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ABSTRACT

Static tests at SA/V (ratio of surface area of glass to solution volume) 20,000 m^{-1} on SRL 200 glass compositions show that, at long test periods, the simulated nuclear waste glass (nonradioactive) leaches faster than the corresponding radioactive glass by a factor of about 40, although comparative tests, done through 560 days, at lower SA/V, 2000 m^{-1}, indicate little difference in the leach behavior of the two types of glasses. The similarity in leach behavior between radioactive and simulated glasses at SA/V of 2000 m^{-1} or lower is also observed for SRL 165/42 and 131/11 compositions. The accelerated glass reaction with the simulated glass 200S is associated with the formation of crystalline phases such as clinoptilolite (or potassium feldspar), and a pH excursion. The radiation field generated by the fully radioactive glass reduces the solution pH. This lower pH, in turn, may retard the onset of increased reaction rate. The radiation field generated by the radioactive glasses does not directly affect the stability of the glass surface alteration layer under those conditions where the radioactive and simulated glasses react at the same rate. These results suggest that the fully radioactive nuclear waste glass 200R may maintain a much lower leach rate than the simulated 200S, if the lower pH in the 200R leachate can be sustained. Meaningful comparison tests between radioactive and simulated nuclear waste glasses should include long-term and high SA/V tests.

INTRODUCTION

There has been interest in the comparison of the leach behavior between fully radioactive and simulated nuclear waste glasses [1-6] ,to assess the differences in reaction mechanism, type, and sequence of secondary phases, and the relative durability among the two types of glasses. The results from these comparisons will provide confidence in the use of the large amount of data generated in the studies of simulated nuclear waste glass for the modeling of performance of radioactive glasses. Most of the previous comparison studies [1,2,4] have been performed at a low to intermediate ratio of glass surface area to solution volume (SA/V $\leq$ 1100 m^{-1}) and for time periods of less than one year. These studies have generally concluded there is little difference in leach behavior between the two glass types. The study reported here reinvestigates that conclusion by utilizing an extensive test matrix, with SA/V ranging between 340 to 20,000 m^{-1} on three waste glass compositions, for time periods planned up to eight years. The early results reported from this study [3,6] are consistent with other studies [1,2,4], in that the leach beahvior of simulated waste glasses is similar to that of fully radioactive glasses. However, the longer-term tests at higher SA/V suggest that the leach beahvior of the two types of glass diverges, under certain conditions. In this paper, the longer-term comparison of the leach behavior is discussed.

EXPERIMENTAL

The experimental details have been reported previously [3]. Briefly, three groups of glass compositions, designated 165/42, 131/11, and 200 have been used. The fully radioactive waste glass compositions (R glasses) were made in the SRL in-cell minimelter, using corresponding glass frits plus sludge from various high-level waste tanks at Westinghouse Savannah River Site. The simulated glass compositions (S glasses) were made to have the same compositions as the R glasses, but with no actinides. The glasses were tested at 90°C in EJ-13 water (repository groundwater equilibrated with tuff rock) at SA/V = 340 m^{-1} (monolith), 2000 m^{-1} (powder), and 20,000 m^{-1} (with glass 200 powders only). These tests have been in progress up to 30 months and most of the tests were done in duplicate. The test vessel is a 22 mL 304L stainless steel vessel with a copper gasket. The solution analyses include leachate pH (at room temperature), cations, selected anions, and actinides. Analyses were done on solutions filtered through 0.45 and 0.005 μm filters, and the errors associated with solution analyses are estimated to be less than 10%. The leached glass surfaces were examined optically and with SEM/EDS (scanning electron microscopy/energy dispersive spectroscopy), TEM (transmission electron microscopy), and SIMS (secondary ion mass spectroscopy).

