CONF 861207-84

TRANSPORT AND REACTION KINETICS AT THE GLASS:SOLUTION INTERFACE REGION: RESULTS OF REPOSITORY-ORIENTED LEACHING EXPERIMENTS

TEOFILO A. ABRAJANO, JR. AND JOHN K. BATES

Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439

CONF-861207--84

ABSTRACT

MAP 2 DE87 006975

Repository-oriented leaching experiments involving Savannah River Laboratory (SRL) 165 type glass under a γ -radiation field ($1 \pm 0.2 \times 10^4$ R/h) have been performed by the Nevada Nuclear Waste Storage Investigations (NNWSI) project. In this communication, we discuss glass surface analyses obtained by SEM, nuclear resonance profiling, and SIMS together with leachate solution data in relation to a mechanism that couples diffusion, hydrolysis (etching and gelation), and precipitation to qualitatively describe the release of different glass components to the leachant solutions. The release of mobile (e.g., Li) and partly mobile (e.g., B) species is controlled primarily by interdiffusion with water species across the interdiffusion zone. Glass components that are immobile in the interdiffusion zone are released to the solution by etching. For prediction of long-term steady-state concentrations of glass components with low solubility, the relative rates of release from the glass and secondary mineral precipitation must be taken into account.

INTRODUCTION

High-level nuclear waste generated by the Defense Waste Processing Facility at Savannah River Laboratory (SRL) will be converted to a glass waste form for repository disposal. Previous studies, that were designed to monitor and model the corrosion of the glass waste form [1,2], have focused mainly on preliminary glass compositions (frits 211 and 131) and used generic conditions during testing. These studies suggested that protective layers that form from insoluble glass matrix elements or reconstituted surface layers act as a major control of long-term elemental release from the glass. Other researchers [3], studying the corrosion of nuclear waste and natural glasses, have argued that feedback effects attributable to "saturation" of partially hydrolyzed glass are responsible for the release trends of all glass species. In each of these previous studies the models developed have been able to adequately describe the experimentally observed reaction progress.

In this paper we discuss the results of leaching experiments involving the current SRL reference glass based on SRL 165-type composition. The experiments were done using variables relevant to the Nevada Nuclear Waste Storage Investigations (NNWSI) repository site at Yucca Mountain, Nevada, and included EJ-13 groundwater (J-13 water pre-reacted with tuff), NNWSI-relevant waste package components, and a gamma radiation field. By the use of these specific conditions we hope to generate results that will be useful in projecting the long-term performance of glass in the NNWSI repository site.

We present surface analytical and solution data that suggest that during the length of the present experiments (182 days) processes different from those discussed above [1,2,3] are controlling the glass reaction. Specifically, the reacted glass consists of three regions that take part in the reaction process. These are an interdiffusion zone that penetrates into the bulk glass, a "gel" that forms outward from the interdiffusion zone, and the surface of the "gel". The release of elements from the glass is incongruent and is controlled by the diffusion of mobile

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

components through the interdiffusion zone and by the etching of immobile components from the surface. The "gel" is a structurally transformed layer that appears to be relatively passive to interdiffusion. The nature of the "gel" layer is nevertheless important because its etching rate determines the release of immobile matrix components. These observations are significant in that they provide the first concerted (surface analytical and solution) description of the reaction of SRL 165-type glass and in that they are different from those noted previously for nuclear waste type glasses [1,2,3], e.g., interdiffusion is still controlling release after 182 days, etching of the surface is occurring, and no protective layer has been observed.

To explain these results we draw upon existing models of glass corrosion and develop a mechanistic rationale to reconcile the observed surface analytical and solution data. The model has also been extended to project long-term corrosion behavior by accounting for the precipitation of secondary products from solution. A description of the long-term performance is presented and empirically the results are not dissimilar from those presented previously [3]. However, application of the long-term model can only be made with certainty when more information is available concerning the interaction kinetics of the glass/repository system.

