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INITIAL COMPARISON OF LEACH BEHAVIOR BETWEEN FULLY RADIOACTIVE AND SIMULATED NUCLEAR WASTE GLASSES THROUGH LONG-TERM TESTING. PART 1. SOLUTION ANALYSIS

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PART 1. SOLUTION ANALYSIS

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ABSTRACT

A comparison of glass reactivity between radioactive sludge based and simulated nuclear waste glasses has been made through long-term testing of both glass types for SRL 165, SRL 131, and SRL 200 frit compositions. The data demonstrate that for time periods through 280 days, differences in elemental release to solution up to 400% are observed. However, in general, differences in glass reactivity as measured by the release of boron, lithium, and sodium are less than a factor of two. The differences in reactivity are not large enough to alter the order of glass durability for the different compositions or to change the controlling glass dissolution mechanism. A radiation effect exists, mainly in the influence on the leachate pH, which in turn affects the glass reaction mechanism and rate. The differences in reactivity between fully radioactive and the simulated glasses can be reasonably explained if the controlling reaction mechanism is accounted for. Those differences are glass composition and leaching mechanism dependent. Lithium is found to have the highest elemental release in an ion-exchange dominated glass reaction process, while lithium has a lower release than boron and sodium in a matrix dissolution dominated process, where boron and sodium are usually among the most concentrated solution species.

A. INTRODUCTION

Most testing to evaluate the performance of HLW glasses has been done using simulated nonradioactive analogs of the same general composition as the radioactive glass. To apply the knowledge gained in those studies to the assessment of the performance of the fully radioactive production glass, we have to demonstrate that the experiments with simulated glasses are an adequate representation of reaction that will occur with the actual production glasses. We have to assess: (1) do both glass types react by the same controlling mechanism, thereby producing the same secondary phases in the same sequences; (2) is there an effect due to the radioactivity that is not adequately simulated using the nonradioactive glass; (3) is there an effect of using glass that may not contain all the nonradioactive components that will be present in the sludge, supernate, and frit feeds to the actual production process since simulated glasses are generally produced using pure starting materials and the minor components are ignored; and (4) is there a difference in the durability of the two glass types.

The work reported here addresses the above concerns by comparing the reactivity of actual radioactive glasses with that of simulated nonradioactive glasses with closely matching compositions. The present study builds on testing of radioactive glass that has been performed by Westinghouse Savannah River Company (WSRC) [1-6] by extending the duration of testing to longer time periods, by using a range of glass surface area to solution volume (SA/V) ratios, and by performing tests in a silicate water. The test matrices allow for an evaluation of reactivity at selected time periods where solution compositions and the structure of the reacted glass layers can be compared. However, the tests are not intended to provide a complete elucidation of the reaction mechanism and, therefore, the number of sample periods are limited, especially at the early stage of the tests. A comparison between the leaching of radioactive and nonradioactive glasses has also been done as part of the joint Japanese, Swiss, Swedish (JSS) Program. Results from that program [7] indicate that after one year testing there may be a factor of two difference in reactivity between the glass types. The JSS tests were done in an inert gas atmosphere and at a relatively low SA/V. Both conditions would be representative of a saturated storage environment which may mitigate reactivity differences. The present tests are designed to evaluate glass reactivity under conditions that may be more representative of an unsaturated environment.

B. EXPERIMENTAL

The detailed experimental parameters for this study have been reported before [8]. Only a brief description of the glasses and the tests is provided here.

1. Glasses

Three groups of glass compositions were used in this study. They are: (1) 165 based glasses (165/42R is from glass frit 165 type plus sludge from tank 42 and 165/42S is the simulated analog), (2) 131 based glasses (131/11R is from glass frit 131 type plus sludge from tank 11 and 131/11S the simulated analog), and (3) 200 based glasses (200R is from frit 200 type plus sludge from tank 8 and 12 and 200S is the nonradioactive glass). These radioactive glasses were made by WSRC using an in-cell minimelter and represent glasses developed as the process engineering matured. The radioactive glasses are sludge based glasses and these contain nearly the full complement of radionuclides expected in the production glass. The lack of the actual supernatant feed reduces the amount of ^{137}Cs from that of the production glass. However, ^{137}Cs will decay during the thermal period and the glasses used in testing are fair representatives for the evaluation of long-term storage behavior.

