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INTEGRATED TESTING OF THE SRL-165 GLASS WASTE FORM

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ABSTRACT

Integrated testing of the important components of a glass waste form waste package has been performed in order to gain a better understanding of the processes of radionuclide release and transport in the near field environment. Based upon an interpretation of the depth of penetration of hydrogen in reacted SRL-165 glass we have modeled the radionuclide release from the glass as a combined process of (1) the diffusive exchange of alkalis and boron in the glass for hydrogen species in the solution ($D=10^{-16}$ cm²/s) and (2) surface dissolution. Surface dissolution controls the release of components not exchanged by diffusion and takes place at a rate of 1.5-3.0 $\mu\text{m}/\text{yr}$. Subsequent to release the radionuclides may remain in the leach solution, diffuse into the tuff, or precipitate as secondary phases. Precipitation is particularly important for plutonium and americium. Diffusive transport of radionuclides through the tuff takes place at an extremely slow rate, $D=10^{-16}$ cm²/s. As such, the mass of radionuclides incorporated in the tuff by diffusion during the tests is inconsequential relative to that in the leach solution (with the exception of plutonium) and can be ignored in mass balance calculations. Mass balance calculations based upon the release of radionuclides by surface dissolution of the glass waste form are in good agreement with observed solution chemistry when allowances are made for a pulse of dissolution early in the tests. This pulse may be due to either the rapid dissolution of high-energy surface features early in the integrated tests, or an initially high surface dissolution rate that decreases with time as silica saturation is approached [1], or a combination of the two.

INTRODUCTION

The prediction of waste form performance under repository conditions for 10,000 years must be based on the results of laboratory testing of at most a few years duration. The predictions can only be successful if a thorough understanding of the processes at work in the test system and the relationship of these processes to the repository case can be obtained. As part of the Nevada Nuclear Waste Storage Investigations Project (NNWSI), we have conducted an integrated test of the reference glass waste form planned for use by the Defense Waste Processing Facility. The test included the glass waste form, reference NNWSI groundwater, and a polished wafer of Topopah Spring tuff, the candidate repository rock. The test was run in a stainless steel reaction vessel, to represent the container material, and in a gamma radiation field to provide information on the effects of radiolysis. At the conclusion of the tests, all components in the system were examined to determine the extent of alteration caused by the reaction conditions.

The purpose of this study is to develop an understanding of the variation in leachate solution chemistry in terms of the dissolution, precipitation, and diffusion properties determined by direct analyses of the individual components in the integrated tests. By performing direct analysis of system components we hope to obtain the necessary mechanistic data to aid in long-term extrapolation of laboratory test data.

DESCRIPTION OF THE EXPERIMENT AND SOLUTION CHEMISTRY RESULTS

The experiments described here are part of a larger study of the effects of gamma irradiation on the dissolution of a waste glass proposed for use by the Defense Waste Processing Facility (DWPF). The full test matrix included testing of samples of glass reacted with a reference groundwater (J-13) that had been equilibrated for two weeks at 90°C with crushed tuff (producing eJ-13 water), both in the presence of Topopah Spring tuff and in the absence of tuff. The glass used was made from SRL-165 black frit that had been doped with uranium, or with uranium and other actinides. In both cases the frit was also doped with cesium and strontium. Blanks using only eJ-13 water or water plus tuff were also run.

The experiments were run in temperature controlled ovens set at 90°C in the Argonne National Laboratory (ANL) gamma radiation facility. The ovens were positioned to achieve a dose rate of 1×10^4 R/hr inside the 304L stainless steel test vessels. The glass samples (2 disks per vessel) were laid on a stainless steel support rack, leaving room below it for a wafer of tuff that had been polished on one side. The tuff wafer was positioned on the bottom of the vessel with the polished side facing up. All experiments were run in duplicate for periods of 14, 28, 56, 91, and 182 days. The glass surface area to solution volume ratio was 0.3 cm^{-1} . Complete details of the test, including a full tabulation of analytical results are given by Abrajano et al.[2]. Details of a similar series of experiments conducted with a dose rate of 2×10^5 R/h are given in Bates et al.[3].

