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ACCELERATED GLASS REACTION UNDER PCT CONDITIONS*

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ABSTRACT

Static leach tests similar to the PCT were performed for times up to two years to assess the long-term reaction behavior of high-level nuclear waste glasses similar to those expected to be produced at the Defense Waste Processing Facility. These tests show the reaction rate to decrease with the reaction time from an initially high rate to a low rate, but then to accelerate to a higher rate after reaction times of about one year, depending on the glass surface area/leachant volume ratio (SA/V) used. The solution concentrations of soluble glass components increase as the reaction is accelerated, while the release of other glass components into solution is controlled by secondary phases which form during the reaction. The net result is that the transformation of glass to stable phases is accelerated while the solution becomes enriched in soluble components that are not effectively contained in secondary phases. The rate becomes linear in time after the acceleration and may be similar to the initial forward rate. A current model of glass reaction predicts that the glass reaction will be accelerated upon the formation of secondary phases which lower the silicic acid solution concentration. These tests show the total silicon concentration to increase upon acceleration of the reaction, however, which may be due to the slightly higher pH that is attained with the acceleration. The sudden change in the reaction rate is likely due to secondary phase formation.

INTRODUCTION

The long-term behavior of high-level nuclear waste glasses to be emplaced in a geologic repository must be predicted on the basis of observations made in short-term laboratory experiments and cannot be simple extrapolations of experimental data [1,2]. The underlying basis of many models of glass corrosion is that the rate-determining step for glass corrosion is the hydrolysis of the bond between a network silicon and an $-\text{OSi}(\text{OH})_3$ group to release silicic acid [3]. The glass reaction rate is modeled using a reaction affinity approach in which the rate is expressed as a function of the difference between the silicic acid concentration in solution and a "saturation" concentration. According to this model, the reaction slows as the silicic acid concentration approaches "saturation" with respect to the glass and eventually proceeds at a low rate [2-7]. Simulations have shown that leachate solutions may become saturated with respect to secondary phases during the reaction, and that these phases may control the solution chemistry at long reaction times such that the solution composition does not attain "saturation" conditions and the reaction rate remains high [4,6]. The long-term reaction rates predicted by computer simulations may be different depending on the assemblage of secondary phases formed [8].

In order to address the issue of long-term glass reaction rates, tests were performed to characterize the effects of secondary phase formation on the subsequent glass reaction. High glass surface area/leachant volume ratios (SA/V) were used to attain highly concentrated leachate solutions conducive to secondary phase formation after very little glass had reacted. These solution conditions have been likened to those expected under stagnant leaching conditions after long reaction times at lower SA/V [9], and so may provide a measure of the glass reactivity relevant to long-term disposal in a waste repository.

Observations of accelerated reactions upon secondary phase formation has been described previously. Experiments performed with monolith samples in steam have shown that the glass reaction rate may be significantly increased upon secondary phase formation [10,11]. Other tests with European glass compositions in aqueous solutions have also shown increased reaction rates after long reaction times and secondary phase formation [2,12]. Zeolite formation (analcime) was interpreted to reduce the silicon concentration in solution to below the "saturation" value and so accelerate the reaction rate in these tests[8]. These results suggest that the constant, low reaction rate often observed in short-term tests cannot, in general, be used to predict the long-term glass reaction rate. Also, if the precipitation of these phases is delayed due to slow nucleation kinetics, the glass may react under "saturation" conditions for long times prior to nucleation, and then show accelerated reaction when the phases nucleate. The work described here was performed to assess the conditions under which secondary phases are formed, which phases form, and how they affect the long-term glass reactivity of high-level waste glass compositions relevant to the U.S. vitrification program.

EXPERIMENTAL

Tests were performed using glass compositions representative of those expected to be produced by the Defense Waste Processing Facility (DWPF). Two compositions were tested: SRL 202, which represents a coupled-feed glass fabricated with a simulated average DWPF waste loading, and a SRL 131-based formulation, which is similar to the EA composition and represents a glass of acceptable durability. Both glasses were doped with radionuclides to study their distribution upon glass corrosion in tests at different SA/V. Only the results of tests with SRL 202 glass are discussed in this paper. The glass composition is given in Table I. Tests were performed similar to the Product Consistency Test (PCT) protocol [13] for reaction times up to two years. Glasses were crushed and the size fraction between 74 and 149 μm used in all tests. Glass was reacted in a tuff ground water solution (referred to as EJ-13) at 90°C. Tests were performed using either 1 gm of glass in 10 mL of leachant or 5 gm of glass in 5 mL of leachate to attain SA/V values of about 2000 m^{-1} or 20,000 m^{-1} , respectively. Tests were performed in 304L stainless steel vessels.