RESULTS

The comparison of the normalized release (based on 0.45 μm filtrates) of B, Li, Na, and Si for all the glass compositions tested at 2000 m^{-1} is shown in Figure 1. For 165/42 compositions at times up to 560 days, the normalized Li and Si releases are similar for both R and S glasses. The B and Na releases from 165/42R are higher than those from 165/42S, but by less than 150% (Figures 1a and 1b). For 131/11 compositions at times up to 280 days, the B, Li, Na, and Si releases from 131/11S are higher than those from 131/11R, with differences being less than 300% (Figures 1c and 1d). For 200 compositions at times up to 280 days, the B, Li, Na, and Si releases from 200S are generally higher than those from 200R (Figures 1e and 1f). The trends of the solution results from testing each of these glasses at 340 m^{-1} (not shown here) are similar to these results at 2000 m^{-1}. While the differences that are measured for the reactivity of the R and S glasses are analytically significant, the absolute differences are relatively small and the trends in the data suggest for each glass type (R and S) the same reaction processes are rate-controlling.

However, the leach behavior of the 200-based composition at 20,000 m^{-1} indicates that there may be a large difference in the long-term reactivity between R and S glasses. Figure 2 shows that the glass dissolution reaction for 200S glass at 20,000 m^{-1} is greatly accelerated between 182 and 364 days. The increased reaction rate was verified by two additional tests terminated at 300 and 390 days. The normalized release in terms of B, Na, Li, and Si increased by a factor of 35, 23, 9, and 10, respectively, from 182 to 364 days. The solution pH increases from 11.82 to 12.29 (Figure 2). The 100-200 mesh glass powder of 200S transforms into a cake-like material that adheres to the walls of the test vessel and a large quantity of white crusty precipitated material forms on top of and between the glass powder (Figure 3c). Examination of the reacted surface layers on the glass samples by both SEM and AEM (analytical electron microscopy) reveals rapid thickening of the surface layers, with abundant crystalline phase formation, as shown in Figure 3. The anion concentrations of phosphate, sulfate, chloride, and fluoride also increases up to 70 times, as the rate increases, although the original content of these anions in the bulk glass are low (which suggests a preferential release of these anions from glass).

On the other hand, the release rate for 200R at 20,000 m^{-1} shows almost no increase at all during the same interval, and the slow release trend extends through 560 days (Figure 2). The leachate pH of the 560-day test of 200R is still 11.64, similar to the pH at 15 days. The various anion concentrations of 200R are nearly constant throughout of the 560-day period. At 364 days, the leach rate of 200S is 39, 31, 16, and 9 times higher than 200R in terms of B, Na, Si, and Li release, respectively. The pH of 200S is 0.6 unit higher than the corresponding pH of 200R, at 364 days.