Solution concentrations for lithium, uranium, and plutonium are given in Table I. The final solution pH for all tests, including those with tuff but without glass was in the range 6.5 to 7.5. Plutonium analyses were done in three different ways: using unfiltered directly sampled leach solution, using filtered (5 nm filter) directly sampled leach solution, and using leach solution acidified in the test vessel. Comparison of the results from these three solution types showed that more than 90 percent of the plutonium

Table I: Solution concentrations (mg/l) for lithium, uranium, and plutonium in experiments using equilibrated J-13 water with polished Topopah Spring tuff wafers, alone or with uranium doped or actinide doped SRL-165 glass. Plutonium concentrations are for the unfiltered solutions and do not include material plated on the vessel walls.

Sample ID	Time (days)	Li conc.	U conc.	Pu conc.
NO GLASS				
G-251	14	<0.22	<.007	na
G-253	28	<0.39	<.007	na
G-258	91	0.20	<.002	na
URANIUM GLASS				
G-211	14	1.24	0.386	na
G-213	28	1.70	0.491	na
G-215	56	2.41	0.625	na
G-217	91	3.22	0.703	na
G-220	182	3.75	0.771	na
ACTINIDE GLASS				
G-231	14	0.86	0.244	1.63E-04
G-233	28	1.52	0.445	5.47E-04
G-235	56	2.08	0.504	8.12E-04
G-237	91	2.51	0.577	1.16E-03
G-239	182	3.81	0.587	5.38E-05

recovered was precipitated on the stainless steel reaction vessel walls. Of the plutonium found in the unacidified solutions, generally more than 50 percent was in a form that would not pass through the 5 nm filter. Results for americium were qualitatively similar to those for plutonium.

The other major cations in solution were sodium (50 to 60 ppm), silicon (generally 40 to 80 ppm Si), and calcium (10 to 18 ppm). Results from the acidified solution analyses were calculated as normalized release rates. These showed that releases followed the pattern of $\text{Li} \geq \text{Na} \geq \text{B} \geq \text{Si}$. In experiments without tuff, the normalized release of uranium was similar to that for boron; in the experiments with tuff present, the normalized uranium release was somewhat less than that for boron. Total plutonium release, including the greater than 90 percent found on the vessel walls, was less than that for boron. These normalized releases do not include the amount of material sorbed onto the tuff or back reacted onto the glass.

HYDRATION PROFILES

In-depth analysis of the hydrogen concentrations in hydrated SRL-165 glass was performed in an attempt to 1) determine the mechanism or mechanisms by which the glass is hydrated and 2) to obtain an estimate of the rate at which the glass surface is dissolved that is independent from that which could be obtained from solution chemistry. The dissolution rates obtained from these experiments provide a measure of the "source term" to be used in subsequent mass balance calculations.

In this study the reaction,

was used to obtain depth profiles of hydrated glasses. This reaction has a narrow (6 KeV) isolated resonance at 6.405 MeV. The sample is bombarded by monoenergetic ^{15}N ions from a linear accelerator. At 6.405 MeV the nuclear reaction occurs at the surface of the sample. At higher energies the reaction occurs within the sample at a depth where the ^{15}N energy falls to that of the resonance energy. The gamma-ray intensity is proportional to the hydrogen concentration. Hence, a plot of gamma intensity versus incident energy can be related to concentration versus depth.

The hydrogen profiles were obtained from SRL-165 samples that were hydrated between 7 and 91 days at a gamma-dose rate of 1×10^4 R/hr and from runs previously performed at 2×10^5 R/hr [3]. Henceforth, these runs are referred to as the low-dose rate and high-dose rate experiments, respectively, and are shown in Figures 1 and 2. The most important feature of these profiles is the development of a steep concentration gradient at the diffusion front. This feature is indicative of a diffusion process where the effective diffusion coefficient has a strong dependence on the concentration of the diffusing species, in this case H_2O . Depth profiles for Na, Li, and B obtained by SIMS analysis [1] are complementary to that of H indicating that hydration takes place by interdiffusion of hydrogen for these cations.

