

Conf-920430-73

A COMPARISON OF GLASS REACTION AT HIGH AND LOW S/V: PCT vs. MCC-1\*

ANL/CP--74206

DE92 010887

W. L. Ebert and J. K. Bates

Chemical Technology Division  
ARGONNE NATIONAL LABORATORY  
9700 South Cass Avenue  
Argonne, IL 60439-4837

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.

1/10/1992

Submitted to  
1992 International High-Level Radioactive  
Waste Management Conference  
Las Vegas, Nevada  
April 12-16, 1992

\*Work supported by the U.S. Department of Energy, Office of Environmental  
Restoration and Waste Management, under Contract W-31-109-ENG-38.

**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.

**MASTER**

## A COMPARISON OF GLASS REACTION AT HIGH AND LOW SA/V: PCT VS. MCC-1

William L. Ebert and John K. Bates  
Argonne National Laboratory  
9700 South Cass Avenue  
Argonne, IL 60439-4837  
(708) 252-6103 / 4385

### ABSTRACT

Leach tests have been performed at SA/V of 10, 2000, and 20,000  $\text{m}^{-1}$  using actinide-doped borosilicate waste glass (SRL 131 and SRL 202) to assess the effects of the SA/V on the mechanism and rate of the glass reaction. Solution results are presented which show the major effect of the SA/V to be dilution. Higher SA/V result in higher leachate pH values being attained due to initial ion exchange reactions. The higher pH values then accelerate hydrolysis of the glass. Colloids rich in aluminum and iron form at high SA/V after very little glass has reacted. Actinides released during glass reaction sorb onto these colloids which eventually become large enough to settle out of solution. The measured response is sensitive to the SA/V of the test, and is dominated by ion exchange at 10  $\text{m}^{-1}$ , by matrix dissolution at 2000  $\text{m}^{-1}$ , and by colloid formation at 20,000  $\text{m}^{-1}$  within laboratory test timeframes.

### A. INTRODUCTION

Static leach tests are being used to measure the production consistency and differentiate the durabilities of borosilicate glasses used in the vitrification of high-level waste. The range of many test variables used for testing glasses destined for use in waste disposal are defined by the anticipated repository environment, including the temperature, pressure, and groundwater chemistry. The effects of other test variables that may affect the measured response need to be fully understood prior to using the results of such tests to assess the durability of waste glass in various environments.

An important test variable in static leach tests is the glass surface area/leachant volume ratio (SA/V). The major effect of the SA/V on the glass reaction is through dilution of the leachate: tests at low SA/V have larger volumes of solution per unit area of glass than do tests at higher SA/V. The solution concentrations of tests at lower SA/V will,

therefore, change at a lower rate per unit mass of glass reacted. Since the rate of glass reaction is known to be dependent on the solution chemistry, the response of a glass in tests at different SA/V may be different, and both the mechanism and rate of glass reaction may change with the SA/V.

Two static leach tests used to measure the durability of glass produced for the purpose of high-level nuclear waste disposal are the MCC-1 test [1], which measures the response of glass monoliths at an SA/V of 10  $\text{m}^{-1}$ , and the Product Consistency Test (PCT) [2], which measures the response of powdered glass at an SA/V of  $\sim 2000 \text{ m}^{-1}$ . Both tests are usually performed at 90°C with DIW as the leachant for short time periods (usually 7 to 28 days). Because of the different solution volumes, the leachates in the PCT test will become concentrated at a greater rate than the leachates in the MCC-1 test as the glass reacts. Differences in the resulting solution chemistries may affect both the mechanism and the rate of glass reaction. It is necessary to understand changes in the reaction which occur as the SA/V changes in order to relate glass durabilities measured in tests at different SA/V.

The results of static leach tests have also been used to derive the algorithm describing the glass reaction kinetics in computer models to be used for long-term predictions of glass behavior under potential repository environments [3]. Laboratory tests are also necessary to validate the computer model prior to simulations of glass reaction to long reaction times. Tests at high SA/V have been suggested as an experimental means of accelerating the glass reaction to simulate long-term behavior, wherein tests performed at equivalent products of SA/V and the reaction time are assumed to provide equivalent extents of reaction [4,5]. Before tests at high SA/V can be used to model long-term reaction behavior, it must be demonstrated that the reaction mechanism is the same in laboratory tests at high and low SA/V or that differences can be accounted for.

We have performed a series of experiments at 10, 2000, and 20,000 m<sup>-1</sup> at 90°C wherein SRL 131 and SRL 202 glasses were reacted in a J-13 groundwater solution or deionized water for times up to one year. These tests are being performed to compare the reaction in a dilute solution under MCC-1 test conditions of 10 m<sup>-1</sup> to that in a more concentrated solution under PCT conditions of 2000 m<sup>-1</sup>. Tests at 20,000 m<sup>-1</sup> were also performed to demonstrate the effects of SA/V separate from any differences resulting from sample preparation, such as surface finish and strain. Reaction times were selected to demonstrate the temporal reaction trends and to provide tests run for equivalent products at (SA/V)\*time. The leachate solutions were analyzed to compare the mechanism and kinetics of the glass reaction at different SA/V. These tests were performed to provide detailed solution results with accompanying solids analyses which can then be compared to the results of computer simulations. Solids analyses are in progress and will be presented elsewhere.