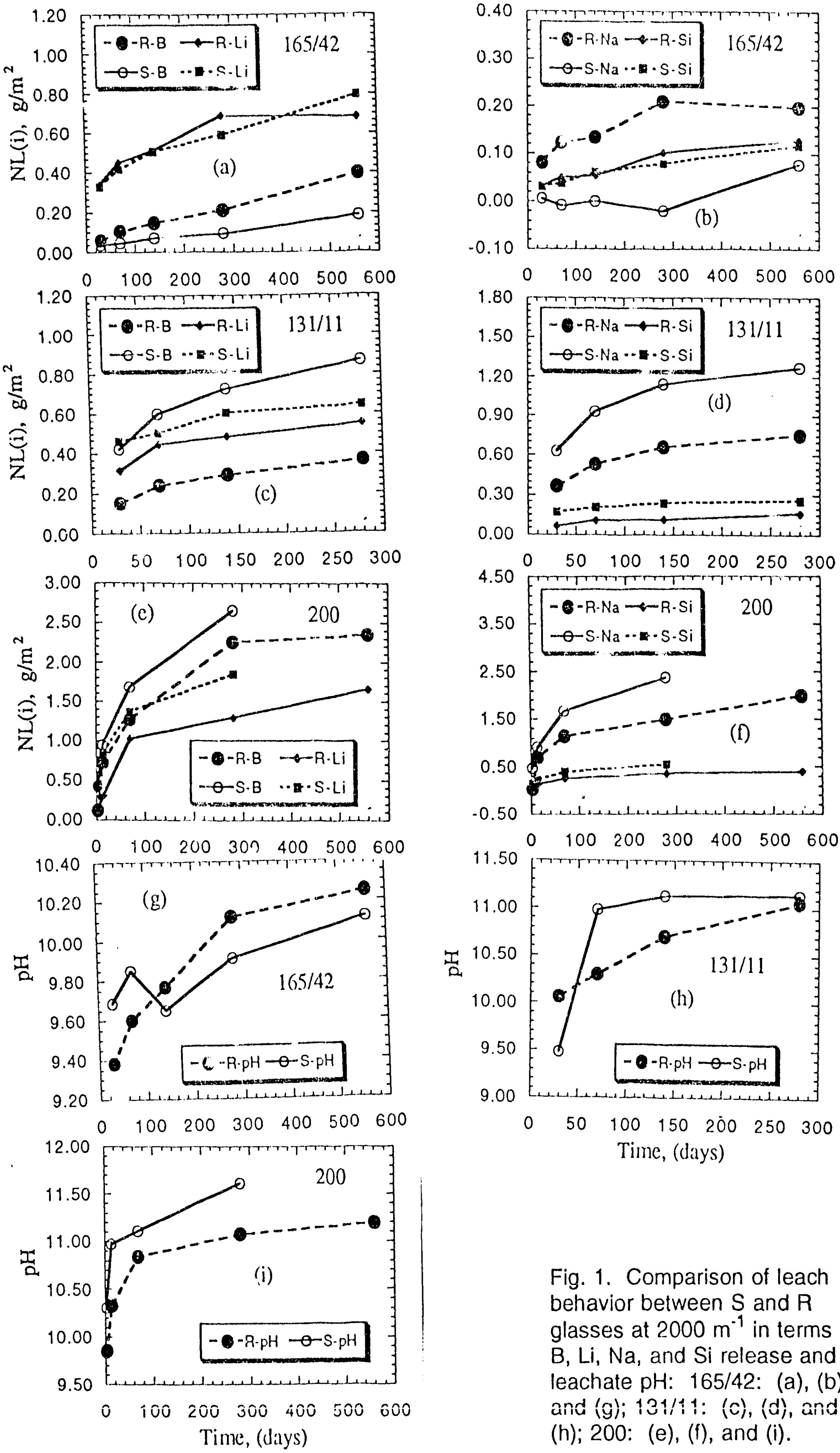

Fig. 1. Comparison of leach behavior between S and R glasses at 2000 m^{-1} in terms of B, Li, Na, and Si release and leachate pH: 165/42: (a), (b), and (g); 131/11: (c), (d), and (h); 200: (e), (f), and (i).