To verify that the advance of the hydration front is indeed diffusion controlled, its thickness [measured as the distance from the surface to a depth where the hydrogen concentration drops to one-half of the surface value, $x(C/C_0=0.5)$] has been plotted versus the square root of time (Figures 1 and 2). For short duration runs (< 28 d) these data yield a linear trend that extrapolates through the origin, substantiating diffusion controlled advance of the hydration front. The slope of the linear portion of these trends yields the effective diffusion coefficient $[x(C/C_0=0.5)=(Dt)^{1/2}]$, which is $1 \times 10^{-16} \text{ cm}^2/\text{s}$ for both low and high-dose rate experiments. This result is similar to that obtained from soda-lime glass hydrated at 90°C in deionized water [4]. The data also demonstrate that the radiation field does not influence the diffusive transport of hydrogen through these glasses.

Figure 1. Hydrogen depth profiles in SRL-165 glasses leached in a gamma field of 2×10^5 R/hr. Inset, plot of the distance from the surface to where the hydrogen concentration drops to 50 percent of the surface value versus the square root of run time.

Figure 2. Hydrogen depth profiles in SRL-165 glasses leached in a gamma field of 1×10^4 R/hr. Inset, plot of the distance from the surface to where the hydrogen concentration drops to 50 percent of the surface value versus the square root of run time.

At longer run times (228d) the depth to the hydration front remains nearly constant. This approach to "steady-state" results when the rate of advance of the diffusion front (decreasing due to the square-root dependence on time) approaches the rate of surface dissolution. Hence, the diffusion front no longer advances with respect to the surface. This result is extremely important as it allows us to determine the surface dissolution rate from its equivalence with the advance of the diffusion front. In practice, the calculation of dissolution rate depends upon identification of the onset of steady-state behavior. Although the number of data presented here is admittedly small, it is still possible to constrain the dissolution rate quite closely. For the high-dose rate experiments defining the approach to steady state behavior at either 28 or 56 days results in dissolution rates of 1.5 and 2.4 $\mu\text{m}/\text{yr}$, respectively, while approach to steady-state behavior at 28 days in the low-dose rate experiments results in a dissolution rate of 3 $\mu\text{m}/\text{yr}$. These rates are somewhat slower than those obtained for soda-lime glasses (9 $\mu\text{m}/\text{yr}$) hydrated at 90°C in deionized water [4]. For the subsequent mass-balance calculations dissolution rates of 1.5 and 3.0 $\mu\text{m}/\text{yr}$ will be used. The effects of increased dissolution rates, e.g., those found in soda-lime glass, will also be considered. It is also important to note that the surface dissolution rate determined from the hydrogen profiles is that appropriate for intermediate to long time frames. During the initial stages of the test higher dissolution rates probably occurred. Abrajano and Bates [1] have concluded that the dissolution rate may vary due to the kinetics of "gel" layer formation. This causes the dissolution rate to decrease as silica saturation is approached. This variation will have important implications in mass balance calculations as the mass released per unit time by surface dissolution will be greatest early in the experiments.

DIFFUSION PROFILES IN THE TUFF WAFERS

At the conclusion of the glass dissolution experiments, the rinsed tuff wafers were sent to LLNL for examination using the ion microscope. Prior to examination, a thin coating of high purity aluminum was applied to the polished side of the wafer to reduce sample charging. In one case the unpolished side was also examined to determine whether polishing the wafer affected the diffusion results; the measurements on the unpolished surface gave diffusion coefficients indistinguishable from those obtained on the polished surface. Depth profiles were obtained for 24 mass numbers using a 25 μm diameter, negatively charged oxygen ion primary beam rastered over a 100 X 100 μm area. The beam was kept focused on the same location on the sample surface, thereby excavating a crater. The material sputtered from the crater produced secondary ions. The positively charged secondary ions were monitored to provide a record of count rate for each mass number versus time. A National Bureau of Standards trace element glass, SRM 612, was used to determine the secondary ion yield of the trace elements relative to that of Si. These relative ion yields were used to convert ratios of trace element to Si intensities to abundances [5]. Since no standard was available for plutonium, its relative ion yield was assumed to be identical to that of uranium. Estimated precision for relative concentrations within a single sample is +/- 10 percent, while absolute concentrations can be determined to within a factor of two. The sputtering rate is held constant during a profiling run, and at the end of the run the depth of the crater is measured using a Dektak model IIA. We estimate that the depths are accurate to +/- 5 percent of the calculated value shown on the profile plots.