2. Leach Tests

Each glass is tested in both monolithic and powder form. The monolith tests are done at SA/V = 340/m, while the powder tests are done at SA/V = 2000 and 20,000/m. The leachant is J-13 well water equilibrated with tuff rock. The test vessel is 22 mL 304L stainless steel vessel with a copper gasket, and the tests are done at 90°C usually in duplicate. Some of the tests have been in progress for more than 20 months. The solution analyses of all the terminated tests include leachate pH, cations, selected anions, total carbon, and actinides with a standard deviation of about 10%. The surface analyses consist of SEM/EDS, SIMS, and TEM/EDS. Only the results from solution analyses are presented here.

C. RESULTS AND DISCUSSION

The available solution data indicate that the leach behavior of the radioactive and simulated glass for each composition type is different. Therefore, the data are presented first as radioactive/nonradioactive glass pairs for each glass composition type tested. Secondly, a comparative overview of the performance of both glass types over different compositions is presented. It is important to note that the tests are scheduled to run for times up to eight years and any conclusions from the current results are tentative.

1. 200-Type Glasses

The solution data for both the monolith tests at SA/V = 340/m and for the powder tests at SA/V = 2000/m and at SA/V = 20000/m for the 200-type glasses show that the radioactive 200R reacts less than the corresponding nonradioactive 200S. The leaching behavior of 200R and 200S is compared at SA/V = 2000/m and at SA/V = 20000/m in Figure 1. 200R shows consistently lower leaching than 200S for all the elements. This includes the matrix elements boron and silicon and the alkalis lithium and sodium. The differences range between 60% to 400%. The pHs of the leachates in 200R are always lower than those in 200S (Figure 1e and 1f). A separate study [9] on the radiation effect indicates that nitrogen related acids and organic acids are produced when a humid atmosphere is exposed to β and γ radiation and the acids produced tend to reduce the leachate pH. Note the pH difference for tests at SA/V = 20,000/m is smaller than that at SA/V = 2000/m. This is because the radiation effect is less dominant at the higher SA/V conditions.

Glass dissolution usually begins with a dealkalization step, characterized by the exchange of hydronium/alkali, followed by matrix dissolution step, which is characterized by a congruent release from the glass. The elemental concentrations measured in solution are a combination of these two release processes plus solubility limited secondary phase formation that occurs at the glass surface. The short-term solution data for the 200-type glasses suggest that the dominant glass reaction process for both 200R and 200S is matrix dissolution even at the shortest time tested. At later times or at higher SA/V (20,000/m), solubility effects also become important. Figures 1a to 1d illustrate the relative normalized release values for individual elements of both 200R and 200S glasses. Initially, a nearly congruent release of boron, sodium, and lithium is evident for both glasses. Silicon exhibits lower normalized release than those of boron, lithium, and sodium since silicon exhibits a solubility controlled formation of clay phases [10]. It is also interesting that the longer the term of the test the greater the deviation from congruent release. The leachate of 200S at SA/V = 2000/m has higher elemental concentrations than 200R and a greater separation in release values is observed between boron, sodium, and lithium (Figure 1a. vs. Figure 1b) for 200S. This divergence in normalized release values suggests that as the solution approaches saturation, elements are being selectively incorporated into secondary phases. The normalized release values have the order of: 200S at 20,000/m > 200R at 20,000/m > 200S at 2000/m > 200R at 2000/m (Figure 1) and the order of deviation from the