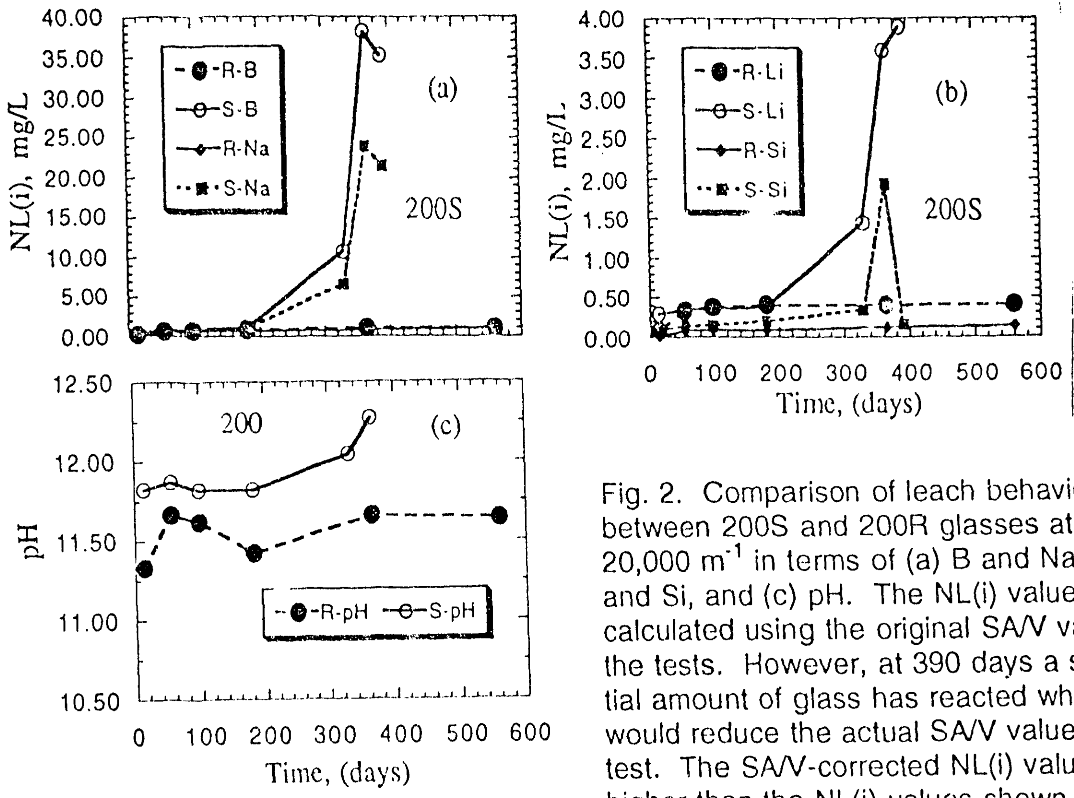

Fig. 2. Comparison of leach behavior between 200S and 200R glasses at 20,000 m^{-1} in terms of (a) B and Na, (b) Li and Si, and (c) pH. The NL(i) values are calculated using the original SA/V value of the tests. However, at 390 days a substantial amount of glass has reacted which would reduce the actual SA/V value of the test. The SA/V-corrected NL(i) values are higher than the NL(i) values shown above.

The uranium concentration in the leachate, of 200S at 20,000 m^{-1}, also increases by a factor of 13, after the acceleration. This is somewhat surprising, due to the basic pH of the leachates, which would suggest a low solubility for uranium. It is possible that the increased U in solution was a result of the higher concentration of anions in the rate-accelerated glass leachate. During acceleration, the concentration increases are 22 times for F^- (7 to 147 mg/L), 21 times for Cl^- (9 to 187 mg/L), 13 times for HPO_4^{-2} (77 to 950 mg/L), and 70 times for SO_4^{-2} (165 to 11550 mg/L). The retention of actinides or rare earth elements by waste glasses has been found to decrease dramatically, when the glasses are tested in brine solutions or other solutions, where anion concentrations are high [7,8].

The surface layers are also significantly different before and after acceleration. The surface layer of 200S at 20,000 m^{-1} before acceleration is a single-layer structure as shown in Figures 3d and 3e. The layer thickness grows slowly with time, being about 150 nm thick (Figure 3d) at 98 days, and about 300 nm (Figure 3e) at 182 days. After acceleration, the surface layers increase to about 6500 nm in thickness with two distinct regions (Figure 3f). The crystalline region has a thickness of about 2000 nm. There is a large amorphous alteration region (more than 4500 nm in thickness) below the crystalline region as shown in Figure 3f. Several types of phases have been identified in the crystalline region. A dominant phase is the elongated prism-shaped crystals with a composition of Si, 61.5; Al, 22.8; K, 9.0; Ca, 4.0 element wt%. The composition shows significant variations in the amounts of K and Ca, depending on the location of the phase in the surface layer being examined. The electron diffraction pattern of the phase matches well with the crystal spacing of a clinoptilolite [9]. The ideal formula for this zeolite phase is $(Na_2,K_2)O{\cdot}Al_2O_3{\cdot}10SiO_2{\cdot}8H_2O$ (Ca and Mg also present; Na, K >> Ca) [9]. However, the composition, d-spacings, and the morphology of this phase are also consistent with a K-feldspar phase. Formation of K-feldspar from zeolite has been well documented [9], but since the phase observed is extremely sensitive to electron irradiation, an indication of containing water, it is more likely the phase is clinoptilolite. The other phases are a