EXPERIMENTAL

Test Matrix

The design of the present experiments has been described previously [4,5,6]. Briefly, two glass disks were placed together in individual Type 304 L stainless steel vessels with measured amounts of pre-reacted J-13 water (EJ-13). The glass surface-area-to-solution-volume (SA/V) ratio for these experiments was nominally set at 0.3 cm⁻¹. In another set of experiments a polished tuff core wafer was also added to the vessel, along with the glass. Both sets were run at a temperature of 90°C, with a γ -dose rate of $1.0 \pm 0.2 \times 10^4$ R/h, and with SRL 165 type glass doped with uranium (SRL U) or uranium plus transuranic elements (SRL A).

Test Components

The leachant (EJ-13 water) used in the present experiments was prepared by reacting J-13 groundwater with caliche-free Topopah Spring tuff at 90°C for 14 days [4,7]. The EJ-13 composition used in the present experiments ($\mu\text{g/mL}$) is Al, <0.10; B, 0.14; Ca, 11.9; Fe, <0.01; Li, 0.046; Mg, 0.95; Na, 45.4; Si, 30.6; Sr, 0.043; U, <0.001; F⁻, 2.45; Cl⁻, 7.70; NO₃⁻, 8.35; NO₂⁻, <0.2; SO₄²⁻, 18.6; and pH = 7.61. Potassium and HCO₃⁻, which were not analyzed, have values of ~5 and 122 in J-13 groundwater. The composition of the SRL 165 U/A glasses used here (wt % oxide) is Al, 4.08; B, 6.76; Ba, 0.06; Ca, 1.62; Fe³⁺, 11.3; Fe²⁺, 0.35; Li, 4.18; Mg, 0.70; Mn, 2.27; Na, 10.8; Ni, 0.85; Si, 52.8; Ti, 0.14; Zn, 0.04; Zr, 0.66; ²³⁷Np, 1.3E-2; ²³⁹Pu, 3.7E-2; ²⁴¹Am, 9.5E-4; U, 0.96; Cs, 0.072; Sr, 0.11; P, 0.29.

Sample Description

All the glass disks were core-drilled from cast bars and were then wafered to size. The disks were cleaned ultrasonically three times with ethanol. One of the two disks used in each test had one side polished to 600 grit. Therefore, three different types of glass surfaces were present

in each test; both faces of one disk and the bottom side of the other disk are as cut, the top side of the other disk is polished to 600 grit, and the sides of the disks are as cored.

Analyses

To adequately describe the reacted glass surfaces, several analytical techniques were used. Microscopic, SEM/EDS, and SIMS analysis of the reacted glasses were performed using instruments and procedures discussed previously [4]. Nuclear resonance profiling for hydrogen was performed on selected SRL U glasses by F. Ryerson of Lawrence Livermore National Laboratory (LLNL) in the laboratory of Professor W. Lanford (State University of New York, Albany). The hydrogen concentration as a function of depth was studied using the nuclear reaction: $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + 4.43 \text{ MeV}$, which has an isolated resonance energy at 6.385 MeV. More extensive discussion of the technique can be found in [8]. Solution analyses utilized standard techniques [5].

RESULTS AND DISCUSSIONS

Characteristics of Reacted Surface Layers

Figure 1 illustrates the progressive modification of the as-cut SRL U glass surface as a function of reaction time. After 14 days of reaction, "scales" about $0.3 \mu\text{m}$ across were observed to form homogeneously on the surface (bright features in Fig. 1a). On the other extreme, the as-cut surface reacted for 182 days has surface fabric that has a "woven" or "chain mail-like" appearance. Similar features on altered SRL glass surfaces have been described as "cellular" [4] or "honey combed" [1]. Note that because these samples have been dessicated (i.e., removed from solution, dried in air, and exposed to high vacuum conditions) prior to examination under the SEM, the actual physical appearance of the surface during the leaching experiment may not be the same as that shown in Fig. 1. In fact, the "chain mail-like" morphology is comparable to well-documented gel dessication textures formed during sol-gel processing [e.g., 9]. This series of photomicrographs (Fig. 1) indicates that the glass surface is altered in a manner whereby the features indicative of freshly cut glass surface (e.g., stress marks, sharp edges) are replaced by features indicative of significant alteration of the glass structure.

