WILLIAM L. EBERT AND JOHN K. BATES

Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4837

ANL/CP--70460

ABSTRACT

DE91 006506

The analytical expression used to model glass reaction in computer simulations such as EQ6 is compared to the results of experiments used to support the simulations. The expression correctly predicts the acceleration observed in experiments performed at high glass surface area/leachant volume ratios (SA/V) upon the formation of secondary phases. High resolution microscopic analysis of reacted glass samples suggests that the accelerated nature of the reaction after secondary phase formation is due to changes in the reaction affinity (i.e., is a solution effect) and not a change in the glass reaction mechanism. The composition of solutions in contact with reacted samples reflect the effects of the secondary phases predicted in the model. Experiments which lead to the generation of secondary phases within short reaction times can be used to identify important secondary phases which must be included in the data base of computer simulations to correctly project long-term glass reaction behavior.

APR 12 1991

INTRODUCTION

A primary goal in waste management is to obtain long-term release rates of radionuclides from spent fuel and high-level waste glass to demonstrate that the radionuclide containment of these waste forms meet acceptance criteria to be established for the high-level waste repository. An approach taken by the Yucca Mountain Project (YMP) is the use of a computer simulation to project the long-term reaction behavior of spent fuel and glass. The computer simulation is supported by experiments used to develop models incorporated into the codes and by experiments designed for code validation. While code development has benefited from models derived from simple tests of glass durability, such as the MCC-1 test, experiments which accelerate the reaction or otherwise characterize the long-term behavior of the glass reaction are required to validate model performance during the long storage times relevant to repository isolation. In this communication, we consider the relationship the expression used to model glass reaction in the EQ6 and other computer codes and experiments performed at high SA/V and elevated temperatures. Results from these experiments are related to the long-term predictions of computer simulations and to the results of reactions performed at lower SA/V and lower temperatures which achieve smaller reaction progresses to assess the role of secondary phases in the glass reaction.

BACKGROUND

Simulation of glass/water reactions requires the use of an analytical expression to describe the dissolution of the glass into the aqueous phase. In the simulation, an incremental amount of glass is dissolved, and the resulting solution composition is compared to a thermodynamic data base to determine if the solution is supersaturated with respect to any secondary phases. If supersaturation occurs, these phases are allowed to precipitate and the solution chemistry is changed until equilibrium is achieved. The resulting solution then influences the release of the next increment of the

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.

glass dissolved. The ability of the computer simulation to project the glass reaction over long time periods depends on the accuracy of the analytical expression used to describe the influence of the solution chemistry on the kinetics of the glass dissolution and of the data base to predict the secondary phases precipitated. Experiments must, therefore, be designed to address the accuracy of both parts of the simulation.

The "master equation" describing the glass reaction in most computer codes is that proposed by Aagaard and Helgeson [1] to describe mineral dissolution. The expression is given in simplified form in Eq. 1:

$$\frac{dm_i}{dt} = SA \ k_i \left(1 - \frac{Q}{K} \right) \quad (1)$$

where m_i is the number of moles of species i released from the mineral (or glass), SA is the surface area, k_i the reaction rate coefficient, and the parenthetic term is the reaction affinity where Q is the ion activity product and K is the equilibrium constant of the dissolving solid. If all material released from the glass goes into solution, then $m_i = VC_i$ where V is the solution volume and C_i the molar concentration, and Eq. 1 can be rewritten as

$$\frac{dC_i}{dt} = \frac{SA}{V} \ k_i \left(1 - \frac{Q}{K} \right) \quad (2)$$

This is the form utilized in geochemical codes based on solution equilibrium such as EQ3/6. In order to apply Eq. 2, the terms k_i and K must be defined. Both k_i and K are functions of temperature and mineral or glass composition. SA and V are experimental (or simulation) variables and Q is a dependent variable computed after each dissolution step. Under infinitely dilute conditions, Q is zero and the affinity term is one and k_i can be measured as dC_i/dt . If the glass dissolves stoichiometrically, then all k_i values will be the same and a single rate coefficient k can be used to describe the glass reaction. The compositional dependence of k can be measured directly by reacting several glasses of interest under dilute conditions.