Table I
SRL 202 Glass Composition

Oxide	SRL 202	Oxide	SRL 202	Oxide	SRL 202
Al ₂ O ₃	3.84	MnO ₂	2.21	U ₃ O ₈	1.93
B ₂ O ₃	7.97	MoO ₃	0.05	ZrO ₂	0.10
BaO	0.22	Na ₂ O	8.92	ZnO	0.02
CaO	1.20	NiO	0.82		
Cr ₂ O ₃	0.08	PbO	0.01	Am ₂ O ₃ ^a	0.0004
CuO	0.40	SiO ₂	48.9	PuO ₂ ^a	0.01
Fe ₂ O ₃	11.4	SrO	0.03	NpO ₂ ^a	0.01
K ₂ O	3.71	TcO ₂ ^a	0.03		
Li ₂ O	4.23	ThO ₂	0.26		
MgO	1.32	TiO ₂	0.91	Total	98.6

^aDopant added to produce SRL 202A glasses.

Upon termination of a test, vessels were opened and the leachant sampled at the reaction temperature. The leachant was filtered through 0.45 μm filters which had been pre-heated to the reaction temperature to remove any suspended glass particles from the leachate. Aliquots were taken from the filtrate for pH, anion, and cation analyses. The leachates from some tests were further filtered through approximately 6 nm filters to determine the amounts suspended and dissolved in solution. Details are given elsewhere [14].

The reacted glass was gently rinsed with deionized water and allowed to dry prior to analysis. The reacted solids were analyzed using optical microscopy, scanning electron microscopy (SEM), and analytical electron microscopy (AEM) to identify secondary phases and characterize the extent of glass reaction.

RESULTS

The aliquots taken for pH measurement were allowed to cool to room temperature prior to analysis. The final pH values are shown in Figure 1 for tests with SRL 202 glass at 2000 and 20,000 m^{-1} . The average value of duplicate tests are plotted, and the differences in the pH values of duplicate tests are all within the size of the symbol. The data points are connected for clarity. The initial pH increase is large at short reaction times at both SAV; the pH increases to higher values in tests at 20,000 m^{-1} at all times. The pH then increases slowly beyond about 28 days at both SAV.

The solutions filtered through 0.45 μm filters may include suspended material, while the solutions filtered through 6 nm filters are assumed to contain only dissolved material. The solutions with the suspended material best represent the total extent of glass reaction, and these data are plotted as a function of reaction time in Figure 2 for several glass components. The values plotted are the normalized elemental mass losses, which are the measured concentrations, in ppm, less the amount in the initial leachant solution, divided by the mass fraction of that element in the unreacted glass, and divided by the SAV of the test. The lines drawn in the figures are provided to show the data trends and do not represent analytical fits to the data. Further filtration of the leachates through 6 nm filters did not reduce the measured levels of alkali metals, boron, or silicon beyond the 15% analytical limit at either SAV, but did reduce the measured concentrations of aluminum, iron, and manganese [14]. Reaction at 2000 m^{-1} resulted in the nonstoichiometric release of glass components: the alkali metals and boron are released to a greater extent than silicon at all times tested. The release rates of the alkali metals and boron are initially high but continually decrease as the reaction continues. Uranium is released to solution at a rate similar to silicon for the first 14 days in tests at 2000 m^{-1} , but the uranium concentration remains nearly constant thereafter.

Figure 1.
Leachate pH Values (25°C)
vs. Reaction Time for Tests With
SRL 202 Glass at (♦) 2000 m^{-1}
and (■) 20,000 m^{-1} .