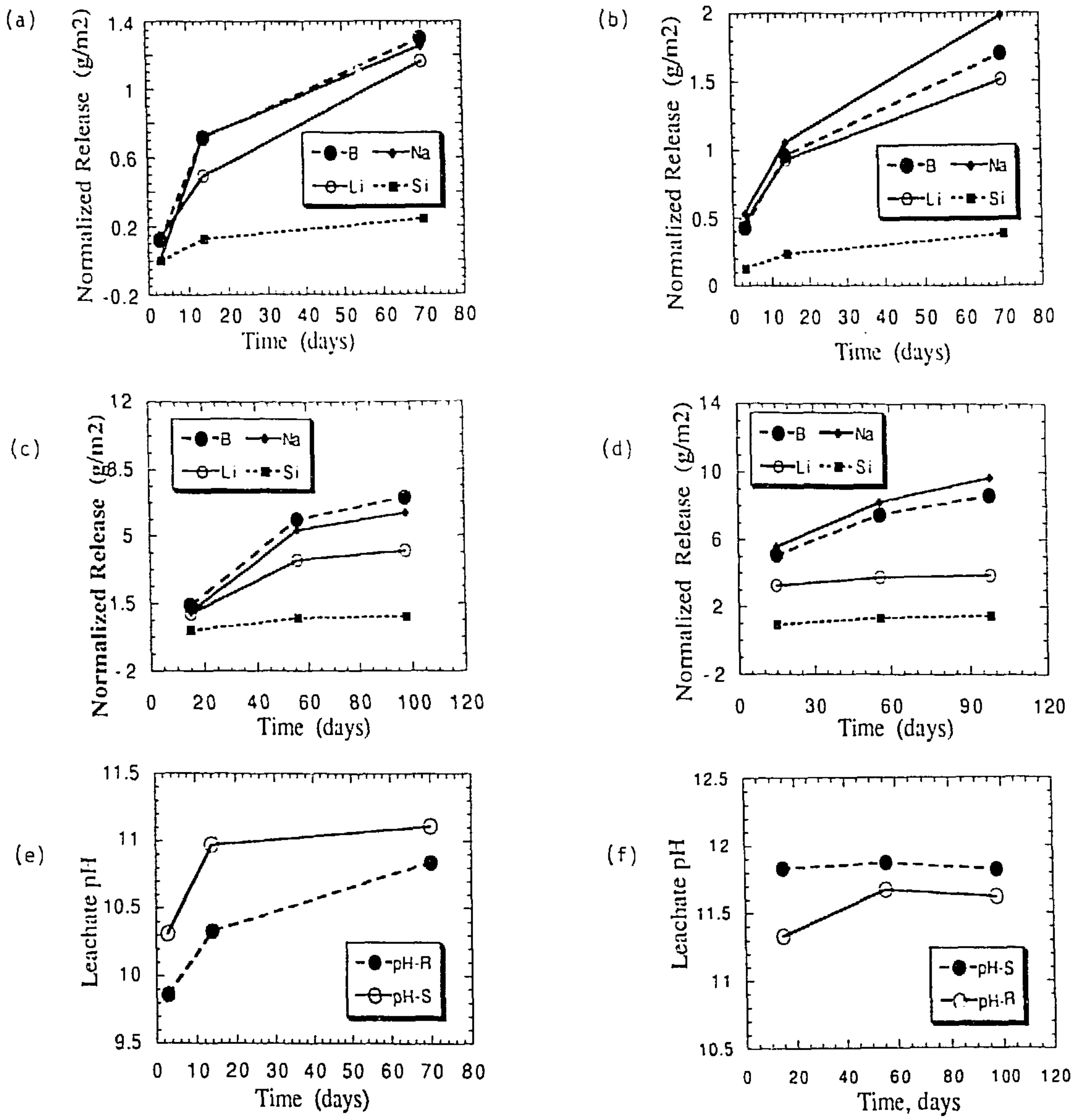

Figure 1. Comparison of Normalized Release Among Different Elements for (a) 200R at SA/V = 2000/m, (b) 200S at SA/V = 2000/m, (c) 200R at SA/V = 20,000/m, (d) 200S at SA/V = 20,000/m, (e) Comparison of Leachate pH between 200R and 200S at SA/V = 2000/m, and (f) Comparison of leachate pH between 200R and 200S at SA/V = 20,000/m.

congruent dissolution is also the same. The largest effect of solubility control is on the concentrations of lithium. The longer the reaction, the greater the normalized lithium release value deviates from those of boron and sodium. The lithium release is the least among boron, sodium, and lithium, which suggests that there should be lithium enrichment in the surface clay phases.

If matrix dissolution is the dominant elemental release process for both 200R and 200S glasses, an explanation can then be offered for the finding that 200R leaches less than 200S. The rate for a matrix dissolution controlled glass reaction depends on the concentration of the nucleophilic species, hydroxide. The pHs are lower in 200R solutions compared to the 200S solutions due to the radiation effect of 200R, and the hydroxide concentrations in 200R solutions are lower than those of 200S. It is the lower hydroxide concentrations that decreases the dissolution rate of 200R in comparison with 200S.

2. 165/42-Type Glasses

In contrast to the dissolution results for the 200-type glasses discussed above, the radioactive glass 165/42R shows a slightly greater reactivity than its counter part, 165/42S, as shown in Figures 2a and 2b. The differences range from 10% to 150%. The pHs in Figure 2c show an interesting "cross over" where the pHs of the 165/42R are initially lower than those of 165/42S and they become higher in the later part of the glass reaction. The relative elemental release values for each glass are also different than those in 200-type glasses as shown in Figure 2, where lithium has concentrations of 4 to 10 times larger than those of boron, sodium, or silicon.