The definition of a thermodynamic equilibrium constant, K , for a metastable phase requires the glass to be modeled as a stable phase and the addition of an ad hoc term to account for residual reaction. Grambow [2] has modeled silicate glass simply as amorphous silica and was able to fit experimental data using Eq. 2 to determine the value of k . Bourcier [3] has modeled the glass to be a solid solution of stable endmembers of major glass components. The equilibrium constant of this ideal solution was then determined and used in Eq. 2. Both approaches have successfully reproduced experimental results from tests with dilute leachates, such as the MCC-1 and flow-through tests, prior to secondary phase formation.

If secondary phases form, then species released from the glass may be present in the solution or incorporated in a secondary phase. Mass balance requires that material lost from the glass either enter secondary phases (including colloids). If the secondary phases are in equilibrium with the solution (as assumed in the computer simulations) then the solution concentrations are fixed by the solubility limits of the secondary phases. Once the solution concentration of the species i becomes constant, both Q and the affinity term in Eq. 1 becomes constant and the rate of glass reaction becomes constant. Species released from the glass become incorporated into secondary minerals while the solution concentration remains constant. At this point of the reaction, Eq. 2 is no longer relevant because $m_i \neq VC_i$ and Eq. 1 must be used. Accordingly, the rate depends on the solution chemistry through the affinity term: the lower the solubility limit of the secondary phase, the higher the affinity and the higher the rate.

It is, therefore, necessary to know which secondary phases form to be able to compute the solubility limits and the reaction affinity which control the reaction rate. Grambow has selected phases for computer simulations which can be fitted to experimental results, although the selected phases, except for analcime, have not been observed in experiments. The EQ3/6 package selects the most stable phase in its data base to form. These phases have also not been observed experimentally. In order to instill confidence in the simulations, agreement must be shown between the phases that are experimentally observed and those used in computer simulations, otherwise the projected rate and extent of reaction is of questionable use. Also, in most instances the thermodynamically most stable phase is not the phase formed initially, rather the kinetically favored phase is usually formed first and the system matures over time as less stable phases give way to more stable phases [4]. Because they may control the solution chemistry for long times, these metastable phases as well as the more mature stable phases must be accounted for to correctly model the reaction progress. These intermediate phases may only be identified through experimentation.

To generate secondary phases, the solution must first become supersaturated. From Eq. 2, the rate the solution concentration increase slows as the solution becomes more concentrated in a self-slowing fashion as described by the affinity term. In order to accelerate the approach to saturation, the reaction can be performed at elevated temperatures to increase k or at high SA/V ratios. The accelerating effect of high SA/V ratios occurs because by minimizing the leachant volume or increasing the glass SA, both the amount of glass which must react and the time of reaction required to attain supersaturated conditions are minimized. Both high temperature and high SA/V are usually required to reach supersaturation within a reasonable time period. Note that the rate of depletion of a species from the glass (dm_i/dt in Eq. 1) depends only on the solution chemistry.

The effect of temperature on glass reaction has been well studied, but the effect of SA/V on glass reaction mechanisms is less studied [5]. The usual experimental approach to achieve high SA/V ratios utilizes powdered samples to provide a large surface area. The work of Allen et al. [6] and of Van Iseghem et al. [7] has shown secondary phases to be generated after about one-half year at elevated temperatures in experiments using powdered glass and small leachant volumes. These workers have identified several secondary phases formed on the reacted solids. The formation of these phases was coincident with an increase in reaction rate as measured by the increase in soluble species in solution. We have used an alternate technique which generates secondary phases within a few days on monolith samples. This is done by restricting the amount of water in contact with the glass by performing experiments in a steam ($T > 100^\circ\text{C}$) or vapor ($T < 100^\circ\text{C}$) atmosphere [8]. In a steam atmosphere, reaction occurs within a small volume of water which condenses on the glass surface. Very high SA/V ratios are attained and the reaction is accelerated upon formation of secondary phases. Both methods accelerate the reaction progress and produce secondary phases within a laboratory time-frame. A disadvantage of using powders is that all the reacted solids must be analyzed to assure that all secondary phases are identified. Also, analysis of the reacted glass is restricted in that the layer thickness may be difficult to ascertain due to irregular particle shapes. An advantage of the use of powders is that a large volume of leachate solution is available for post-test analysis. At the same time, a maximum SA/V that can be achieved is established by the minimal volume of leachate which can be separated from the glass for analysis. An advantage of using monoliths is that all secondary phases form on a single sample which greatly simplifies solids analysis. The reacted glass is easily cross-sectioned for layer analysis and secondary phases can be picked from the sample for individual analysis.