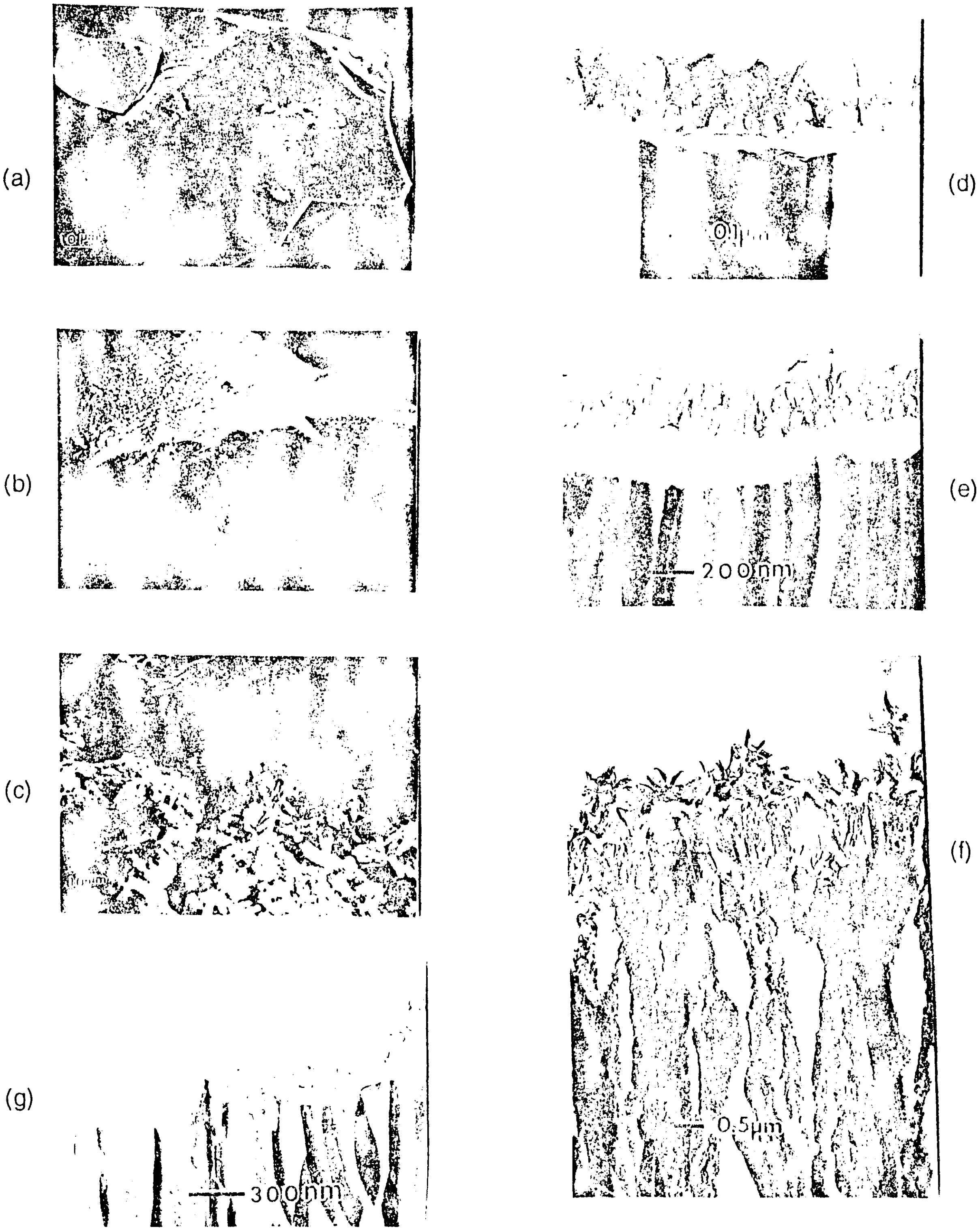

Fig. 3. Surface layer examination on reacted 200 glass compositions at 20,000 m^{-1}: SEM micrographs of the top surface views on 200S samples reacted for (a) 98 days, (b) 182 days, and (c) 364 days; TEM micrographs of cross-sections on samples reacted for (d) 98 days of 200S, (e) 182 days of 200S, (f) 364 days of 200S, and (g) 364 days of 200R.

Fe-rich clay as shown in Figures 3d-3g, an almost pure amorphous Si phase that is both isolated from and in close vicinity with the clay phase, and a Si-Ca phase which is a button-like mass.

Figure 3g is a TEM micrograph of 200R glass reacted for 364 days. The surface layer thickness is 150-300 nm, which is similar to that of 200S at 182 days. The compositions of the surface layer in the 364-day sample of 200R are also similar to the layer composition of 200S before acceleration.

DISCUSSION

The results, on tests done at 340 and 2000 m^{-1}, show only small differences in leach behavior between radioactive and simulated glasses of 165/42, 131/11, and 200 compositions for time periods up to 560 days. On the other hand, the tests at SA/V of 20,000 m^{-1} show up to a factor of 40 difference in leach rates between 200R and 200S glasses within 364 days.

To explain the observed leach behavior, the correlation between solution pH and the extent of reaction is instructive. For the 200-based glasses, the solution pH values for all of the 340 and 2000 m^{-1} tests to date and 20,000 m^{-1} tests prior to 330 days are lower for the R glass compared to the S glass. This pH lowering is attributed to the radiation effect which generates various acids in the system [6]. For the 200 and 131/11-based compositions, the reaction is dominated by network hydrolysis. This process is favored by higher solution pH values, and thus when the radiation effect lowers the leachate pH, the R glasses initially react more slowly