(a)

(b)

(c)

Figure 2.
Normalized Elemental Mass
Loss vs. Reaction Time for Tests
with SRL 202 Glass at (a)
 2000 m^{-1} (b) and (c) $20,000 \text{ m}^{-1}$
(■)Li, (▲)Na, (●)B, (◆)K, (○)Si,
and (□)U. The lines are drawn
to show data trends but do not
represent analytical fits.

The alkali metals and boron are also released to a greater extent than silicon in tests at $20,000 \text{ m}^{-1}$. The release of the alkali metals and boron slows with time through about 182 days, but suddenly increases after a reaction time between 182 and 364 days. Figure 2c shows the same data as in 2b replotted to show the release behavior at short times. Beyond 182 days, the release of the alkali metals and boron proceeds at a nearly constant rate that is similar to the rate measured during the first three days. The degree of increase in the solution concentrations is different for the different glass components: boron is increased the most followed by sodium, potassium, and lithium. While lithium is released to the greatest extent at short reaction times (see Figure 2c), its release remains nearly constant between about 91 and 182 days and is only slightly accelerated beyond about 182 days. The release of silicon to solution is increased between 182 and 364 days, but the silicon concentration increases only slightly beyond 364 days. The uranium solution concentration increases slightly at very short reaction times, but then decreases beyond about 14 days and is not significantly affected by the increased reaction rate which occurs after about 182 days.

Solids Analysis

The appearance of the reacted glasses from tests before and after acceleration was visibly distinct. Glass reacted at 2000 m^{-1} at all times and at $20,000 \text{ m}^{-1}$ for 182 days or less appeared unreacted to the unaided eye, while glass reacted for 364 days or more at $20,000 \text{ m}^{-1}$ was covered with a white crusty material. The surfaces of some samples were inspected using an SEM. The surfaces of the highly reacted samples were covered with a porous, flaky material, while the other samples had surfaces that looked slightly roughened relative to the unreacted glass. To better characterize the surface layers, reacted glass particles

were isolated, potted in an epoxy resin, and then thin-sectioned using an ultramicrotome for AEM analysis [15]. The thin-sectioned samples were analyzed to characterize the thickness, structure, and composition of the reacted glass after different reaction times. Figures 3 -c show the reacted surface of SRL 202 glass reacted at $20,000 \text{ m}^{-1}$ for 14, 182, and 364 days. The layer formed after 14 days is seen to be composed of small laths of material and has separated from the underlying glass. Some chattering of the unreacted glass (horizontal fracturing in the photomicrographs) has occurred during microtomy due to differences in the hardness of the glass, layer, and epoxy. After 182 days of reaction, the thickness of the layer has increased slightly, but the general appearance of the layer has not changed. Selected area electron diffraction (SAED) shows the layer to be polycrystalline, although a moderate degree of ordering of the microcrystallites that comprise the layer can be seen perpendicular to the glass surface. A much thicker layer having two distinct regions is formed after 364 days of reaction, as shown in Figure 3c. The outer part of the layer appears similar to the layer formed after 182 days, and has a similar thickness and similarly oriented laths. The inner part is much thicker and appears to be composed of smaller, more randomly oriented microcrystallites. The SAED analysis shows the crystallites in the inner and outer parts of the layer to have similar structures. Layers formed on glass reacted at 2000 m^{-1} were thin and had an appearance similar to those shown in Figure 3 a and b at all reaction times.

Figure 3. Photomicrographs From AEM Analysis of SRL 202 Glass Reacted (a) 14 days, (b) 182 days, and (c) 364 days.

Table II
Compositional Analyses of Reaction Layer, Elemental Weight Percent*

Element	Glass Composition	364-Day Outer Layer	364-Day Inner Layer
Si	60	58	57
Mg	1.6	1.6	0.7
Al	4.7	13	10
K	4.6	0.3	0.9
Ca	1.5	0.6	1.5
Ti	1.1	1.0	2.1
Mn	2.7	5.0	5.5
Fe	14	21	22
B	9.8	0.5	0.5

*Normalized to 100% total of elements listed.

Compositional analysis using energy dispersive X-ray spectroscopy (EDS) in the AEM shows the inner and outer layers formed on the sample reacted 364 days also have similar compositions, as given in Table II. Also included in Table II are the results of WDS analysis for boron obtained in the SEM. The entire layer is depleted in boron and sodium and enriched in aluminum, calcium, magnesium, manganese, and iron, relative to the bulk glass. The layer formed in other tests had similar compositions. The results of structural and compositional analyses of the layers are consistent with their being a smectite clay phase.