The two techniques are complementary in the sense that the reaction can be tracked through solution analysis (with powdered glass experiments), secondary phase formation (both powder and steam experiments), and by complete analysis of the reacted glass (steam experiments). Both solution and solids analyses may be used to validate the models used in computer simulations, and to demonstrate that experimental techniques used to accelerate the reaction do not significantly change the mechanism or nature of the reaction.

EXPERIMENTAL RESULTS AND DISCUSSION

Detailed analyses of the reacted solids can be used to in reaction mechanisms or compare the alteration of glass under various conditions. Generation of similar reaction products provides evidence that an experimental technique of accelerating the reaction progress does not alter the reaction mechanism. We have previously shown [8] that the reaction layers of glass reacted in a steam atmosphere become very thick after precipitates form, indicating an increase in the reaction rate. We have since analyzed the layers of samples of SRL 202 glass reacted in steam that have not (yet) generated secondary phases and samples that have generated secondary phases using analytical electron microscopy (AEM). While the solutions in contact with all samples reacted in vapor may become supersaturated with respect to several mineral phases, nucleation of these phases may or may not occur within the testing time. Nucleation may be related to slight differences in the volume of water in contact with the glass. We have also analyzed samples of SRL 165 glass reacted in liquid water at 90°C for comparison [9]. SRL 202 glass is the current reference glass for WSRC waste while SRL 165 glass was an earlier reference glass. The compositions are given in Table I. Figure 1a shows the reaction layer of an SRL 165 type glass reacted for 278 days at a SA/V of 30 m⁻¹ at 90°C. Figure 1b shows a typical layer formed on SRL 202 glass in steam at 200°C which did not generate secondary phases. The particular sample shown had reacted 57 days without precipitating minerals from the solution. This is an extreme example of delayed nucleation; most samples form precipitates within 10-14 days at 200°C. Note the similar appearance of the layers on these two samples. Both layers are depleted in alkali metals and enriched in alkaline earths and other elements of low solubility relative to the unreacted glass. Both appear to be growing separate from the glass; note the region of epoxy between the layer and the glass. It appears that reaction continues at the exposed glass surface beneath the layer. High resolution microscopy reveals lattice images of a crystalline phase identified as smectite clay within the otherwise amorphous layers of both samples [10]. These are interpreted to form in situ within the layer and to be distinct from mineral phases precipitated from the solution. Figure 1c shows the layer formed on SRL 202 in steam at 200°C after 7 days on a sample on which many secondary mineral phases did precipitate from solution. Note that the layer is much thicker than that formed in Figure 1b. High resolution electron microscopy shows there to be an abundance of microcrystallites throughout the layer with lattice spacings similar to those found in the other layers. Figure 1d shows a typical section of this layer. The crystallites in the other layers had a similar appearance.