than the S glasses (Figures 1h and 1i). On the other hand, the dominant reaction process for the 165/42 compositions during the time periods examined is ion-exchange. The initial lower pH for 165/42R compared to 165/42S (Figure 1g) favors the ion-exchange reaction more in the R glass than in S glass. As the ion-exchange reaction continues, the solution pH increases, which in turn begins to promote the network hydrolysis reaction. This explains why 165/42R is slightly more reactive than 165/42S (Figures 1a and 1b) in terms of B and Na.

The accelerated reaction of 200S after 330 days can also be correlated with solution pH. Solution pH is known to be one of the dominant effects on nuclear waste glass reaction [10,11]. Initially at 20,000 m^{-1}, the 200S glass leachates have pH values of 11.82 ± 0.05 during 15, 56, 98, and 182 days, while the 200R have pH values of 11.65 ± 0.13 between the 15 and 560 days. Additionally, the leach rates of both 200S (before acceleration) and 200R (up to 560 days) decrease with time, and the leach rate for 200R at 20,000 m^{-1} is always lower than corresponding 200S. However, after 330 days the pH of the 200S glass exceeds 12.0 and the reaction rate of 200S greatly increases, while the pH of 200R leachate at 560 days is still similar to its pH at the beginning of the test (Figure 2c) and shows no sign of pH excursion. This lower pH for 200R may retard the onset of increased glass reaction rate. It is possible that no reaction acceleration for 200R will occur if the radiation effect of 200R can maintain the leachate pH below 11.8. The similarity, in the thickness, composition, and morphology of the surface alteration layers between the 182-day sample of 200S (Figure 3e) and the 364-day sample of 200R (Figure 3g), suggests that the radiation field of radioactive glass has not produced any direct effect on the development of surface alteration layers.