Most of the elements that are released from the glass are present in the rock in substantial concentrations. It is generally impossible to detect diffusion of these elements from the solution into the rock. However, if an element is totally absent from the rock while at the same time present in the solution in reasonable quantities, diffusion or infiltration of that element from the solution into the rock will be relatively simple to detect. Plutonium is such an element; of 28 attempted profiles only one gave an ambiguous result. Uranium profiles are nearly as reliable as plutonium, but occasionally a crater appears to intersect a grain of material with high uranium content, thereby obscuring the diffusion profile. Lithium provides much less reliable data because of its higher abundance in the rock and its relatively heterogeneous distribution. Only about half of the profiles that found unequivocal evidence of diffusive transport of uranium and plutonium gave unambiguous results for lithium.

The concentration (C) versus depth (x) data were fit to a solution to Fick's 2nd Law for diffusion from an infinite source into a one dimensional semi-infinite medium with constant surface concentration, given by

$$C = C_0 \operatorname{erfc}(x/2(Dt)^{1/2}),$$

where C_0 is the surface concentration. From this fit, D, the diffusion coefficient was obtained and the true surface concentration of the rock determined. Two general types of profiles were obtained. The most common profile was a single diffusion curve, with the results for all three elements giving diffusion coefficients that were in excellent agreement. An example of this type is given in Figure 3. The second type of profile showed a break in the curve at an intermediate depth in the profile. This type of profile is seen most clearly for lithium, but the effect can also be seen in the companion profiles for uranium and plutonium, although it is less pronounced. This step is interpreted to be caused by a microcrack in the crater region. This crack would provide a rapid transport path relative to the matrix path, allowing some material to get to deeper locations in the wafer. The concentration of radionuclides in the crack may be different from that in the main volume of the solution. At the base of the crack, matrix diffusion would begin again. An example of this type of curve is shown in Figure 4.

Distribution coefficients were calculated for each of the elements for which a successful diffusion profile was obtained by dividing the concentration of the element in the surface layer of the rock by the concentration in solution. The results were very consistent except for the 182 day plutonium samples. The solution concentration of plutonium dropped sharply between 91 and 182 days (see Table I). When the distribution coefficients were calculated using a solution concentration of 0.001 ppm for the 182 day samples, the data were in agreement with the other samples. This suggests that the lowering of the plutonium concentration occurred near the end of the 182 day period. Details of the calculations for both diffusion and distribution coefficients are given in Phinney et al. [6].

The data for diffusion and distribution coefficients are summarized in Table II. Sample G-239 was reacted in the presence of the actinide-bearing glass for 182 days. Nine profiles were obtained from the rock surface for this sample; thus we can get a meaningful average and standard deviation for the single rock sample. The average apparent diffusion coefficients for all three elements are in remarkable agreement. The distribution coefficients for plutonium and uranium are both much higher than the results obtained by batch sorption studies [7]. The distribution coefficient for lithium is lower than that for uranium, as would be expected. The most probable reason for lithium to show any tendency to be retarded during transport is ion exchange with the alkali feldspar in the rock.

Figure 3. Depth profile for Li, U, and Pu in tuff reacted with actinide doped SRL-165 for 182 days. The curves are the model diffusion profiles determined from these data.

Figure 4. Depth profile for Li in tuff reacted with actinide doped SRL-165 for 182 days. The curve is the model diffusion profile determined from the near surface data ($< 0.6 \mu\text{m}$). The divergence between the model profile and the data at depth may be due to a diffusional "short-circuit" along a microcrack (see text).

The data for all samples, including G-239, were also averaged. The results, as shown in Table II, gave a higher value for the diffusion coefficient by about a factor of four. The values found for the distribution coefficients are indistinguishable from the single sample data.

The product of the apparent diffusion coefficient and the distribution coefficient should give a diffusion parameter that eliminates the effects of retardation by sorption or ion exchange. This product is shown in Table II. For both sets of data, the values show a wide range for the product, rather than the agreement that would be expected if diffusion were significantly slowed by the process of solid and liquid partitioning. In contrast, the measured apparent diffusion coefficients were in excellent agreement. This suggests that the process that limits the diffusion rate for all three elements is the same and that it is much slower than the effects due to element redistribution among the phases.