Although differences in normalized releases are observed between the fully radioactive and the simulated glass of 165/42-type, the solution kinetics analysis indicates that the dominant release process for both 165/42R and 165/42S is an ion-exchange reaction. The exchange of hydronium ions from solution for the alkalis in the glasses is the rate-determining step and the rate of the glass reaction depends on the concentration of the hydronium ions. Since the pH is initially lower in 165/42R as a result of radiation effects, the leaching of 165/42R is faster than 165/42S due to the higher concentration of hydronium ion in 165/42R. We, therefore, observe slightly higher normalized releases in 165/42R compared to 165/42S. The main glass reaction process can be presented as:

$$\text{Glass-O}^{-+}\text{R} + \text{H}_3\text{O}^+(\text{solution}) = \text{Glass-OH} + \text{R}^+(\text{solution}) + \text{H}_2\text{O}$$

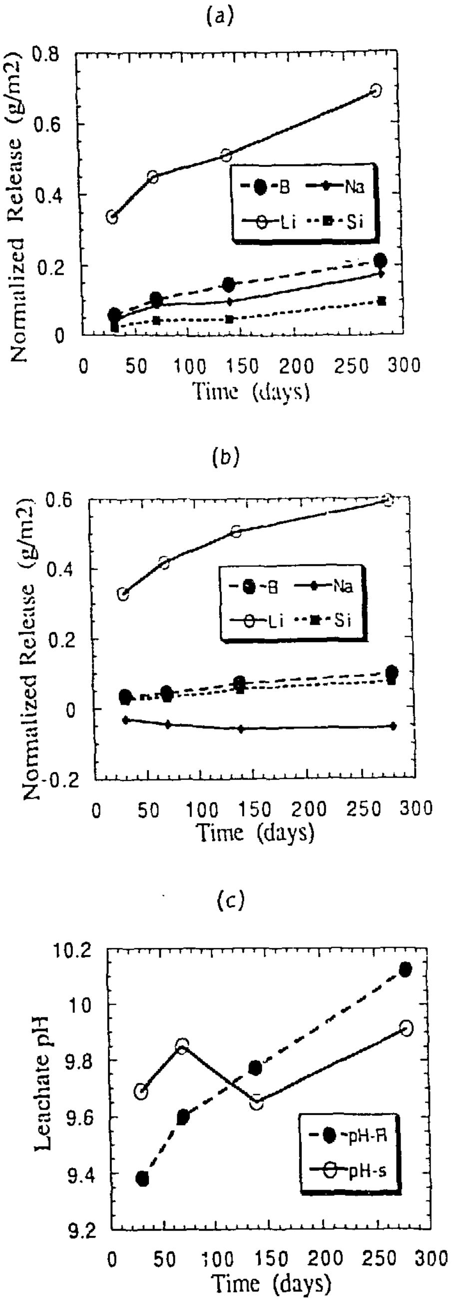

Figure 2. Comparison of Normalized Release among Different Elements at SA/V = 2000/m for (a) 165/42R, (b) 165/42S, and (c) Comparison of Leachate pH between 165/42R and 165/42S at SA/V = 2000/m.

where R^+ is a symbol for alkali element. As the reaction proceeds, hydronium ions are consumed more rapidly from the leachate of 165/42R. The pH of the leachate increases, and the pH "cross over" occurs (Figure 2c). The relative elemental concentration levels (Figure 2) also agree with an ion-exchange controlled glass reaction mechanism. Although lithium, sodium, and potassium in the glass have the same chance to exchange with hydronium ions, lithium is consistently released more rapidly in 165-based glass [12] and has the least chance to be exchanged back to glass surface because of its high hydration energy, its large hydrated radius, its low mobility in solution [11]. Additionally, lithium shows little tendency for 165-based glasses to be incorporated into the reacted layers under hydrothermal test conditions [12]. The normalized release of lithium, therefore, is usually the greatest among all the elements in the leachate for an ion-exchange-controlled glass dissolution. The measurable concentrations of boron and silicon are indicative that the glass dissolution is a collection of multiple processes since boron and silicon are usually released through matrix hydrolysis reactions. These multiple processes may include water diffusion, ion-exchange, matrix dissolution, or hydrolysis, solution saturation, and secondary phase precipitation.