Another possible explanation for the observed rate acceleration is the formation of a suite of crystalline phases in 200S samples but not in 200R samples. As the glass reaction progresses, the solution concentration increases. The increased solution concentration lowers the glass reaction affinity [12] and glass reaction rate decreases with time before acceleration. When the solution concentration reaches the solubility limit of a given secondary phase and the nucleation barrier is overcome, the formation of the secondary phase reduces the solution concentration (activity) and increases the glass reaction affinity, resulting in glass reaction acceleration. Figures 3a to 3c show the gradual increase in the formation of surface precipitates. At 98 days (Figures 3a), few surface precipitates are visible. The amount of surface precipitates increases at 182 days (Figure 3b). The surfaces are fully covered with white precipitates (Figure 3c) at 364 days (note that Figures 3b and 3c are at the same magnifications). The dominant zeolite phase (e.g., clinoptilolite) present in the 330, 364, and 390-day samples is not observed for samples up to 182 days, and this zeolite phase may be a main contributor to the acceleration of 200S at SA/V of 20,000 m^{-1}. However, the origination of these phases in 200S, not in 200R, may still be a result of the high solution pH of 200S.

The reduction in glass reaction affinity results from the decrease in solution concentrations (activities) of the elements that make up the secondary phases. However, reduction in elemental concentrations is usually difficult to assess directly from the concentration measured. This is because many factors, such as solution pH, ionic strength, and glass dissolution, influence solution activities besides secondary phase formations. Table I is a list of concentrations of the relevant species for the formation of clinoptilolite (or K-feldspar) before and after acceleration of 200S at 20,000 m^{-1}. In general, the boron and alkali concentrations keep increasing with time and have large increases during the acceleration period. The Al concentration decreases more than four times during acceleration. The Si concentration also decreases eventually, reaching a level of 600 mg/L at 390 days. The reduction in observed concentrations of Si and Al correlates with the formation of the zeolite phases and serves as evidence for the reaction affinity control.

CONCLUSIONS

Static tests at SA/V of 340 and 2000 m^{-1} up to 560 days on three SRL nuclear waste glass compositions show similar reactivity and leach trend between radioactive and simulated nuclear waste glasses with similar chemical compositions. A large difference in reactivity (up to a factor of about 40 in leach rates of boron) has been observed between 200R and 200S glasses when tested at SA/V of 20,000 m^{-1} within one year. The accelerated glass reaction with the simulated glass 200S is associated with the formation of crystalline phases such as a clinoptilolite (or K-feldspar), and a pH excursion. The radiation field generated by the fully radioactive glass reduces the solution pH. This lower solution pH, in turn, may retard the onset of increased reaction rate. The radiation field of the radioactive glass has not been found to have any direct effect on the development of the surface alteration layers on glasses. These results suggest that radioactive glass 200R may leach much less than the corresponding simulated glass 200S under similar test conditions, if the leachate pH of 200R can be kept lower than that of 200S. In

Table I

Leachate Concentrations (mg/L) (0.45 μm Filtrate) of 200S at 20,000 m^{-1} Before and After Acceleration*

Days	B	Li	K	Al	Si
98	499 ± 1	107 ± 5	191 ± 1	4.7 ± 0.1	608 ± 3
182	642 ± 14	117 ± 16	287 ± 11	3.4 ± 1.1	833 ± 12
300	6389	439	1783	1.1	2421
364	22275	1071	4467	0.8	1444
390	20924	1190	4706	0.4	661

*The values with errors are calculated from the duplicate tests and the remaining values are from s singular test that has an analytical error of less than 10%.

modeling the performance of glass, all factors, such as the radiation-induced pH reduction in the leachate discussed above, that influence glass reaction must be accounted for to make adequate long-term predictions. Meaningful comparison tests between radioactive and simulated nuclear waste glasses should include long-term and high SA/V tests.

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