Compositional analysis of the layers using X-ray spectroscopy (EDS) shows them to all be depleted in alkali metals and boron. The layer generated in liquid solution at 90°C was enriched in several elements having low solubilities, such as the alkaline earths and aluminum. This results from partial dissolution of the silicate network and a compression of the residual layer. The layer generated in vapor on the sample which did not precipitate secondary minerals from solution maintained a level of

Table 1
Compositions of SRL 165 and SRL 202 Glasses

Oxide	SRL 165 Oxide wt %	SRL 202 Oxide wt %	Oxide	SRL 165 Oxide wt %	SRL 202 Oxide wt %
Al ₂ O ₃	4.08	3.84	MoO ₃	<0.01	0.05
B ₂ O ₃	6.76	7.97	Na ₂ O	10.85	8.92
BaO	0.06	0.22	NiO	0.85	0.82
CaO	1.62	1.20	PbO	-	0.01
Cr ₂ O ₃	<0.01	0.08	SiO ₂	52.86	48.95
Cs ₂ O	0.07	-	SrO	0.11	0.03
CuO	-	0.40	TiO ₂	0.14	0.91
Fe ₂ O ₃	11.74	11.41	ZnO	0.04	0.02
K ₂ O	-	3.71	ZrO ₂	0.66	0.10
Li ₂ O	4.18	4.23	ThO ₂	-	0.26
MgO	0.70	1.32	UO ₂	0.96	1.93
MnO ₂	2.79	2.21			
			Total	98.49	98.58

Figure 1. Photomicrograph of (a) SRL 165 Glass Leached at $SA/V = 30 \text{ m}^{-1}$ at 90°C for 278 Days, (b) SRL 202 Glass Reacted in Steam at $SA/V > 4000 \text{ m}^{-1}$ at 200°C for 57 Days with No Secondary Phase Formation, (c) SRL 202 Glass Reacted in Steam at $SA/V > 4000 \text{ m}^{-1}$ at 200°C for 7 Days with Secondary Phase Formation, and (d) High Resolution Image of Layer in (c) Near the Outer Surface.

low solubility elements similar to the unreacted glass. The silicate network does not dissolve to a significant degree in the vapor environment because the silicon solubility limit is quickly reached in the vapor environment. The layer on the sample reacted in vapor to form secondary minerals on the outer surface was depleted in several elements with low solubilities. The presence of secondary phases which contain these elements provides a more stable phase than the layer for elements of low solubility. As the glass reacts, species such as aluminum can be removed from the layer and contained in a phase such as analcime while maintaining a low solution concentration.

The formation of secondary phases will alter the chemistry of the solution in contact with the glass. Analysis of the solution provides another measure of the reaction progress and can be compared to the compositional analysis of the layers and to the results of computer simulations. We have characterized the solution produced during reaction in steam to better relate the extent of reaction and secondary phase formation to the computer simulation results. The solution in which the reaction occurs at 200°C in the saturated steam environment evaporates from the sample and condenses on the cool reaction vessel when the reaction is terminated. Dissolved salts are left as residue on the sample surface as the solution evaporates. We have allowed several reacted samples of SRL 202 glass to reequilibrate in water vapor at room temperature to redissolve these salts and approximate the solution in which the glass reacted. Experiments were performed with two samples included in each reaction vessel. Immediately upon terminating the experiment, the reacted samples and the water on the vessel bottom were removed from the vessel. One sample was retained for later analysis. A small amount of DIW and the other reacted sample were placed back in the vessel and the vessel resealed. The initially dry sample became wetted upon exposure to the water vapor and droplets formed within a few days due to osmotic pressure gradients. Solution volumes ranging from 0.01 to 0.04 mL were removed using a micropipet, diluted with deionized water, acidified with HNO_3 , and analyzed by ICP. Approximately 0.006 mL of solution remained on the sample. This residual volume was included in the calculations to determine the amount of species in solution. The resulting solution composition is only an approximation of that present during reaction since precipitates may form upon evaporation or quenching that do not redissolve during reexposure. The phase solubilities will differ at 200°C in saturated steam and at 25°C in water vapor, but selected species that are highly soluble may be expected to have similar high solubilities in both cases. For example, the alkali metals Li and Na as well as boron may be representative of the solution at high temperatures. Table II shows the dilution-corrected concentrations for a highly reacted sample containing an abundance of secondary phases (referred to as sample 3) and for two samples which reacted to a lesser extent and generated no secondary phases (referred to as samples 1 and 2). The water recovered from the vessel bottom of several tests was analyzed to show the highly concentrated solution condensed on the sample did not drip off the sample during reaction or during termination. A drop of 0.05 mL volume, for example, would be diluted about 4X by the 0.20 mL of water in the vessel bottom. The pH would increase from about 6 to 9 if dripping had occurred. The measured pH of the recondensate on the glass sample was 10 for all samples independent of the visual extent of reaction and the water in the vessel bottom had a pH value near 6. The solution analyses are presented as the mass of species in the recondensed solution and as the mass in the solution per micrometer of the measured layer thickness of the reacted glass. The thickness of the reaction layers formed on these samples were measured using an SEM. Included in the table are the theoretical mass and mass per micrometer of species (Na, Li, B) that would be released if the measured reaction layer was totally depleted. It is assumed that the outer surface