The nature and extent of surface alteration was further examined using surface profiling techniques. Nuclear resonance profiles for H of polished SRL U glass surfaces reacted for various durations are shown in Fig. 2. The hydrogen distribution with depth of the surface reacted for 14 days resembles diffusion profiles where the diffusion coefficient depends on concentration (i.e., "S"-shaped) [10] and is interpreted as such [cf. 11]. We will refer to the region that exhibits this type of profile as an interdiffusion zone. Equally well-defined diffusion profiles for hydrogen were found for glass surfaces reacted for 7, 14, and 28 days in our previous experiments [4,11]. Surfaces reacted for 28 to 182 days in the present experiments are somewhat different from the 14-day profile and show what we interpret to be a step H-profile (Fig. 2). Starting from the low intensities of the bulk glass, the H concentration increases outward in a manner similar to that described for the surface reacted for 14 days. It appears, however, that the interdiffusion zone has encroached deeper into the glass as the reaction progressed. In addition, a second zone that appears to have more water than the interdiffusion zone has formed on the surface. The down-pointing arrows in Fig. 2 mark the approximate onset of this second zone. We believe that

Figure 1. SEM Comparison of the Surfaces of SRL U Glass from Experiments. (a) 14 days, (b) 28 days, (c) 56 days, and (d) 182 days. The magnification in all micrographs is 1000X and the marker below the figures represents 10 μm .

Figure 2. Nuclear Resonance Profile of H in SRL U Glasses. (a) 14 and 28 days, no tuff; (b) 182 days, no tuff. The regions of interest are identified in the profiles. These are the bulk glass, the transition zone, and the "gel" layer.

the development of this second zone is related to the formation of the SEM-observable features described above (Fig. 1) and refer to this zone as a "gel" layer or partially hydrolyzed glass. It is immaterial to the present argument whether this outer layer is a true gel or not. What is important is that an outer layer, whose network structure appears to be fundamentally different from that of the bulk glass or the interdiffusion zone, forms during leaching. It is prudent to recognize that the H-profiles alone cannot be (and were not) used to justify the presence of this "gel" layer because analytical artifacts cannot be fully discounted. The physical observations using the SEM (Fig. 1) are the strongest arguments for the presence of a structurally altered glass surface. It is to these SEM observable surface features that we are associating the formation of step H-profiles (Fig. 2). We note that because dessication of this "gel" layer after termination of the experiments most certainly has occurred, the observed "water" concentrations are minimum amounts. Vacuum loss and thermal effects during analysis may also have decreased these near-surface concentrations [cf. 8,11]. Lastly, the H-profile for the glass reacted for 182 days (Fig. 2b) provides strong evidence that a second process, in addition to interdiffusion, is controlling the introduction of "water" into the glass.

The description of the reacted glass surface is further enhanced by considering the SIMS profiles for selected glass components (Fig. 3). Again, only SIMS profiles of surfaces that were polished prior to leaching are presented, although as-cut surfaces profiled yielded essentially the same results. Intensities were normalized to Si and the bulk glass intensities. Silicon was used as a normalization "standard" because the absolute intensity of Si, SiO, and Si₂O were constant to within 10% throughout the sputtering process and did not show any systematic variation across the reacted zones and bulk glass except for slight enrichment in the first 50 Å. Silicon intensity also showed no systematic variation across the surface layers and bulk glass during ion microprobe profiling of SRL A glasses for actinide elements (unpub. data). After reaction for 14 days, Li, Na, and B appear depleted relative to the bulk. When considered with the H nuclear resonance profiles, it appears that Li, Na, and B exhibit complementary diffusion profiles to H in the interdiffusion zone, although the depth to which Li is "completely" depleted in the layer is clearly greater than that of Na and B. This depletion trend corresponds well with the normalized elemental loss trends (see below) which also show the same order of relative depletion. Glasses reacted for longer periods show increasing depletion depths for each element (Li, Na, B). Figure 4 summarizes the relation between reaction time and depletion depth for Li. An approximation of the minimum thickness of the "gel" layer may be made from the Li profiles if it is assumed that Li is evenly leached out of this layer and that the Li intensity began rising as soon as the gel/interdiffusion zone boundary is reached (Fig. 4). These minimum estimates compare well with the estimates of "gel" thickness from the H profiles and are presented in Table I. A sputtering rate of 71 Å/min was calibrated directly by surface profilometry (Dektac).