Table II: Summary of apparent diffusion coefficients (D_{app}), distribution coefficients (K), and their product. Diffusion coefficients are in units of 10^{-16} cm²/sec. Distribution coefficients are in units of ml/gm.

Element	D_{app}	Std. Dev	Dist.Coeff	Std Dev.	Product*
G-239 data only					
Lithium	0.34	0.47	7	3	1.8
Uranium	0.31	0.22	28	12	6.9
Plutonium	0.4	0.18	4890	3002	1670
All Data for samples with glass					
Lithium	1.7	2.6	16	13	36
Uranium	1.5	1.8	34	22	51
Plutonium	1.4	1.5	7610	6578	10300

* Product is the average of individual product values

Integration of the diffusion profiles over the surface of the tuff wafers yields the amount of material actually incorporated in the tuff surface by diffusive transport. For a surface concentration of 8 ppm Pu, the total amount of Pu diffused into the polished surface of a tuff wafer after 91 days is 3.4×10^{-9} g. The Pu concentration measured by alpha-spectrometry in the polished surface of a tuff wafer from a duplicate experiment is 4.3×10^{-9} g, in excellent agreement with that predicted from the diffusion profiles. The total amount of Pu in the unfiltered solution after 91 days is 1.7×10^{-8} g; therefore, the mass of Pu in the tuff is approximately 25 percent of that in the solution. However, it should be noted that most of the total inventory of Pu released is precipitated on the reaction vessel and recovered in the acidified solutions. In the 91 day experiment the acidified solution contained 3.5×10^{-7} g of Pu. The combined mass of Pu diffused in the tuff and that in solution represents only 6 percent of the total inventory released and so the amount of Pu in the tuff wafer is not significant in the mass balance calculations for this experiment. In the absence of precipitation, incorporation of Pu in the tuff by diffusion would be an important process for Pu. Its importance will be even greater on a repository scale where the available tuff surface area will be greatly increased relative to that in these experiments.

MASS BALANCE

In this section we will attempt to model the experimentally determined leachate compositions (or, in some cases leachate plus acidified solution compositions) based upon the known sources and sinks of material within the system. As a means of simplification the SRL-165 glass is considered the only source of material in the system. In practice this requires that we restrict the discussion to components that have low concentrations in eJ-13 water and cannot be derived from rock-water interaction in large quantities. Since the eJ-13 water has already been equilibrated with the tuff, this simplification is justified. In-depth analysis of the tuff wafers has also demonstrated that the tuff is not a significant sink for materials in the system for elements other than plutonium. Hence, in the absence of precipitation on the glass, mass balance for these experiments can be modeled simply as the release of glass components to the leachate solution, provided that the amounts of materials precipitated onto the vessel walls and sample holders are included as "solution" samples. The input parameters to the model are (1) the geometry, composition and density of the glass cylinders, (2) solution volume, (3) experiment duration and (4) the leaching mechanism of the SRL-165 glass. The first 3 data are given by Abrajano et al.[2].

We have chosen to represent the leaching mechanism as a combination of alkali-boron-hydrogen interdiffusion and surface dissolution. The alkalis and boron will be released to the solution by diffusion while the majority of other components are released by surface dissolution. Therefore, the concentration of alkalis and boron in solution should vary linearly as the square root of time, while that of other components should display a linear variation with time. The alkali and boron release should not be retarded initially by the surface dissolution rate, since the alkalis and boron would be instantaneously and quantitatively removed from the surface once they reached it via diffusion. At present we do not have sufficient data to determine the chemical diffusion coefficients of the individual species (B^{3+} , Na^{+} , Li^{+} , H^{+} , H_2O^{+}) participating in the interdiffusion process, so a kinetic model for diffusive release will not be considered here.

Mass loss from the glass cylinders is largely a function of surface dissolution. We expect the interdiffusion process to have little effect upon mass loss if interdiffusion takes place by exchange of hydronium ions for alkalis and boron as opposed to exchange of hydrogen ions. The predicted mass loss from the glass cylinders is calculated from the density of the glass cylinder and the change in its dimensions due to surface dissolution at a constant rate for a known time. The dissolution rate used in the calculations is that determined from the hydrogen penetration rate data. The predicted mass losses for each of the two cylinders in a given experiment are compared to the observed values for these cylinders in Figure 5; predicted solution compositions are determined similarly by considering the amount of an element released by a certain mass loss and the solution volume. The variation of the predicted mass loss and the predicted solution concentrations in subsequent figures is virtually linear in time because the model uses a constant dissolution rate and the extent of dissolution is small. Therefore, the abscissa in these figures can also be viewed as a time axis.