## B. EXPERIMENTAL

Samples were prepared from SRL 131 and SRL 202 frits provided by Westinghouse Savannah River Company (WSRC). The starting material was doped with U, Np, Pu, and Am, remelted, annealed, and cast into bars. These actinide-doped glasses are referred to as SRL 131A and SRL 202A. An SRL 202 glass doped only with uranium was also prepared and is referred to as SRL 202U. Cores approximately 1 cm in diameter were drilled from the bars and sectioned into disks approximately 0.9 mm thick. All surfaces of the disks were then ground to a final 600-grit finish and washed to remove fines. The remaining glass in the bar was crushed and sieved to separate the -100+200 mesh fraction for use in the tests. The powdered glass was washed to remove fines. Representative samples of both the monolith disks and the powdered glass were surveyed in a scanning electron microscope (SEM) to verify acceptability prior to use and to assure that no measurable alteration had occurred during sample preparation. The surface area of the powdered glass available for reaction was approximated using the average mesh openings of the sieves and is calculated to be  $2 \times 10^{-2}$  m<sup>2</sup>/g. The nominal size of the grains was confirmed using an SEM. The surface area of each monolith disk was computed from the measured diameter and thickness.

Samples of the actinide-doped glasses were dissolved and analyzed to determine their compositions. These are given in Table 1. The leachant solution was prepared by reacting J-13 groundwater with pulverized tuff (<100 mesh) at 90°C for 28 days. The solution was then cooled

Table 1. Composition of SRL 131A and SRL 202A as Oxide wt %

	SRL 131A	SRL 202A
Al <sub>2</sub> O <sub>3</sub>	3.27	3.84
B <sub>2</sub> O <sub>3</sub>	9.65	7.97
BaO	0.16	0.22
CaO	0.93	1.20
Cr <sub>2</sub> O <sub>3</sub>	0.13	0.08
CuO	0.02	0.40
Fe <sub>2</sub> O <sub>3</sub>	12.66	11.41
K <sub>2</sub> O	3.86	3.71
Li <sub>2</sub> O	3.00	4.23
MgO	1.31	1.32
MnO <sub>2</sub>	2.43	2.21
MoO <sub>3</sub>		0.05
Na <sub>2</sub> O	12.08	8.92
NiO	1.24	0.82
PbO		0.01
SiO <sub>2</sub>	43.76	48.95
SrO	0.01	0.03
TiO <sub>2</sub>	0.65	0.91
ZnO	0.02	0.02
ZrO <sub>2</sub>	0.22	0.10
ThO <sub>2</sub>		0.26
U <sub>3</sub> O <sub>8</sub>	2.73	1.93
TcO <sub>2</sub>	0.03	0.03
Am <sub>2</sub> O <sub>3</sub>	0.0004	0.0004
PuO <sub>2</sub>	0.009	0.01
NpO <sub>2</sub>	0.009	0.01
Total	98.1	98.59

to room temperature and filtered and is referred to as EJ-13 solution. The solution composition is given in Table 2. Tests with SRL 131A and SRL 202A were performed in 22 mL 304L stainless steel Parr vessels. Tests with SRL 202U were reacted in 30 mL Teflon vessels. Nominal SA/V of 10, 2000, and 20,000 m<sup>-1</sup> were achieved by placing 1 monolith disk in about 17 mL of leachant, 1 g of powdered glass in 10 mL of leachant, or 5 g powdered glass in 5 mL leachant. This provided sufficient leachate for complete solution analysis after each test.

Table 2. Composition of EJ-13, ppm

Al	1.1	Si	46
B	0.16	pH	8.2
Ca	5.1	HCO <sub>3</sub> <sup>-</sup>	120
K	7.3	F <sup>-</sup>	3
Li	0.05	Cl <sup>-</sup>	9
Mg	0.39	NO <sub>3</sub> <sup>-</sup>	16
Na	54	SO <sub>4</sub> <sup>=</sup>	35

### C. RESULTS AND DISCUSSION

The leachates of tests with powdered glass were filtered through 0.45  $\mu\text{m}$  polycarbonate filters at  $\sim 90^\circ\text{C}$  to remove suspended glass particulates prior to analysis. This solution was analyzed for pH, anions, cations, and actinides. An aliquot was further filtered through approximately 60  $\text{\AA}$  filters and analyzed for cations and actinides. The amount of suspended material present can be computed by difference. Reacted solids were rinsed with DIW and allowed to dry at room temperature in a dust-free environment. Samples were then analyzed with optical microscopy, scanning electron microscopy with x-ray spectroscopy (SEM/EDS), analytical electron microscopy (AEM), and secondary ion mass spectrometry (SIMS). Tests scheduled for one year or less have been completed and longer term tests are ongoing. This report will highlight differences in the solution results of tests at different SA/V. Solids analyses will be presented elsewhere.

#### 1. Leachate pH

The leachates from tests at  $10 \text{ m}^{-1}$  and the filtrates from tests at 2000 and  $20,000 \text{ m}^{-1}$  were allowed to cool to room temperature prior to pH analyses. The average pH values of duplicate tests are shown plotted against the reaction time in Figure 1. Differences in the results of duplicate tests are within the size of the symbols except for the tests at  $10 \text{ m}^{-1}$  run 238 days. The measured pH is seen to increase significantly above the pH of the initial leachant (8.2) in tests at 2000 and  $20,000 \text{ m}^{-1}$  after only a few days. The pH in tests at  $10 \text{ m}^{-1}$  increased slowly. Tests at  $20,000 \text{ m}^{-1}$  had pH values about 1.5 and 1.0 units higher than tests at  $2000 \text{ m}^{-1}$  after equal reaction times through about 200 days for SRL 131A and SRL 202A glass, respectively. At 280 days, tests with both glass types at  $2000 \text{ m}^{-1}$  showed a slight increase in pH while the pH in tests at  $20,000 \text{ m}^{-1}$  remained nearly constant through 364 days.