The measured depletion depth of Li, defined as the depth at which Li concentration is half the bulk glass value, can be compared to the normalized depletion depth estimated from the relation $ND(Li) = NL(Li)/\rho$ where $ND(Li)$ and $NL(Li)$ (see below) are the normalized depletion depth and normalized release of Li, respectively, and ρ is the bulk glass density (~2.7 g/cc) (Table I). The difference between these two depths represents the aggregate thickness of the glass matrix that has been removed by etching. It is clear from Table I that significant etching (0.4-1.2 μ m) must have occurred. Independent evidence of etching comes from the observed behavior of Si in the reacted surface layers and from corresponding solution release patterns (see below). Because the SIMS and ion microprobe profiles showed no systematic variation of Si concentration

a

b

Figure 3. SIMS Profile for Selected Elements in SRL U Glasses. (a) 14 days, no tuff; (b) 182 days, no tuff.

Figure 4. Li SIMS Profile for SRL U Glasses Reacted for 14, 28, 56, 91, and 182 Days. Also shown are the minimum gel thicknesses for each profile.

Table I. Region Thicknesses in Reacted Glass

Reaction Period (Days)	Gel ^{a,d}	Region Thicknesses (μm)			Depletion Depths (μm)	
		Interdiffusion ^a Zone	Glass Etched ^c	Sid	Li ^e (Measured)	Li ^f (Projected)
14	0.05	0.10	0.40	0.55	0.10	0.50
28	0.08	0.15	0.80	0.72	0.14	0.94
56	0.09	0.13	1.06	0.74	0.18	1.24
91	0.12	0.17	1.15	1.409	0.41	1.56
182	0.16	0.18	1.21	1.14	0.64	1.85

^aAs measured using nuclear resonance profiles.

^bAs measured using SIMS.

^cAs calculated by taking the difference between the Li depletion depth calculated from $(NL)_{Li/p}$ and the Li depletion depth measured using SIMS profiles (see last two columns).

^dAs calculated from $(NL)_{Si/p}$.

^eActual depletion depth measured from SIMS profiles.

^fNormalized depletion depth of Li based on $(NL)_{Li/p}$, this value includes the etched, "gel," and interdiffusion regions.

^gValue based on one test, all other values based on two tests.

from the surface layers to the bulk glass, it is unlikely that significant release of Si via diffusion or concentration of Si via shrinkage or reprecipitation has occurred. If etching is the only mechanism responsible for Si release, $ND(Si)$ must equal the etching depth estimated from the Li data. Indeed, Table I shows these two values are in good agreement.

It appears from the surface data that the early stages of interaction of glass with EJ-13 solution is dominated by the interdiffusion of hydrogen species from the liquid with mobile and partly mobile glass components. Boron appears to belong to the latter category as indicated by its behavior in the interdiffusion zone, i.e., B is significantly fractionated from Si during interdiffusion. Except for the initial "instantaneous" surface exchange of network modifiers in the glass for proton or hydronium in solution, etching or network dissolution must have gone on concurrently with the interdiffusion process, although at a slower rate. This etching process must be slow enough to allow both an interdiffusion zone and a "gel" layer to develop. The rate of growth of both the "gel" layer and interdiffusion zone decreased with time as measured by SIMS and nuclear resonance techniques. The observation that Si concentration in the "gel" layer and interdiffusion zone is constant and similar to that of the bulk glass suggests that etching is the dominant mechanism of Si release to solution.

Solution Chemistry and Release Kinetics

The coupled etching (gelation)-interdiffusion process that emerges from the above discussion has been demonstrated in previous aqueous corrosion studies of commercial glasses [e.g., 13,14]. However, studies on nuclear waste glass corrosion [e.g., 1,2,3,] have concluded that other processes will control the long-term release of various glass components (see introduction section), and that interdiffusion is an important factor governing release only in the very short time frame. In the discussion below, we will compare the predictions of the etching (gelation)-interdiffusion mechanism to the observed solution release trends. We will show that incorporation of "gel" saturation effects and secondary phase

precipitation to the above mechanism can adequately describe both the experimental results and long-term repository interactions.

