant reaction mechanisms.

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