The lines emanating from the origin display the predicted mass losses for surface dissolution rates of 9 $\mu\text{m/yr}$ (solid) and 3.0 $\mu\text{m/yr}$ (Figure 5). For both cases the fit to the observed data is poor. The model underestimates the release for short duration experiments and overestimates the release for longer duration experiments. The surface dissolution rate near the start of the experiments appears to be much larger than that inferred from the hydrogen profile analyses. One possible explanation is a higher dissolution rate due to lower silica concentration in the solutions for the early stages of the experiments [1]. Another possible mechanism is the rapid dissolution of low radius of curvature, high activity surface features produced during sample preparation. The amount of material released by such a process will vary from

sample to sample, but will always be reflected by an incremental early mass loss in each experiment. The result of both processes would be an early pulse of material delivered to the solution, which can be represented as a non-zero intercept in Figure 5. In order to test this hypothesis we assume that rapid dissolution processes instantaneously release $3-4 \times 10^{-4}$ g of material at the start of each experiment. The subsequent mass loss is determined by linear surface dissolution at the rates previously determined by hydrogen depth profiling, $1.5-3 \mu\text{m/yr}$. The results are shown as the cross-hatched region in Figure 5. The results are in good agreement with the majority of observed data; the greatest discrepancies are for short term experiments where the contribution of the initial release is proportionately largest. These processes should also be observed in the solution concentrations of components controlled by matrix dissolution, but may not be seen for the alkalis where rapid diffusive exchange should be the controlling factor.

Inspection of surfaces of all the experimental components has not revealed the precipitation of any uranium-rich phases, nor has uranium been significantly depleted by diffusion into the tuff wafers. Hence, the solution concentrations should reflect only the surface dissolution of the glass. The observed solution concentrations of uranium are plotted against the predicted values in Figure 6. The trends mimic those of the mass loss data indicating that uranium release may be controlled by bulk dissolution; however, there is significant curvature to the data, suggesting that there may be some diffusion process involved in the uranium release. Again, these trends cannot be reconciled without calling upon either a variable dissolution rate or an additional dissolution process early in each experiment. The initial U release used in Figure 6 is consistent with the initial mass loss observed in Figure 5. Subsequent linear surface dissolution at the experimentally determined rates predicts solution concentrations (cross-hatched region) that are in good agreement with the observed data. Plots of predicted versus observed Pu release yield results similar to that of U.

It should be noted that the variation in normalized uranium leachate concentration versus the square root of time is linear. This type of parabolic release is typically considered to be evidence of a diffusion controlled process. However, at this time, in-depth analysis of uranium in the glass surfaces is incomplete (Bates, unpublished data). Therefore, the possibility of diffusive loss of uranium suggested by the solution data cannot be corroborated by direct analysis at this time. Studies of cation self-diffusion in silicate melts and glasses has demonstrated that the mobilities of high-charge density cations such as U^{4+} and U^{6+} are low relative to those of the alkalis [8]. As such, we have chosen to consider uranium release as a dissolution controlled process. This assumption may change should uranium depth profiles in the hydrated glasses substantiate diffusive release.

Lithium should be released to the solution by alkali-hydrogen interdiffusion and, therefore, its concentration in the leachate solution should disagree with that predicted by the linear dissolution model. The trend of the data on a plot of observed versus predicted (equivalent to time) solution concentration (Figure 7a) displays a parabolic release curve for lithium. If a y-intercept of $1 \mu\text{g/ml}$ is assumed as the possible initial release, subsequent linear surface dissolution (cross-hatched region) fails to match the observed data. The concentration of lithium in solution has been plotted versus the square root of time in Figure 7b and displays a linear trend extrapolating through the origin. The solution data confirm the diffusive release of lithium that was determined by direct observation of glass hydration. Further, the zero intercept in Figure 7b indicates that the contribution of alkalis to solution due to rapid dissolution of surface features is small compared to early diffusive release of exchangeable alkali cations.