The normalized release of selected glass components as a function of reaction time is shown in Fig. 5 [see 4,5 for details]. The absolute amounts of Si and Na added to the leachate from the glass are considerably less than the starting levels in EJ-13 solution; and the variance of normalized release for both elements is greater in the glass-containing experiments than in the corresponding blanks. Nevertheless, systematic temporal variations are well reproduced in two sets of replicate runs adding credence to, at least, a qualitative description of the release patterns of these elements in EJ-13 solution. In comparison, the interpretation of the release patterns of Li and B does not encounter these difficulties because the concentrations of these two elements in EJ-13 solution as well as in the blank experiments are much lower than observed in the final leachate.

The normalized release rate of Li brackets the upper limit of mobile cation release from the glass to the EJ-13 solution. It is commonly thought that network-modifying ions such as Li and Na are released from the glass via the following reactions:

or

where X is a network-modifying ion of valence n, and R can be any network former. In reference to the discussion of surface layers (above), the exchange reactions just noted are predominantly occurring in the interdiffusion zone. As the exchange sites move deeper into the glass, the release of the leachable species becomes slower. If no other process (e.g., network hydrolysis) is occurring, the release of mobile ions and the growth of the alteration layer follow parabolic kinetics. Sullivan [12] has shown that these release kinetics are not altered even if the concentration dependence of the diffusion coefficients is incorporated into the interdiffusion equation.

The normalized release of Li and Na from the glass in the present experiments can, in fact, be adequately described by parabolic kinetics (Fig. 5c). The release patterns of these elements in our previous experiments also followed parabolic kinetics [4]. In spite of their comparable mobilities, the normalized release of Na is consistently lower than Li. We believe that this, in part, is due to the high initial concentration of Na in EJ-13 water. The rate of release of B is also parabolic with respect to time but is consistently lower than Li and Na. This "incongruity" is probably the result of the lower mobility of B. It appears that the boron-oxygen bonds in SRL glasses are actually being hydrolyzed

Figure 5. Variation of Normalized Concentrations of Li, Na, Si, and B as a Function of Reaction Time for (a) SRL U + EJ-13 + Tuff and (b) SRL A + EJ-13 + Tuff. Similar data for Li and Na plotted as a function of $t^{1/2}$ [(c) no tuff, (d) with tuff].

within the interdiffusion zone leading to the observed solution release pattern (Fig. 5) and SIMS profiles (Fig. 3). As with the alkalis, the decreased rate of release of B with time can be reconciled with the growth of the interdiffusion zone.

Simple parabolic release patterns of leachable species are, however, to be expected only if etching and/or gelation are not occurring. Network hydrolysis (etching/gelation) will decrease the thickness of the interdiffusion zone potentially complicating its layer growth kinetics and the solution release pattern controlled by this growth. It is instructive to examine explicitly how the rates of gelation or etching influence the growth kinetics of the interdiffusion zone. The solution to this problem is similar to the classic coupled diffusion-dissolution model applied to alkali silicate glass corrosion by Rana and Douglas, and Boksay et al. [13,14] and developed for borosilicate glass by Sullivan, and Godbee and Joy [12,15]. In this model, the rate of growth of the interdiffusion zone was described by an equation of the form [12]:

$$dL/dt = q(t) - v(t) \quad (3)$$

where L is the thickness of the interdiffusion zone, $q(t)$ is the rate of penetration of the interdiffusion zone into the bulk glass, and $v(t)$ is the network dissolution velocity. In the presence of a "gel" layer through which diffusion is fast compared to that through the interdiffusion zone, $v(t)$ becomes the rate of "gel" penetration into the interdiffusion zone.