Several other secondary phases that form during the glass reaction have been identified by AEM analyses of the reacted solids. Bright yellow phases seen on the surface of the reacted glass in tests performed at $20,000\text{ m}^{-1}$ for 364 days or longer were identified as weaverite ($\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$). Also found on the top surface and amongst the reacted glass particles were a milky white phase that has been identified as clinoptilolite ($(\text{Na,K})_6(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 20\text{H}_2\text{O}$) and an amorphous silicon phase. Other AEM analyses are in progress to better characterize these and other phases that may have formed. AEM analyses were also performed on suspended material that was filtered from the leachate. These are discussed elsewhere [16].

DISCUSSION

These results demonstrate that the long-term glass reaction cannot, in general, be modeled using a constant rate derived from short-term tests in which the solution becomes "saturated" with silicon. Sudden increases may occur in both the release of soluble components to solution and the generation of secondary phases at the glass surface. Boron is usually assumed to provide the best measure of the extent of glass reaction because of its high solubility [17]. The boron solution concentration increases the most upon acceleration, while the silicon concentration is only slightly increased. The differences in the release of boron and silicon to solution after 364 days are consistent with the analyses of the reacted glass samples. From Table II, the layers formed are depleted in boron but only slightly depleted in silicon relative to the unreacted glass. Very little silicon released from the glass during the reaction enters solution. Instead, silicon is consumed during the

formation of clay in the reaction layer. Continued reaction occurs at the glass surface beneath the layer. Other glass components, such as the alkali and transition metals, may be incorporated into the clay to varying degrees as the underlying glass continues to react, and their release into solution may be mitigated by the presence of clay layer.

The sudden increase in the glass reaction rate in tests at $20,000 \text{ m}^{-1}$ after 182 days results in changes in both the solution composition and the glass alteration layer. The solution pH is increased slightly and the boron, sodium, and potassium concentrations increase by up to a factor of 10 between 182 and 364 days. The solution concentrations of other glass components, including silicon, are only slightly increased between 182 and 364 days. Clay formed as the primary alteration phase has much small crystal sizes after acceleration of the reaction, which is consistent with its more rapid formation. The continued release of boron occurred at a constant rate of about $0.04 \text{ g/m}^2/\text{day}$ through two years. Longer term tests are in progress to assess if the reaction continues at this rate. Sodium and potassium were released at lower rates that were also constant with time. Silicon and lithium appear to maintain nearly constant solution concentrations at reaction times beyond one year.

While the smectite clay phase appears to be the dominant silicon-bearing phase formed at all reaction times (by volume), other phases may also affect the silicon solution concentration and the reaction rate. Both smectite clay and wecksite are formed at short reaction times long before the reaction is accelerated and likely do not affect the rate. Clinoptilolite and the amorphous silicon phase have only been observed after the reaction has been accelerated, and one or both is suspected to be responsible for the change in the reaction rate. The possible involvement of these and other secondary phases in the observed acceleration of the glass reaction will be further investigated by comparing these experimental results to computer simulations in which the identified phases are allowed to control the solution chemistry.

CONCLUSION

Static leach tests performed for long times show an acceleration of the reaction rate may occur wherein both the generation rate of secondary phases and the release of soluble components to solution increase suddenly after a transient period of low reactivity. These observations are consistent with current models of glass reaction which predict that the formation of secondary phases which reduce the silicic acid concentration in solution will accelerate the glass reaction. The total silicon concentration measured in solution does not decrease with the acceleration, rather it increases slightly due to an increase in the pH. Silicon is consumed by smectite clay which forms at all reaction times and by other secondary phases. The clay phase is not responsible for the acceleration of the reaction and does not restrict access of the leachate to the underlying glass or release of glass components from the glass. Acceleration of the reaction occurs upon the formation of a secondary phase other than the clay (probably a zeolite or an amorphous silicon phase) which consumes silicon and lowers the concentration of non-dissociated silicic acid. Continued reaction occurs stoichiometrically at the glass surface beneath the clay layer with release of glass components to either solution or to secondary phases.

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