Figure 5. Observed mass loss from glass versus that predicted from linear surface dissolution of SRL-165 (the x-axis values are based upon a 9 $\mu m/yr$ dissolution rate). Solid symbols are from actinide doped runs, open symbols from actinide free runs. The solid and dashed curves projecting from the origin are for dissolution rates of 9 $\mu m/yr$ and 3 $\mu m/yr$, respectively. The cross-hatched region is that bounded by the lines for dissolution rates of 1.5 $\mu m/yr$ and 3.0 $\mu m/yr$ after an initial pulsed release of material.

Figure 6. Observed uranium concentration in solution versus that predicted from linear dissolution (x-axis is based on a 9 $\mu\text{m/yr}$ dissolution rate). Symbols as in Figure 5.

Figure 7. (a) Observed lithium concentration in solution versus that predicted from linear dissolution. Symbols and axes as in Figure 5. (b) Observed solution concentration versus the square root of run time.

CONCLUSIONS

All of the components in an integrated test of a glass waste form based on SRL-165 frit have been examined to determine the sources and sinks for materials released from the waste form and the other components present in the tests. Plutonium and americium were mainly found adhering to the reaction vessel walls and the sample supports [2]. A small, but significant, fraction of the plutonium was found in the tuff rock wafers that were included in the tests. Diffusion of uranium and lithium into the tuff was also observed, but the fraction of the total released U and Li that was found in the tuff was not large enough to affect mass balance calculations. Diffusion coefficients for Pu, U, and Li were small (10^{-16} cm²/s) and were indistinguishable for the three elements. Distribution coefficients between the rock and the solution averaged 16 ml/gm for Li, 34 ml/g for U, and 7610 ml/g for Pu. These values indicate that retardation of radionuclide migration by the tuff should be significant for U and Pu in the repository near-field environment provided that matrix flow paths are dominant.

Profiles of hydrogen concentration in the reacted glass wafers showed diffusion limited transport. The model for entry of hydrogen into the glass is exchanged with alkalis and boron, which are released to the leach solutions. The departure of the hydrogen profiles from the behavior predicted by diffusion was used to infer a dissolution rate for the glass surface. This dissolution rate (1.5 to 3.0 μm/yr) was used in mass balance calculations to investigate the mechanism(s) controlling the glass dissolution process. The results of our mass balance calculations indicate that we must invoke either a variable dissolution rate that decreases throughout the duration of the experiments or an initial incremental release of material in order to reconcile the observations. Formation of a gel layer transitional to

diffusion and surface dissolution provides a mechanism by which the surface dissolution rate may vary [1], while rapid dissolution of high-energy surface features early in the runs may provide an initial incremental mass release. On the basis of solution chemistry and mass balance, the two possibilities are indistinguishable and resolution requires further direct analysis leading to a more thorough understanding of the gelation and dissolution kinetics of these materials.

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References

1. Abrajano, T.A. and J.K. Bates, in Scientific Basis for Nuclear Waste Management X, edited by J.K. Bates (Elsevier Science Publishers, New York, 1987, in press).
2. Abrajano, T.A., J.K. Bates, T. Gerding and W.L. Ebert, Argonne National Laboratory Topical Report (1987, in prep).
3. Bates, J.K., T.J. Gerding, T.A. Abrajano, Jr. and W. Ebert, UCRL-15801, Lawrence Livermore National Laboratory, Livermore, CA (1985).
4. Lanford, W.A., K. Davis, P. Lamarche, T. Laursen, R. Groleau, and R.H. Doremus, J. Non-Cryst. Sol., 33, 249-266 (1979).
5. Shimizu, N., M.P. Semet, and C.J. Allegre, Geochim. Cosmochim. Acta 42, 1321-1334 (1978).
6. Phinney, D.L., V.M. Oversby and F.J. Ryerson, UCRL, Lawrence Livermore National Laboratory (1987, in prep).
7. Daniels, W.R. et al., LA-9328-MS, Los Alamos National Laboratory, Los Alamos, N.M. (1982).
8. Hofmann, A.W. in Physics of Magmatic Processes, edited by R.B. Hargraves (Princeton University Press, Princeton, N.J., 1980) pp. 385-417.

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