3. 131-Type Glasses

Figure 3 compares the leach behavior between 131/11R and 131/11S at SA/V=2000/m. These data show that the radioactive 131/11R has a lower reactivity than the corresponding nonradioactive 131/11S. The differences are about 150% to 200% for boron and silicon, while lower differences of about 20-80% are observed for alkalis such as lithium and sodium. The pHs of the leachates in 131/11R are also lower than those in 131/11S beyond 70 days. The relative elemental releases demonstrate that lithium falls between sodium and boron for 131/11R and is lower than both sodium and boron in the case of 131/11S.

The solution kinetics analysis suggests that matrix dissolution is the dominant glass reaction process at longer terms. The lower pHs for 131/11R are responsible for the lower elemental release rates in 131/11R compared to 131/11S, as discussed above for 200-type glasses. However, the solution data for 131-type glasses as discussed below also suggests that ion-exchange plays an important role in glass reaction during the early stage of testing. As discussed above for 165/42 glass, the highest normalized release for an ion-exchange controlled glass dissolution is usually lithium. In the case of matrix dissolution, all the elements are released stoichiometrically. The concentration of released

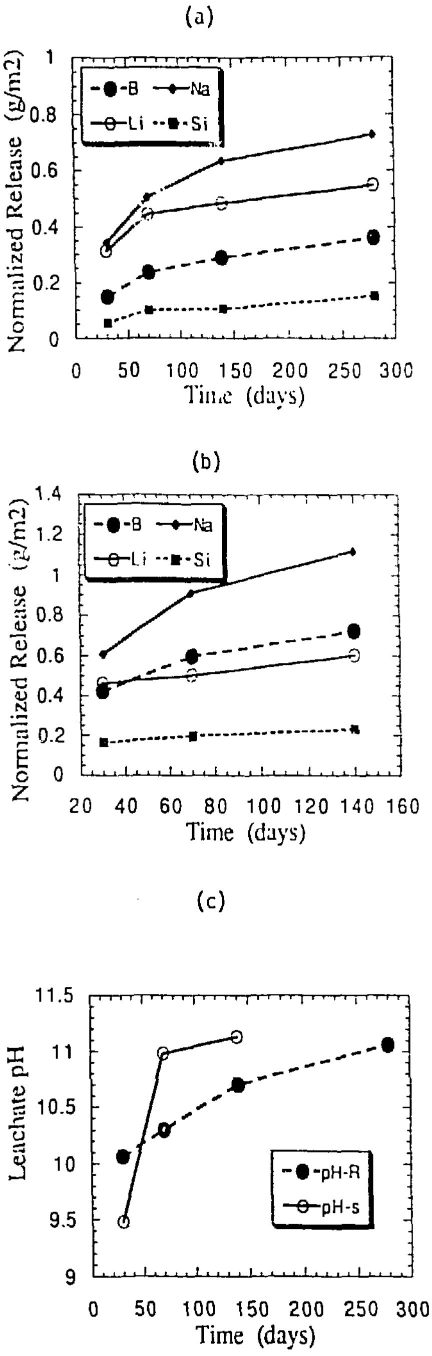

Figure 3. Comparison of Normalized Release among Different Elements at SA/V = 2000/m for (a) 131/11R, (b) 131/11S and (c) Comparison of Leachate pH between 131/11R and 131/11S at SA/V = 2000/m.

alkalis in solution may be reduced due to incorporation into in situ alteration layers, and clay phases. However, the boron is usually very soluble and shows little tendency to be incorporated into alteration layers [13-15]. Only minor amounts of boron have been found to participate in precipitation reactions and the solution concentration of boron has been concluded to be a good indicator of glass reaction [15]. The concentration of boron is, therefore, usually higher than lithium, and potassium but close to sodium, in a matrix dissolution controlled glass dissolution process. In fact, lithium is found to be the least concentrated species among boron, sodium, and lithium for 200 glass type, where matrix dissolution is the dominant process.

As shown in Figure 3, the release of lithium for both 131/11R and 131/S is still higher than or close to boron although lithium is no longer the highest release. This suggests that ion exchange has been an important process in the dissolution of 131/11 type glasses. The boron release is close to sodium, and the highest release is sodium not lithium, suggesting that matrix dissolution is now the dominant process. The solution data also indicate that 131/11S is less durable than 131/11R, and we would expect that 131/11S would switch from an ion-exchange dominated glass reaction to matrix dissolution-dominated process earlier than 131/11R. As a result, the concentration of boron, the most soluble product of matrix dissolution, surpasses the concentration of lithium, the indicator of ion-exchange controlled process earlier during the reaction progress. This is, indeed, the case as shown in Figure 3b, where boron release for 131/11S surpasses that of lithium but not for 131/11R (Figure 3a).