The pH rise at short reaction times is due to glass reaction to release alkali metals which also produces hydroxide [6]. The rate at which alkali is released and hydroxide produced depends initially on the rate at which water enters the glass to ion exchange a proton for an alkali metal and is insensitive to the SA/V of the test. Thus, the amount of hydroxide produced per unit surface area (e.g., as moles/ $\text{m}^2$ ) early in the reaction is similar at all SA/V and the measured pH values reflect the different degrees of dilution. A major effect of the SA/V in static leach tests is that tests at higher SA/V attain higher pH values than tests at lower SA/V after equivalent reaction times. This may lead to a change in the dominant step of the reaction mechanisms as the

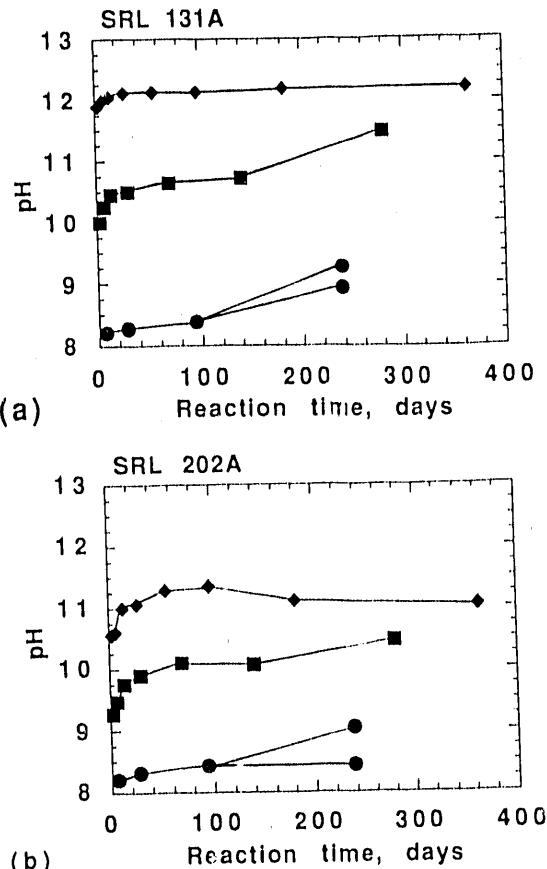


Figure 1. Leachate pH ( $25^\circ\text{C}$ ) vs. reaction time, for tests with (a) SRL 131A glass and (b) SRL 202A glass at (●)  $10 \text{ m}^{-1}$ , (■)  $2000 \text{ m}^{-1}$ , and (◆)  $20,000 \text{ m}^{-1}$ .

reaction proceeds. Ion-exchange reactions involve consumption of protons and prevail at low pH values. Tests at 2000 and  $20,000 \text{ m}^{-1}$  generate basic solutions after very little glass has reacted and so ion-exchange reactions are quenched. The pH of tests at  $10 \text{ m}^{-1}$  remains low enough that ion-exchange reactions continue to dominate the reaction even after 238 days. The change from an ion-exchange dominated reaction to a hydrolysis dominated reaction is usually assumed to occur near a pH of 10. Tests at  $20,000 \text{ m}^{-1}$  have pH values greater than 10 at all times tested, while tests at  $10 \text{ m}^{-1}$  have pH values less than 10 at all times tested. Thus, the dominant reaction steps probably differ in tests at  $10 \text{ m}^{-1}$  and  $20,000 \text{ m}^{-1}$ . Tests at  $2000 \text{ m}^{-1}$  may show a change in the reaction mechanism as the pH increases from below 10 at short reaction times to above 10 at longer reaction times.

Dissociation of silicic acid becomes important at pH values above about 9 ( $pK_{a1} = 9.1$  and  $pK_{a2} = 9.6$  at  $90^\circ\text{C}$  [7]). The relative effects of the pH increase due to ion exchange and the pH decrease due to dissociation of silicic acid on the observed leachate pH are affected by the SA/V of the test through the relative amounts of alkali and silicic acid released from the glass. At high SA/V, very high pH values may be attained before sufficient silicic acid is released to "buffer" the pH rise, while at lower SA/V the silicic acid concentration may become significant before the pH reaches a value of 9. Boric acid may also dissociate and influence the leachate pH.

## 2. Elemental Release

The pH change due to the initial ion exchange reactions affects subsequent hydrolysis reactions which involve a nucleophilic attack of hydroxide to break metal-oxygen bonds [6]. These reactions lead to the destruction of the silicate network and the eventual dissolution of the glass. While ion-exchange reactions result in a pH change due to the generation of hydroxide, hydrolysis reactions do not. This is because one hydroxide is consumed during the breaking of each Si-O-Si bond, for example, and one hydroxide is produced as the resulting  $\text{SiO}_4^{4-}$  species abstracts a proton from a water molecule [6]. Released acids may subsequently dissociate to generate protons which affect the leachate pH. For example, both silicic and boric acids may stabilize the pH.