Gelation and etching are end-members of the hydrolysis reaction:

where $R = H$ or a network former. For etching, one of the product terms represents an aqueous silica species. For gelation, both product terms represent partially hydrolyzed gel species that are still connected to the network, i.e., at least one R in each is a network former. The rate of (4) can be described using the transition state theory as extended to near-saturation conditions by Aagaard and Helgeson [16] [cf. 3]. This has been done in detail [6] with the essential result that the "gel" penetration rate ($v(t)$) is first order in the short term and constant in the long term. For etching, the same relation governs $v(t)$ except that it is possible to relate the activity of hydrolyzed silicon bonds to the concentration of silicic acid in solution [6]. The resulting expression is similar to those described previously [3,12,17] where the etching rate is first order with respect to the degree of silica saturation. This first-order etching formulation can be integrated to show the explicit time dependence of L (i.e., thickness etched), and the solution takes the form [6]:

$$L = k_1 (1 - e^{-k_2 t}) \quad (5)$$

where k_1 is related to the difference between the saturation concentration of the "gel" and the initial concentration in solution for Si , and k_2 is the dissolution rate constant [6]. If no other processes are occurring, the rate of etching will decrease with time in a manner described by (5). Equation 5 also predicts that the reaction will approach a final steady state (i.e., H_4SiO_4 released equals that back precipitated) in a time scale given by $t = 1/k_2$. This would imply, with respect to Eq. 3, that $v(t) = 0$ and the layer growth kinetics is controlled solely by the rate of penetration of the interdiffusion zone ($q(t)$). If "gel" dissolution is the only mechanism controlling the solution trend of Si (i.e., no precipitate formation, see below), Eq. 5 also governs the Si release pattern (i.e., $NL(\text{Si}) \propto L$).

The rate of penetration of the interdiffusion zone into the bulk glass is diffusion-controlled. Therefore, $q(t)$ could be described by solving the diffusion equation with respect to a frame of reference that moves at the rate $v(t)$. For the steady-state case described above (i.e., $v(t) = 0$), $q(t)$, as well as dL/dt , is simply:

$$q(t) = dL/dt = -n_1 t^{-1/2}$$

(6)

where n_1 is a constant related to the diffusion coefficient and the concentration gradient driving the diffusion process [6]. In integrated form, we have ($L = L_0$ at $t = 0$):

$$L = (n_1/2)t^{1/2} + L_0 \quad (7)$$

Thus, the layer growth kinetics of the interdiffusion zone reverts to a simple parabolic function. If, however, a constant driving force for etching or gelation is maintained, $v(t)$ becomes invariant with time. Calculations of $q(t)$ where $v(t)$ is constant have been performed in [12-15] with the essential result that $q(t)$ is parabolic within the time frame $t \ll D/v^2$ (D is the diffusion coefficient and v is the constant etching or gelation velocity) and $q(t)$ is linear at longer times (i.e., $t > D/v^2$). The value of $q(t)$ also approaches $v(t)$ in the time scale $t > D/v^2$ so that we predict that the layer stops growing ($dL/dt = 0$ in Eq. 3) in the same time frame. However, the corrosion of the glass itself does not stop; $q(t)$ and $v(t)$ just proceed at the same rate.

The above discussion provides the basis for understanding the role of transport processes across the interdiffusion zone on the long-term release of leachable species from the glass. The major consequence of the scenario that gelation will have a constant finite rate at infinite time is that transport through the interdiffusion zone will remain as the major controlling process for the release of leachable glass components to solution. Where the "gel" layer serves as an additional (albeit, less effective) barrier to transport (e.g., for B), the coupled rate of interdiffusion and etching will govern the long-term release rate (with explicit provision for the different interdiffusion coefficients in the "gel" and interdiffusion zone [e.g., 12]).

The present mechanism is distinguished from that proposed by [1,2] who alluded to "protective" precipitate layers. We do not see any evidence (i.e., solution or surface data) to support the latter mechanism in the system examined, although it certainly cannot be totally precluded in long-term predictions. These "protective" precipitate layers if and when they form will serve as a second barrier to transport in addition to that provided by the interdiffusion zone. Longer duration experiments that may help clarify these trends are still in progress in our laboratory [18].