4. The Same Order of Glass Durability Among Different Glass Compositions for Both Radioactive Glasses and the Simulated Analogs

The leach behavior of the radioactive and simulated glasses for each composition type (R vs. S glass) was compared above. Also of interest is a comparison between the different composition groups (131, 200, 165) for both the radioactive glasses and the simulated analogs to see whether there is a difference in the order of durability. Figure 4 presents this comparison among the simulated analogs and Figure 5 is for the radioactive glasses. The order of glass durability for the simulated glasses arranged according to the normalized release of the elements of boron, silicon, sodium, and lithium is 165/42S > 131/11S > 200R. The pHs in Figure 4a present the same order as the glass durability for simulated glasses, i.e., the most durable glass, 165/42S, has the lowest pH values while the least durable, 200S, has the highest pHs. The durability order for the radioactive glasses as shown in Figures 5b to 5d is the same as that of the simulated glasses in terms of the boron, silicon, and sodium normalized releases. The pHs of those radioactive glasses in Figure 5a also show exactly the same order as the corresponding nonradioactive glasses in Figure 4a. However, the lithium illustrated in Figure 5e shows that 165/42R leached slightly faster than 131/11R. This is because the lithium release for 131/11R is much slower than that of boron or sodium and it, therefore, does not represent a full measure of durability. This lithium anomaly is not seen in the simulated glass because 131/11S is much less durable than 165/42S and this durability order is maintained even with the comparison between the fastest releasing element of 165/42S (an ion exchange dominated process), lithium, and the lowest released element of 131/11S (a matrix dissolution dominated process), lithium. Therefore, the durability order measured by the major element released into solution for both simulated and fully radioactive glasses is the same: 165/42 > 131/11> 200.

It is seen from surface analyses, which are not covered in this paper, that the durability order defined by the thickness of the reacted layers is the same as it derived from the solution data [10]. The sample surface analyses also provide insight as to alkali depletion due to ion exchange reaction and the incorporation of alkali into clay layers.

D. CONCLUSION

An initial comparison of the reactivity between simulated and fully radioactive glasses has been made as part of the long-term testing program described herein. The short-term data discussed above indicate differences in reactivity for each pair of glass compositions. The difference in reactivity was shown to exist for all the glass types and at each SA/V tested.

Although differences in normalized releases were observed between fully radioactive and the simulated glass of the same type, analyses of the solution data indicates that each type of glass tested generally follows the same controlling mechanism in the glass reaction. The dominant release process for both 165/42R and 165/42S is preferential alkali release, and the normalized lithium concentrations in the leachates are always the highest. The reaction of 200R and 200S is more characteristic of matrix dissolution, and the normalized boron and sodium concentrations are usually higher than the corresponding lithium concentrations, which may also suggest the incorporation of lithium into secondary phase. 131/11R and 131/11S show a reaction characteristic of matrix dissolution for the extended