Tests at  $10 \text{ m}^{-1}$  showed greater scatter in the measured solution concentrations than tests at 2000 and  $20,000 \text{ m}^{-1}$ . Tests at  $10 \text{ m}^{-1}$  are probably more sensitive to surface preparation and analytical uncertainties. The general order of release at  $10 \text{ m}^{-1}$  is  $\text{Na} > \text{Li} > \text{K} > \text{B} > \text{Si}$ . The greater release of alkali metals than boron or silicon is due to the continued dominance of the ion-exchange reactions at  $10 \text{ m}^{-1}$  even after 238 days.

Figure 2 shows the normalized elemental mass losses of several soluble species from SRL 202A glass at 2000 and  $20,000 \text{ m}^{-1}$ . The normalized elemental mass loss is simply the measured concentration, in  $\text{g/m}^3$ , divided by the SA/V, in  $\text{m}^{-1}$ , and by the mass fraction of the element of interest in the glass. Thus, stoichiometric release will result in overlapping  $\text{NL}(i)$  vs. time curves. The curves in Figure 2 clearly do not overlap. The nonstoichiometric release occurs when the reaction is dominated by ion exchange during short reaction times. The alkali metals are released through ion exchange reactions according to a selectivity which is determined

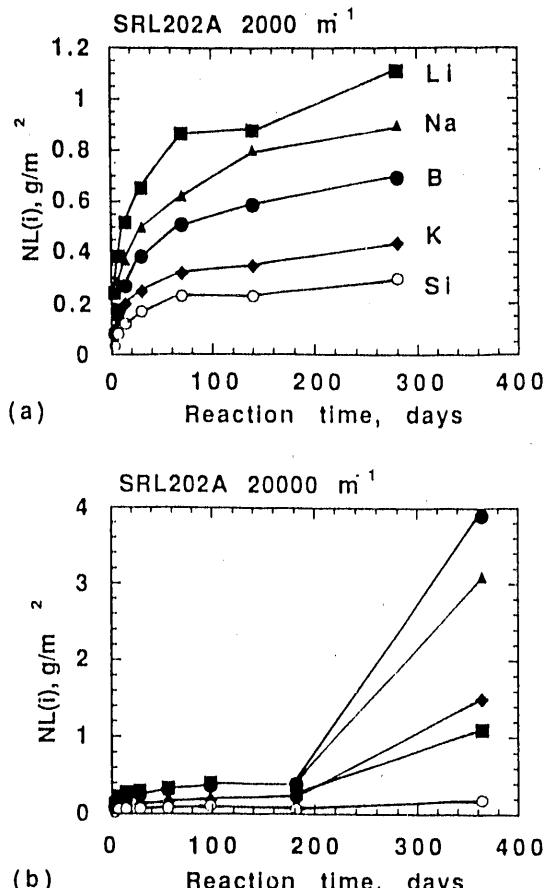


Figure 2.  $\text{NL}(i)$  vs. reaction time for tests with SRL 202A glass at (a)  $2000 \text{ m}^{-1}$  and (b)  $20,000 \text{ m}^{-1}$  for (■) Li, (▲) Na, (●) B, (◆) K, and (○) Si.

by both bond energies and glass structure. At  $2000 \text{ m}^{-1}$ , the release rates decrease as  $\text{Li} > \text{Na} > \text{B} > \text{K} > \text{Si}$  through 280 days. The hydrolysis reactions which release boron and silicon are promoted by hydroxide ions which are generated during ion exchange of the alkali metals. Hydrolysis does not occur to a significant degree at low pH values [6]. Thus, boron and silicon are usually released at a lower rate than the most readily released alkali metal. Boron is preferentially released to silicon due to differences in the bond energies and structures. At longer reaction times (beyond about 70 days at  $2000 \text{ m}^{-1}$ ), the release appears more stoichiometric as hydrolysis reactions dominate the mechanism.

Similar behavior is seen in tests at  $20,000 \text{ m}^{-1}$  (Figure 2b) where preferential release of alkali occurs at short reaction times (through about 14 days) but the release becomes stoichiometric at intermediate reaction times. At longer reaction times, however, tests at  $20,000 \text{ m}^{-1}$  show changes in the solution chemistry due to secondary phase formation and an acceleration of the glass reaction between 182 and 364 days, where NL(B) increases by a factor of about 9. Other elemental concentrations increase less than NL(B) over this time interval, presumably because these elements are incorporated into secondary phases while boron is not. Lithium may still be released from the glass to the greatest extent after 364 days at  $20,000 \text{ m}^{-1}$ , but only about 20% of the lithium released remains in solution while about 80% is in a secondary phase. Analyses of the reacted solids are in progress to identify the phase(s) which contain lithium.

The results plotted in Figure 2 are for solutions filtered through  $0.45 \mu\text{m}$  filters. The leachates of some tests were additionally filtered through approximately  $60 \text{ \AA}$  filters. This was done to quantify what may be considered to be the truly dissolved concentrations. The dissolved concentrations are needed for comparison to solubility products calculated in computer simulations. Filtration reduced the measured concentrations of Al, Fe, Mg, Mn, Ni, and Ti but did not affect the concentrations of B, K, Li, Na, or Si, beyond the analytical uncertainty. Results for tests up to 91 days at  $20,000 \text{ m}^{-1}$  in EJ-13 solution are shown in Table 3 for Al, Fe, Si, and B. Note that the Al and Fe concentrations in the  $0.45 \mu\text{m}$  filtered solutions are reduced beyond 28 days. These results suggest that colloidal

material containing Al and Fe is present at all times tested and that the particulate size increased with the reaction time such that most of the material was either removed by  $0.45 \mu\text{m}$  filters in tests reacted 28 days or more, or that the colloids had settled out of solution during the reaction. Silicon has been seen to form iron-silicate colloids in tests with other glasses [7,8]. Due to the very large Si/Fe ratio in solution, it is unlikely that Fe-Si colloid formation would measurably reduce the silicon concentration in solution. For example, in test 7, approximately 18 ppm of iron is removed by filtration with  $\sim 60 \text{ \AA}$  filters while the analytical uncertainty in the silicon analysis is about  $\pm 36 \text{ ppm}$  for both the  $0.45 \mu\text{m}$  and the  $60 \text{ \AA}$  solution. Unless the Si:Fe ratio in the colloids is very high, colloid formation will not noticeably affect the silicon solution results. Analysis of the reacted solids are required to identify the colloids formed in these tests.