The coupled rate formulation derived above can also be used in the interpretation of the release trend of relatively insoluble glass components. However, because precipitation of secondary precipitates may further modify the observed normalized release, we can generalize the release trend model by coupling the rate law governing elemental release from the glass to a precipitation rate law. Secondary precipitation was not explicitly considered above because no alkali or B-bearing precipitates were observed. Furthermore, Li and B have relatively high solubilities and are not expected to be incorporated to a significant degree in potential alteration minerals. Sodium and Si release to solution may be affected by precipitation (e.g., analcime) and this is expected for longer experimental durations or long-term prediction. The rate formulation describing the combined effect of "gel" saturation and precipitation on the Si release pattern, for example, has the general form:

$$dC(H_4SiO_4)/dt = k_3 \{C(H_4SiO_4)_s - C(H_4SiO_4)\} - k_4 \{C(H_4SiO_4) - C(H_4SiO_4)_p\} \quad (8)$$

where $C(H_4SiO_4)_p$ is the saturation concentration of the precipitate, and k_3 and k_4 are dissolution and precipitation rate constants, respectively. The dissolution rate law will be similar for all matrix elements released at the same rate as Si (e.g., Pu), although the precipitation rate law will be governed by the precipitate of the specific glass component (e.g., $PuO_2 \cdot nH_2O$).

Equation 8 can be integrated from $t = t_{ss}$ (i.e., time when p begins to precipitate) to t , and this has been done in [6] with the following results [cf. 19]:

$$C(H_4SiO_4) = k_3 \{C(H_4SiO_4)_s - C(H_4SiO_4)_{ss}\} + k_4 \{C(H_4SiO_4)_p - C(H_4SiO_4)_{ss}\} e^{k_5(t - t_{ss})} - \frac{k_3 C(H_4SiO_4)_s}{k_5} + \frac{k_4 C(H_4SiO_4)_p}{k_5} \quad (9)$$

where $C(H_4SiO_4)_{ss}$ is the solution concentration of silicic acid at time t_{ss} and $k_5 = -(k_3 + k_4)$. This integrated form describes a Si release rate that decreases with time and achieves steady state in a time scale given by $(t - t_{ss}) = 1/(k_3 + k_4)$. The steady-state concentration, however, is determined not only by the saturation concentration of the precipitating phase but also by the relative rates of gel dissolution and product phase precipitation. What this means is that steady-state concentration, which is not necessarily the saturation concentration of p, is always lower than the "gel" saturation concentration when precipitation is occurring. This is responsible for setting up the steady-state driving force for dissolution discussed above. We cannot completely rule out the possibility that secondary silicates are present but were not observed in the present experiments because the solution concentrations achieved are saturated with respect to a number of potential alteration phases (e.g., analcime, cristobalite, etc.). At very long times when multiple phase precipitation is expected to occur (unless solution flow rates are high), the coupled rate expressions become unwieldy but preserve a pseudo-first order form [6]. If the precipitate contains leachable elements (e.g., Na, alkali earths, etc.), the precipitation rate expression has to be coupled to the parabolic rate expression (or to the coupled diffusion-gelation rate expression) to arrive at a model of release of leachable elements to solution. This qualitatively results in a lower concentration of leachable elements (those contained in the precipitate) in solution as soon as precipitation of the alteration phase begins. If the precipitation rate is much faster than the diffusion rate through the interdiffusion zone, a steady-state concentration determined by the saturation concentration of the alteration phase is quickly achieved. Otherwise, the relative rates of diffusion and precipitation will determine the solution release trend. We are presently considering the implications of a coupled dissolution-precipitation model to the observed release trends of the actinide elements [6].

We did not explicitly consider the effect of pH on the release rates of various glass components to EJ-13 solution because the pH achieved in the present experiments were essentially buffered within a narrow pH range of 6.8 to 7.5. However, pH effects can be explicitly incorporated into the formulations discussed above through the saturation concentrations (e.g., above pH = 9 the solubility of silicic acid increases dramatically)

or through the rate constants of dissolution or diffusion. Higher pH levels than those achieved by the present experiments ($\text{pH} > 9$) will serve to enhance dissolution and gelation effects relative to interdiffusion, but, based on the present results, may not actually exist under repository conditions of NNWSI.