TABLE II
Analysis of Recondensate on Vapor-Reacted Samples of SRL 202

Sample Number	1	2	3
Extent of Reaction	Low	Low	High
Number of Ppts	None	Very few	Many
Layer Thickness, μm	4.0	6.0	21
B, μg	15 (52) ^a	35 (78)	130 (270)
B, $\mu\text{g}/\mu\text{m}$	3.8 (13)	5.8 (13)	6.2 (13)
Li, μg	36 (44)	29 (66)	21 (231)
Li, $\mu\text{g}/\mu\text{m}$	9.0 (11)	4.8 (11)	1.0 (11)
Na, μg	80 (140)	89 (210)	190 (760)
Na, $\mu\text{g}/\mu\text{m}$	20 (36)	15 (36)	9.0 (36)
Si, μg	2	2.1	4.5
Si, $\mu\text{g}/\mu\text{m}$	0.5	0.35	0.21

^atheoretical values assuming total depletion of measured reaction layer.

of the layer was the outer surface of the original glass. These values are given in parentheses next to the measured values. Analysis of the reacted layers shows them to be depleted totally (within analytical error) in boron and sodium. Depletion of lithium has been seen to be nearly complete in previous studies [10] and is assumed here. Silicon is only slightly depleted in the layer relative to the unreacted glass and no theoretical concentrations are given. The silicon in the recondensate is presented as mass per micrometer of layer thickness for comparison.

The total amount of boron in solution increases with the extent of reaction as measured by the layer thicknesses. The mass of boron released per micrometer increases with the layer thickness but attains less than half the predicted concentrations. The total amount of lithium in the recondensed solution is similar to the predicted amount for the least reacted sample but less than the predicted amount for the most reacted sample. The mass of lithium in solution per micrometer layer thickness decreases with increasing layer thickness. Sodium and silicon show similar behavior to lithium in that the amount in solution per micrometer layer thickness decreases with increasing layer thickness. This suggests that lithium is contained in a secondary phase with low solubility in the highly reacted sample and is not representative of the extent of glass reaction. Lithium is usually the most highly leached species in static leach tests and is predicted by EQ3/6 simulation to be contained in petalite after long reaction times. Jantzen has reported the formation of hectorite (a lithium saponite) on SRL 165 glass [11] and glasses with a high phosphate content have been seen to form Li_3PO_4 [8], although no lithium phase has yet been identified on these reacted SRL 202 glass samples.

Sodium and silicon are known to be contained in zeolites (including analcime) identified to form on the surface of sample 3. The formation of secondary phases reduces the solution concentrations of sodium, silicon, and, presumably, lithium. The concentrations per micrometer layer thickness of lithium, sodium, and silicon decrease as the layer thickness increases because these elements are incorporated into secondary phases as the reaction progresses.

While the solution generated by reexposing the reacted glass to water vapor is only an approximation of the solution in which the reaction occurs, interactions between the solution and the secondary phases are evident. Based on the amount recovered per micron layer thickness, the

boron concentration is most representative of the reaction progress of those species analyzed. Lithium, sodium, and silicon show the suspected effects of secondary phase formation to lower the solution concentrations. A more complete analysis of the solution may provide more evidence to relate the solution chemistry to the assemblage of secondary phases that is in equilibrium with it, but these scoping experiments have shown that the solution in contact with the glass in a steam environment can be characterized for comparison to the reacted solids.