Tests at all SA/V and with all glass types showed filtration with  $60 \text{ \AA}$  filters to remove Al, Fe, Mg, Mn, and Ni from the leachate. Routine analyses of the unfiltered leachates were not performed because some leachates have contained suspended glass particles. Analysis of some samples showed filtration with  $0.45 \mu\text{m}$  filters removed small amounts of these elements. The amount removed by both filters increased with the SA/V of the test for both glasses.

The leachates of tests with SRL 202A at  $20,000 \text{ m}^{-1}$  run 364 days which showed higher reaction rates (see Figure 2b) were filtered with  $60 \text{ \AA}$  filters. The concentrations of all elements were reduced after filtration. Soluble elements including the alkali metals,

Table 3. Effect of Filtration on Leachate Analysis

Test No.	Reaction Time (days)	pH	Al, ppm		Fe, ppm		Si, ppm		B, ppm	
			0.45 $\mu\text{m}$ <sup>a</sup>	60 $\text{\AA}$ <sup>b</sup>	0.45 $\mu\text{m}$	60 $\text{\AA}$	0.45 $\mu\text{m}$	60 $\text{\AA}$	0.45 $\mu\text{m}$	60 $\text{\AA}$
1	3	10.86	5.23	1.26	25.7	0.38	276	243	75.3	73.5
2	3	10.89	5.42	1.25	26.8	0.38	283	243	77.0	75.0
3	7	11.03	9.18	1.31	44.2	0.30	351	267	93.8	85.9
4	7	11.01	8.33	-	38.2	-	338	-	92.8	-
5	14	11.23	11.5	-	51.7	-	411	-	111	-
6	14	11.28	12.1	<2.5	54.9	0.75	417	323	111	107
7	28	11.37	6.05	1.80	18.5	0.28	361	360	119	127
8	28	11.38	3.85	1.93	8.37	<0.19	350	362	121	128
9	56	11.37	1.55	-	0.50	-	381	-	148	-
10	56	11.41	1.52	-	0.37	-	385	-	149	-
11	91	11.40	<1.3	<1.1	0.66	<0.23	429	440	177	182
12	91	11.38	2.33	1.70	0.24	<0.23	436	446	180	181

<sup>a</sup>Filtrate solution from  $0.45 \mu\text{m}$  filtration.

<sup>b</sup>Filtrate solution from approximately  $60 \text{ \AA}$  filtration.

boron, and silicon were only reduced by 20-25%, while insoluble species, including Al, Fe, Mn, and Ni, were almost totally removed by filtration. The large difference between NL(B) and NL(Si) at 364 days (see Figure 2b) and the small amount of filterable silicon in the leachate suggest that the silicon is primarily contained in solid secondary phases rather than being suspended in the leachate. Solids analyses in progress to more to completely describe the fate of silicon. Preliminary results have shown a secondary phase to form on the glass surface at all SA/V early in the reaction. The composition of this phase corresponds well with the observed leachate composition in that it contains silicon and insoluble elements but is depleted in alkali metals and boron. Figure 3 shows the phase formed after 14 days in tests at  $20,000 \text{ m}^{-1}$  with SRL 202U glass in EJ-13. It appears that silicon and elements having limited solubilities are incorporated directly into

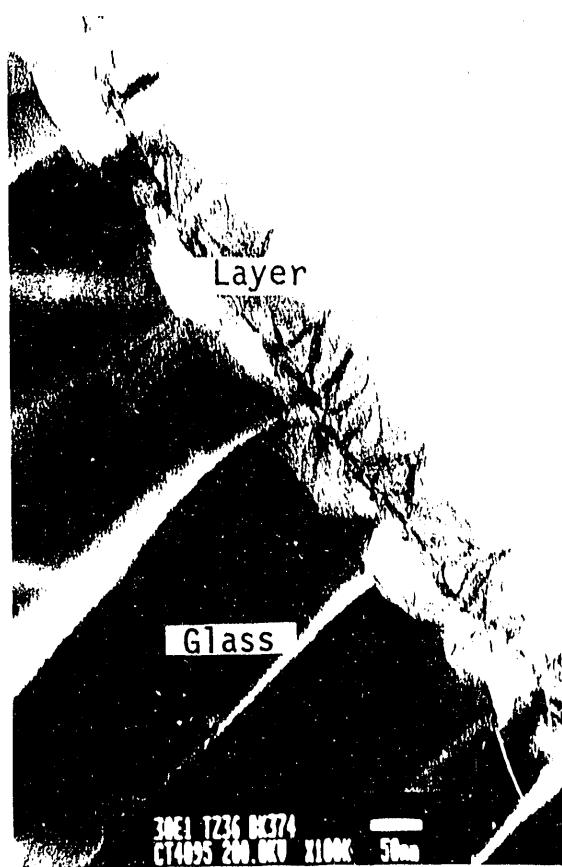


Figure 3. Brightfield Image Showing Secondary Layer Formed on SRL 202U Glass Reacted 14 Days at  $20,000 \text{ m}^{-1}$  in EJ-13.

this phase as the glass reacts. A more detailed description of the glass reaction will be presented elsewhere.