CONCLUSIONS

We have presented results of surface and solution analyses for experiments involving SRL U and SRL A glasses in EJ-13 leaching solution. We interpret the surface and solution data to indicate that under the present experimental conditions, the early stage of interaction of SRL U and SRL A glasses with EJ-13 solution is dominated by the interdiffusion of water species with mobile and partly mobile glass components across an interdiffusion zone. Boron appears to be partly mobile as indicated by its behavior in the interdiffusion zone, i.e., B is significantly fractionated from Si during interdiffusion. Except for the initial "instantaneous" surface exchange of network modifiers in the glass for proton or hydronium in solution, etching or network dissolution must have proceeded concurrently with the interdiffusion process, although at a slower rate. This etching process must be slow enough to allow not only an interdiffusion zone but a "gel" layer to develop.

Gelation or "gel" formation is a partial hydration process whereby some Si-O-Si bonds are broken. It represents the initial stage of etching in that the latter is the process of completely detaching the soluble aqueous silica units from the "gel" surface. The short- and long-term solution release trends of mobile elements (e.g., Li) are controlled by the rate of interdiffusion through the interdiffusion zone. The release of relatively immobile elements (e.g., Si) is governed by the rate of etching. Models were presented to explain the observed and predicted time dependence of individual elemental release trends. However, the application of the model to the actual projection of long-term glass performance under NNWSI conditions can only be done when more complete description of the reaction progress is obtained.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Geologic Repositories, and the Nevada Nuclear Waste Storage Investigations Project.

REFERENCES

1. J. E. Mendel, Compiler, Final Report of the Defense High-Level Waste Leaching Mechanisms Program (Pacific Northwest Laboratory, Richland, WA, PNL-5157, 1984).
2. R. M. Wallace and G. G. Wicks, in Scientific Basis for Nuclear Waste Management VI, edited by D. Brookins (Elsevier Science Publishers, New York, 1983) pp. 23-28.
3. B. Grambow, in Scientific Basis for Nuclear Waste Management VIII, edited by C. M. Jantzen et al. (Elsevier Science Publishers, New York, 1984), pp. 15-27.
4. J. K. Bates, D. F. Fischer, and T. J. Gerding, Argonne National Laboratory, ANL Report No. 85-62, 1986.
5. T. A. Abrajano, Jr., J. K. Bates, W. L. Ebert, T. J. Gerding, Lawrence Livermore National Laboratory, UCRL Report NO. 15825, 1986.
6. T. A. Abrajano et al. (in preparation).

7. V. M. Oversby, Lawrence Livermore National Laboratory, UCRL Report No. 53552, 1984.
8. W. A. Lanford et al., J. Non-Crystalline Solids, 33, 249 (1979).
9. C. J. Brinker and G. W. Scherer, J. Non-Crystalline Solids, 70, 301 (1985).
10. R. H. Doremus, in Treatise on Materials Science and Technology, edited by M. Tomozawa and R. H. Doremus (Academic Press, New York, 1982), pp. 41-69.
11. D. L. Phinney et al., in Scientific Basis for Nuclear Waste Management X, edited by J. K. Bates and W. B. Seefeldt (Elsevier Science Publishing, New York, this volume).
12. T. M. Sullivan, Ph.D. Thesis, University of Illinois, 1984.
13. M. A. Rana and R. W. Douglas, Phys. Chem. Glasses, 2, 179 (1961).
14. Z. Boksay, G. Bouquet, and S. Dobos, Phys. Chem. Glasses, 9, 69 (1968).
15. W. H. Godbee and D. S. Joy, Oak Ridge National Laboratory, ORNL-TM-4333, 1974.
16. P. Aagaard and H. C. Helgeson, Am. J. Science, 281, 237 (1982).
17. J. D. Rimstidt and H. L. Barnes, Geochim. Cosmochim. Acta, 44, 1683 (1980).
18. W. L. Ebert, J. K. Bates, and T. J. Gerding, in Scientific Basis for Nuclear Waste Management X, edited by J. K. Bates and W. B. Seefeldt (Elsevier Science Publishers, New York, this volume).
19. M. Tole, Geochim. Cosmochim. Acta, 50, 379 (1986).
20. The Addenda is available upon request from the authors.