CONCLUSIONS

Solution and solids analyses of tests at high SA/V performed in steam show that the solution chemistry and the rate of glass reaction change upon generation of secondary phases. The increase in the solution concentrations demonstrates an increase in the glass reaction rate which is also reflected by increased layer thicknesses in tests with glass monoliths. Microscopic analysis of reacted glass shows the reaction to produce similar reaction layers in liquid water at 90°C and in steam at 200°C prior to and after secondary phase formation. Thus both temperature and high SA/V accelerate the reaction progress of these glasses so the long-term reaction can be characterized and composed to the results of computer simulations. The model of glass reaction used in computer simulations to project glass reaction to long times or large extents of reaction predicts the reaction to slow as the solution becomes saturated (with respect to the glass) until stable secondary phases form. These phases then establish lower solubility limits for glass components which in turn set the reaction affinity. The predicted behavior is observed in experiments performed at large SA/V. Experiments in a vapor environment can be used to accelerate the glass reaction to the point where secondary phases form. Such experiments are required to generate and identify secondary phases which control the solution chemistry and so the glass reaction rate. Computer simulations used to project the long-term reaction behavior must include these phases in their data base to correctly characterize the reaction.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Project, under subcontract to Lawrence Livermore National Laboratory, SANL 910-005.

REFERENCES

1. P. Aagaard and H. C. Helgeson, "Thermodynamic and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous Solutions. I. Theoretical Considerations," *Amer. J. Sci.* **282**, 237-285 (1982).
2. B. Grambow, "A General Rate Equation for Nuclear Waste Glass Corrosion," in *Scientific Basis for Nuclear Waste Management VIII*, C. M. Jantzen, J. A. Stone, and R. C. Ewing, eds., Materials Research Society, Pittsburgh, PA (1985).
3. W. L. Bourcier, D. W. Pfeiffer, K. G. Knauss, K. D. McKeegan, and D. K. Smith, "A Kinetic Model for Borosilicate Glass Dissolution Based on the Dissolution Affinity of a Surface Alteration Layer," *Mat. Res. Soc. Symp. Proc.* Vol. 176, 209 (1990).
4. D. W. Breck, *Zeolite Molecular Sieves, Structures, Chemistry and Uses*, John Wiley and Sons, Inc., New York (1974).
5. J. K. Bates, "The Role of Surface Layers in Glass Leaching Performance," this volume (1990).

6. C. C. Allen, D. L. Lane, R. G. Johnston, A. D. Marcy, and R. R. Adec, "Hydrothermal Studies of Simulated Defense Waste Glass Plus Basalt," Mat. Res. Soc. Symp. Proc. 44, 451 (1985).
7. P. Ph. Van Iseghem, W. Timmermans, and R. DeBatist, "Parametric Study of the Corrosion Behavior in Static Distilled Water of Simulated European Reference High Level Wastes Glasses," Mat. Res. Soc. Symp. Proc. 44, 55 (1985).
8. W. L. Ebert and J. K. Bates, "The Reaction of Synthetic Nuclear Waste Glass in Steam and Hydrothermal Solution," Mat. Res. Soc. Symp. Proc. 176, 339-346 (1990).
9. J. P. Bradley and J. K. Bates, "Leached Nuclear Waste Glasses: Ultramicrotomy and Analytical Electron Microscopic Characterization," Proc. of the 12th Int. Congress for Electron Microscopy, Seattle, WA, August 13-17, 1990, pp. 444-445 (1990).
10. W. L. Ebert, J. K. Bates, and T. J. Gerding, "The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part 4: SRL 165, ATM-1c, and ATM-8 Glass at 1E3 R/h and 0 R/h," Argonne National Laboratory report ANL-90/13 (1990).
11. C. M. Jantzen and W. G. Ramsey, "Prediction of Radioactive Waste Durability by the Hydration Thermodynamic Model: Application to Saturated Repository Environments," Mat. Res. Soc. Symp. Proc. Vol. 176, 217 (1990).

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.

END

DATE FILMED

06 / 10 / 91