### 3. $(\text{SA}/\text{V})^*\text{Time Scaling}$

It has been suggested that leach tests can be scaled by the product of  $(\text{SA}/\text{V})$  and the reaction time [4]. These scaling arguments predict that tests at  $2000$  and  $20,000 \text{ m}^{-1}$  will generate similar solution concentrations at equivalent  $(\text{SA}/\text{V})^*t$ . From Figure 2b, it is apparent that the boron release best represents the extent of glass reaction without complications due to secondary phase formation. The boron solution concentrations achieved in tests at equivalent  $(\text{SA}/\text{V})^*t$  are shown in Figure 4 for tests with SRL 131A and SRL 202A at  $10$ ,  $2000$ , and  $20,000 \text{ m}^{-1}$ . Scaling is

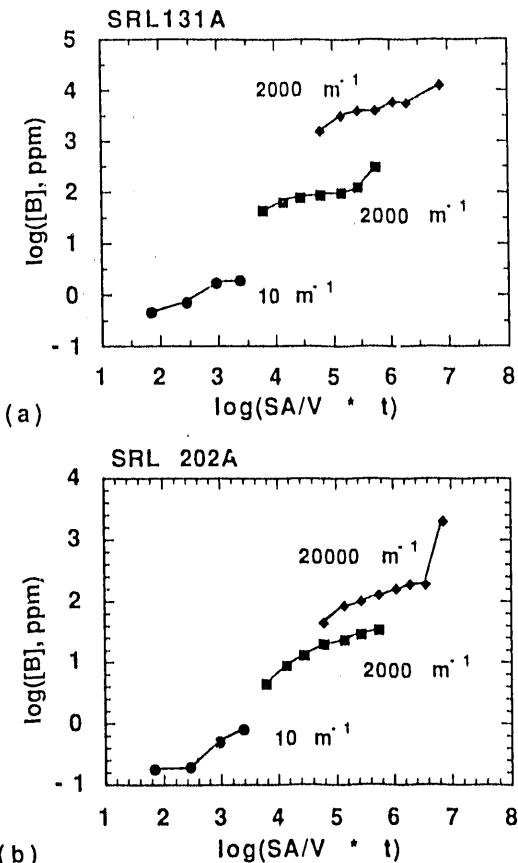


Figure 4.  $\log ([\text{B}])$  vs.  $\log [(\text{SA}/\text{V})^*\text{time}]$  for (a) SRL 131A glass and (b) SRL 202A glass for tests at (●)  $10 \text{ m}^{-1}$ , (■)  $2000 \text{ m}^{-1}$ , and (◆)  $20,000 \text{ m}^{-1}$ .

clearly not observed in these experiments where, at all equivalent  $(SA/V)^*t$ , tests at higher SA/V generate greater boron concentrations. In general, tests with SRL 131A show greater disparity than tests with SRL 202A. This is probably because SRL 131A contains more alkali than SRL 202A (18.94 wt % total oxides compared to 16.86 wt %), and higher leachate pH values are attained due to initial ion exchange. The higher leachate pH values may then accelerate subsequent glass reaction. Failure of  $(SA/V)^*t$  scaling is attributed to differences in the leachate pH values achieved at different SA/V and the resulting changes in the reaction rates. This has been observed in tests with other glass compositions [7,9].

Better agreement has been recently reported for scaling leachate data by  $(SA/V)^*(time)^{1/2}$  [10]. Data for SRL 202A glass shows better correspondence with  $(SA/V)^*(time)^{1/2}$ , but data for SRL 131A glass does not. This indicates that a mechanistic understanding of the glass reaction is required before any single scaling approach can be used to predict long-term glass behavior. Also, the acceleration of the reaction at  $20,000 \text{ m}^{-1}$  observed at 364 days suggests that short-term tests cannot be used to predict long-term glass behavior.

#### 4. Actinide Release

An important issue in the testing of nuclear waste glasses is how the released radionuclides behave when glass is reacted at different SA/V. Differences in the physical and chemical state of the nuclides will affect how readily they may be transported away from the waste package. Analyses were performed on the unfiltered leachate, the filtrate from  $0.45 \mu\text{m}$  filtration, the filtrate from  $\sim 60 \text{ \AA}$  filtration, and an acid strip solution of the reaction vessel to measure the distribution of the doped actinides between fractions that were suspended, dissolved, and sorbed onto the steel vessel. Aliquots were analyzed using alpha spectroscopy.