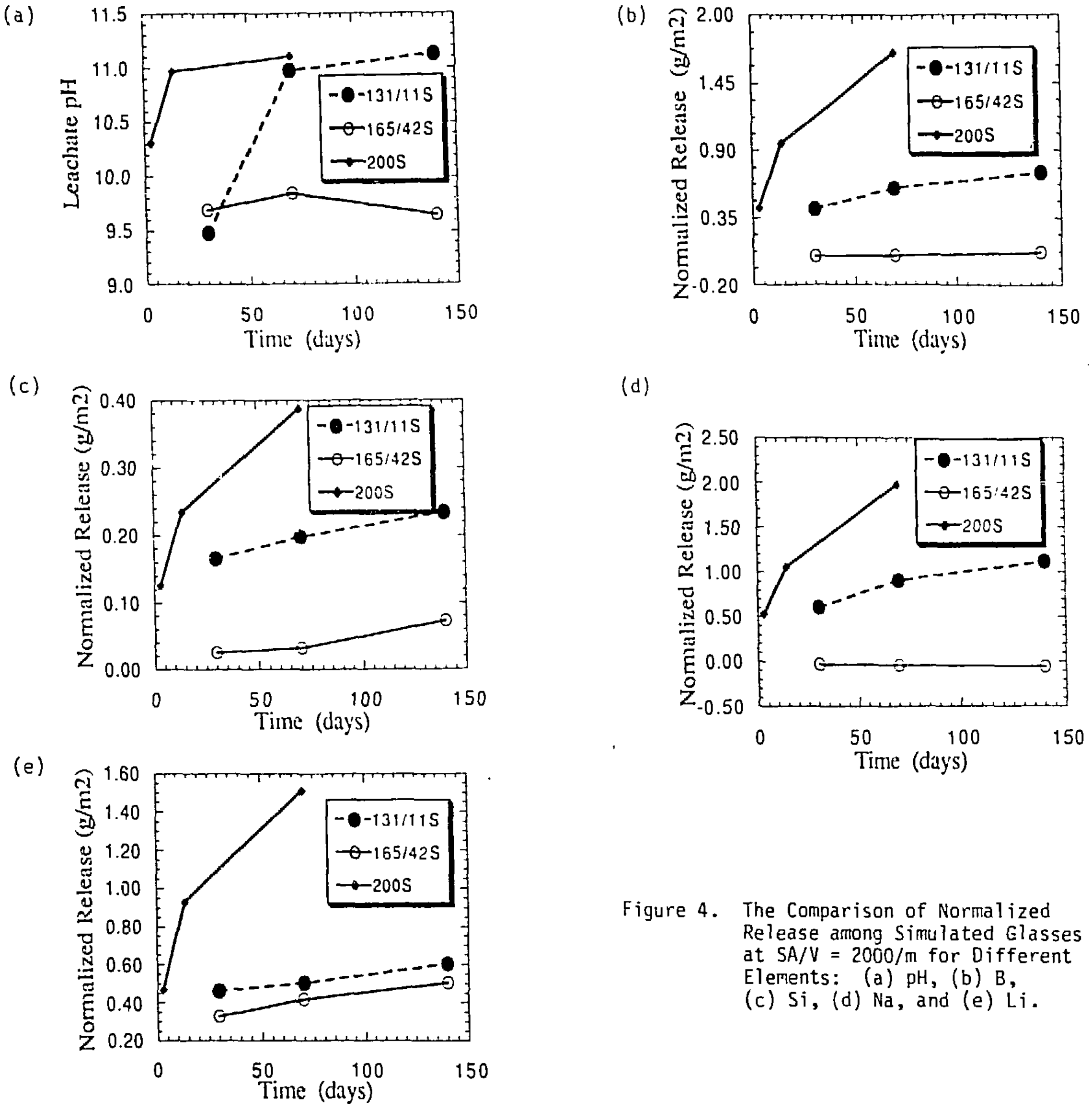

Figure 4. The Comparison of Normalized Release among Simulated Glasses at SA/V = 2000/m for Different Elements: (a) pH, (b) B, (c) Si, (d) Na, and (e) Li.

time periods and an ion exchange dominated reaction in the early test period, where normalized lithium concentrations fall between sodium and boron. The relative glass durability observed for the simulated glasses is 165S > 131S > 200S. The same order of glass durability is preserved for the fully radioactive glass in terms of both glass leach rates and the thickness of the reacted layers.

The pHs for the fully radioactive glasses are usually lower than the simulated glasses due to the radiolysis induced formation of nitrogen related acids and other acids in the leachates. This reduction in solution pHs of the radioactive glasses, combined with the controlling mechanisms revealed above, can be used to explain the observation that the radioactive glass reacts less than the corresponding simulated glass for both 131/11-type and 200-type glasses, but more for 165-type glasses. The controlling reaction mechanism for both 131-type and 200-type glasses is matrix dissolution, i.e., the dissolution rates are proportional to the concentration of the