The mass of neptunium, plutonium, and americium found in the filtrates of the  $0.45 \mu\text{m}$  and  $60 \text{ \AA}$  filters and in the acid soak solution are plotted against the reaction time for tests with SRL 202A glass at  $2000 \text{ m}^{-1}$  and  $20,000 \text{ m}^{-1}$  in Figure 5. Results of analyses of the unfiltered leachates are not included here because (1) particles of glass were suspended in the leachate and gave anomalously high results, or (2) colloidal material attenuated the spectra and prevented quantification. The amount in the  $60 \text{ \AA}$  filtrate is assumed to be dissolved, the difference between the  $0.45 \mu\text{m}$  and  $60 \text{ \AA}$  filtrates suspended, and the amount in the acid soak is assumed to have been sorbed

to the vessel. Note that suspended material was probably removed by the initial filtration using  $0.45 \mu\text{m}$  filters and that the results shown in Figure 5 include only that suspended material which passed through  $0.45 \mu\text{m}$  filter. These plots show a change in the distribution with the SA/V for each nuclide. Neptunium is present in the leachate both as dissolved and suspended material at  $2000 \text{ m}^{-1}$  with very little sorbed to the vessel. At  $20,000 \text{ m}^{-1}$ , neptunium is found in the leachate at short reaction times but in decreasing amounts at longer times. The amount of neptunium sorbed onto the vessel increases with the reaction time.

The plutonium and americium found in solution is primarily associated with suspended material in tests at  $2000 \text{ m}^{-1}$ . The amounts are nearly constant beyond about 28 days. The amount of plutonium and americium on the vessel walls increases with the reaction time. Plutonium and americium are also found suspended in solution at short reaction times at  $20,000 \text{ m}^{-1}$ , but the amount decreases with the reaction time and becomes negligible beyond about 28 days. The amount of plutonium and americium on the vessel walls is nearly constant beyond about 28 days.

We interpret the difference in actinide distribution with respect to SA/V to be due to colloid formation in tests at  $20,000 \text{ m}^{-1}$  after about 28 days. Neptunium, plutonium, and americium are sorbed onto colloids which remain suspended in solution initially but fall out of solution or are removed by the  $0.45 \mu\text{m}$  filter in tests 28 days or longer. The decrease in actinide concentration in the leachate beyond 28 days corresponds with the decrease observed in aluminum and iron (see Table 3) after about 28 days.

The behavior of the actinides in tests at  $2000 \text{ m}^{-1}$  suggests that colloids are also be present in these tests, though with smaller particle sizes [11]. Plutonium and americium have very low solubilities under alkaline conditions of these tests. The plutonium and americium suspended in tests at  $2000 \text{ m}^{-1}$  are probably sorbed onto small Al- or Fe-bearing colloids. These colloids may eventually become large enough that they will be removed by  $0.45 \mu\text{m}$  filters or may settle out of solution. This may be why the amount of neptunium in the leachate decreases after 280 days at  $2000 \text{ m}^{-1}$ . It is unclear if the colloids originate as precipitates within solution or as secondary material spalled from the glass surface which is small enough to become suspended. Analyses of the reacted solid material are in progress to more completely describe the actinide behavior and the origins of the suspended material.

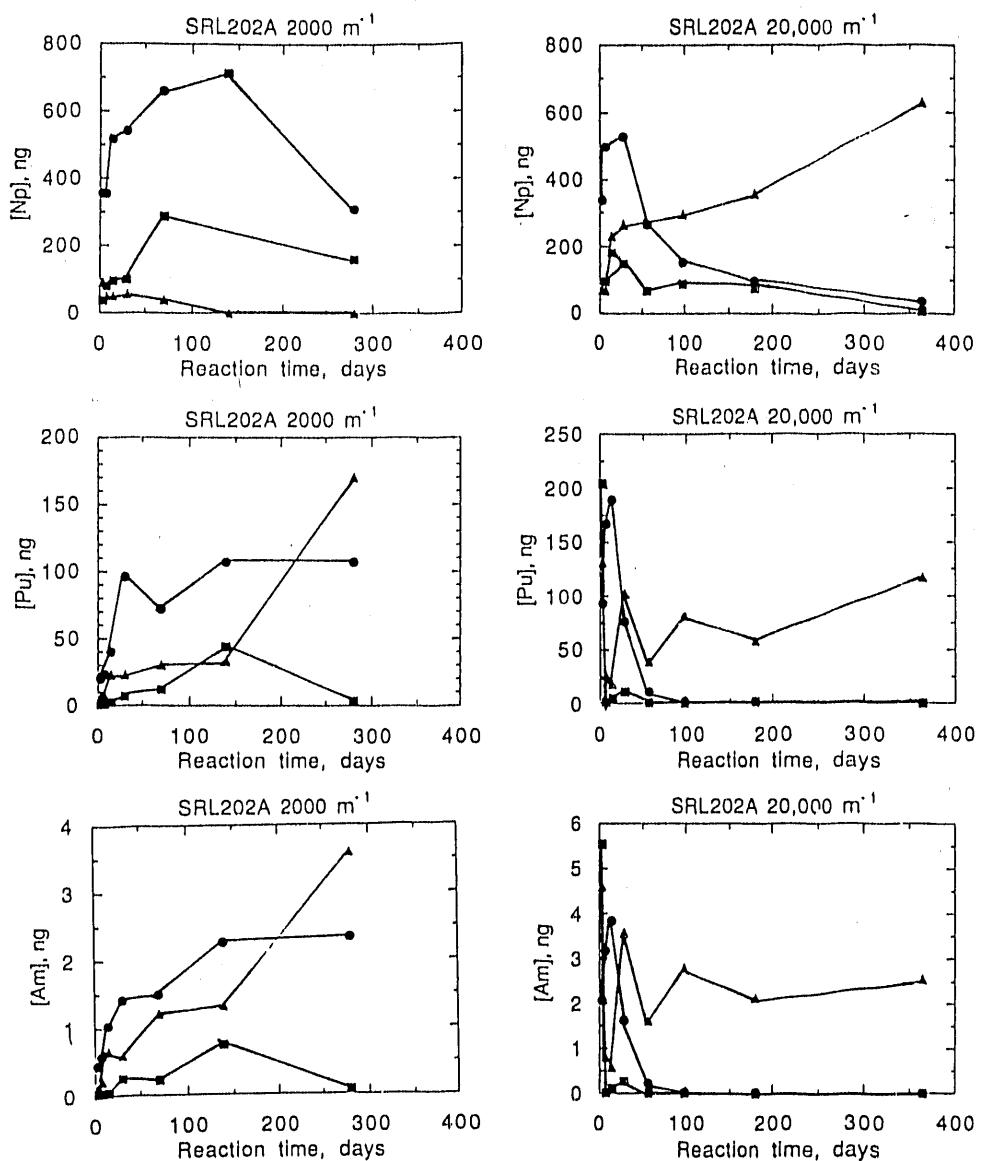


Figure 5. Mass actinide in (●) 0.45  $\mu\text{m}$  filtrate, (■) 60 Å filtrate, and (▲) acid soak solution for tests with SRL 202A glass at  $2000 \text{ m}^{-1}$  for (a) Np, (b) Pu, and (c) Am; and at  $20,000 \text{ m}^{-1}$  for (d) Np, (e) Pu, and (f) Am.

#### D. CONCLUSIONS

The results of these tests show the SA/V used in static leach tests can significantly affect the observed response in tests of three days to one year duration. Physically, the SA/V of a test can only affect the capacity of the leachate to dilute species released by the glass reaction, but the different solution chemistries which result may significantly affect the reaction path. The initial effect of high SA/V is an increased pH rise due to smaller solution volumes per unit glass surface area. The increased pH may then affect subsequent hydrolysis reactions. Greater solution concentrations of glass components at higher SA/V may result in the formation of colloids which may contain released nuclides. The amount of nuclides in the leachate may increase if the colloids are small and remain suspended, or may decrease if the colloids are large and settle out of solution.

The observed reaction behavior in leach tests is dependent on the SA/V of the test as the system progresses from being dominated by ion exchange to being dominated by hydrolysis and matrix dissolution as the pH increases, and finally to a system dominated by the generation of colloids. For example, the MCC-1 test predominantly measures the ion-exchange dominated reaction of the glass while the pH remains near neutral (<10). The PCT attains higher leachate pH values and measures the matrix-dissolution dominated rate prior to colloid or secondary phase formation. Other effects are due to the higher concentrations of glass components in the leachates at high SA/V, such as colloid and secondary phase formation. Observations in tests at high SA/V such as those performed here at  $20,000 \text{ m}^{-1}$  may be dominated by secondary phase formation. Interpretation of glass durability or production consistency tests requires a full understanding of which process dominates the observed response. Likewise, reaction models used for long-term simulation of the glass reaction must be based on test results which probe the appropriate step in the reaction mechanism. For example, the current model used by the YMP accounts only for matrix dissolution and is best supported by tests at SA/V near  $2000 \text{ m}^{-1}$ , where matrix dissolution controls the observed responses.

#### E. ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under contract W-31-109-ENG-38.

#### F. REFERENCES

1. Materials Characterization Center, Nuclear Waste Materials Handbook, Volume 1, Pacific Northwest Laboratory report DOE-TIC-1400 (1981).
2. C. M. JANTZEN and N. E. BIBLER, Product Consistency Test (PCT) for DWPF Glass: Part I. Test Development and Protocol, Westinghouse Savannah River Company report DPST-87-575 (1987).
3. W. L. BOURCIER, D. W. PEIFFER, K. G. KNAUSS, K. D. McKEEGAN, and D. L. 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. L. R. PEDERSON, C. Q. BUCKWALTER, and G. L. McVAY, "The Effects of Surface Area to Solution Volume on Waste Glass Leaching," *Nucl. Technol.* 62, 151 (1983).
5. L. R. PEDERSON, C. Q. BUCKWALTER, G. L. McVAY, and B. L. RIDDLE, "Glass Surface Area to Solution Volume Ratio and Its Implications to Accelerated Leach Testing," *Mat. Res. Soc. Symp. Proc.* Vol. 15, 47 (1983).
6. R. J. CHARLES, "Static Fatigue of Glass. I," *J. Appl. Phys.* 29(11), 1549 (1958).
7. E. VERNAZ, T. ADVOCAT, and J. L. DUSSOSSOY, "Effects of the SA/V Ratio on the Long-Term Corrosion Kinetics of R7T7 Glass," *Ceram. Trans.* (1990).
8. J. W. SHADE and D. M. STRACHAN, "Effect of High Surface Area to Solution Volume Ratio on Waste Glass Leaching," *Ceram. Bull.* 65(12) (1986).
9. S. O. BATES, G. F. PIEPEL, and J. W. JOHNSTON, Leach Testing of Simulated Hanford Waste Vitrification Plant Reference Glass HW-39, Pacific Northwest Laboratory report PNL-6884 (1989).
10. B. GRAMBOW, W. LUTZE, and R. MULLER, "Empirical Dissolution Rate Law for the Glass R7T7 Contacting Halite and Silica Saturated Brines," in *Mat. Res. Soc. Symp. Proc.*, in press.
11. J. C. CUNNANE and J. K. BATES, "Identification of Colloids in Nuclear Waste Glass Reactions," presented at the 93rd Annual Meeting, American Ceramics Society, Cincinnati, OH, April 28-May 2, 1991.

DATE  
FILMED  
5/20/92