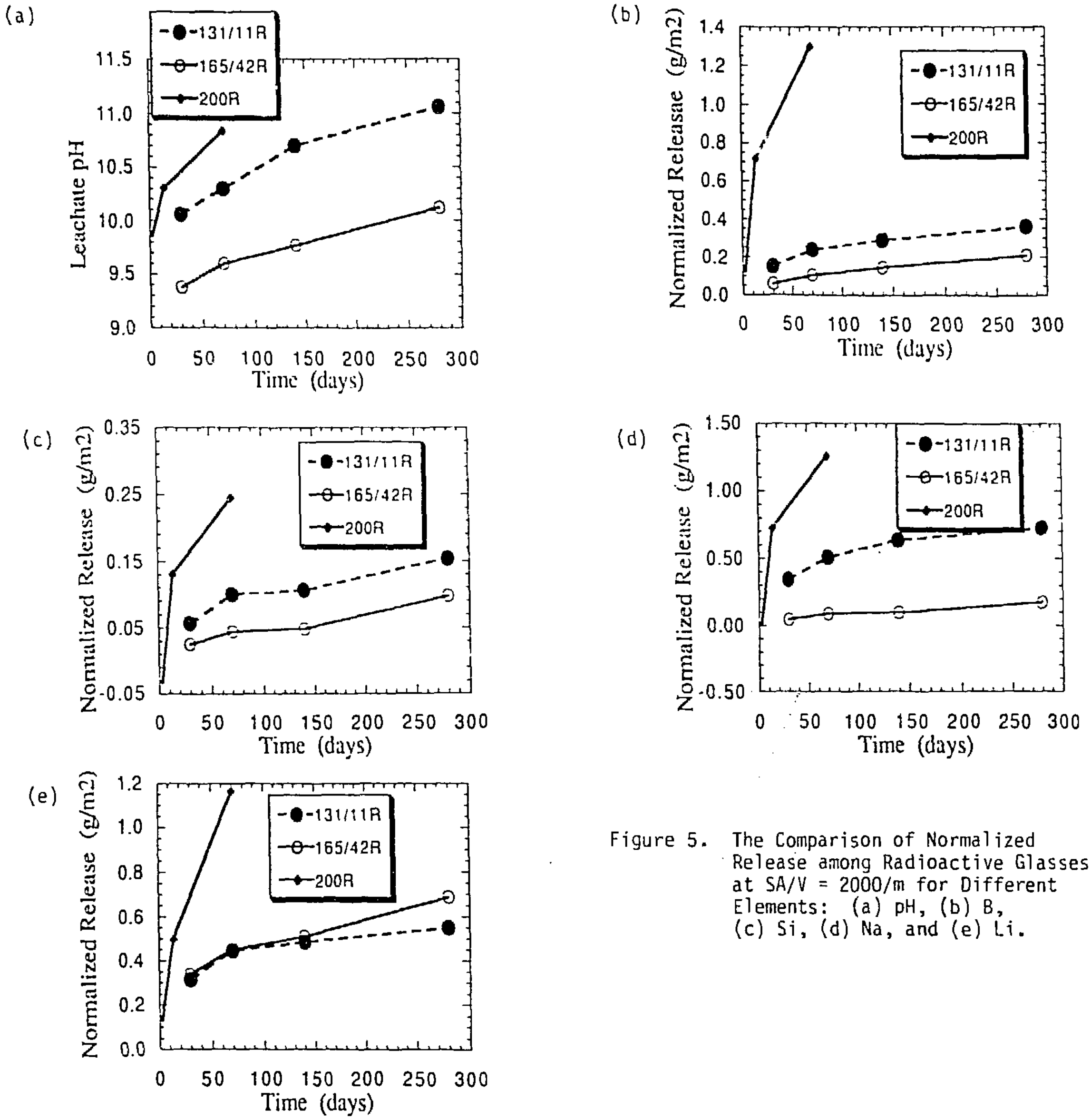

Figure 5. The Comparison of Normalized Release among Radioactive Glasses at SA/V = 2000/m for Different Elements: (a) pH, (b) B, (c) Si, (d) Na, and (e) Li.

nucleophilic species, hydroxide. The pHs are lower in the solutions of the radioactive glasses and, therefore, lower reaction rates are observed for 131/11R and 200R glasses. On the other hand, for the time period reported, 165-type glasses are leached mainly through an ion-exchange reaction mechanism, where the reaction rate depends on the hydronium ion concentration. As the pH is lowered for 165/42R glass due to the radiation effect, the increased concentration of hydronium ions promote the ion exchange process between hydronium ions in solution and the alkalis in glass, resulting a faster release. Thus, as opposed to the 131- and 200-based glasses, the 165/42R glass reacts more rapidly than the 165/42S.

The results demonstrate that under conditions of the reported tests, a radiation effect exists, mainly in terms of the influence on the leachate pH, which in turn affects glass reaction. The differences in reactivity between fully radioactive and the simulated glasses can be reasonably explained if the controlling reaction mechanism is accounted for. The reactivity differences are glass composition and leaching mechanism dependent, and while the difference in reactivity reaches a maximum of 400% for selected elements the overall difference in reactivity is small.

The ongoing static tests will be continued as tests are scheduled to be continued through eight years. Data generated from solution analyses will be combined with surface layer studies to more completely compare the reactivity of the radioactive and nonradioactive glasses and to provide a data base for validation of glass performance models.

E. ACKNOWLEDGMENT

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