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THE REACTION OF SRL 202 GLASS IN J-13 AND DIW

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ABSTRACT

Static leach tests were performed in both 304L stainless steel and Teflon vessels using a synthetic high-level waste glass with either deionized water (DIW) or a tuff groundwater solution as the leachant to assess the effects of the vessel and the initial leachant composition on the extent and nature of the glass reaction. The tests were performed using monolith samples at 340 m^{-1} and crushed samples at 2000 m^{-1} for times up to 1 year. The results show less silicon is released from the glass into the groundwater solution than into DIW at both high and low glass surface area/leachant volume ratios (SA/V), but the alkali metal and boron releases are not affected by the leachant used. Tests performed in a stainless steel vessel resulted in slightly lower leachate pH values, but similar reaction rates to those performed in a Teflon vessel, as measured by the boron release. Blank tests with DIW or EJ-13 in the vessels showed the Teflon vessels to release small amounts of fluoride (1 to 2 ppm) and to acidify the DIW slightly ($4.0 < \text{pH} < 5.6$). The pH values of blank tests with EJ-13 increased from 8.2 to about 8.6 in steel and to about 9.2 in Teflon vessels. The slightly higher pH values attained in Teflon vessels are attributed to outgassing of CO_2 during the test.

INTRODUCTION

Static leach tests are commonly used to measure the durabilities of glasses that may be produced during vitrification of high-level nuclear waste. The response of the glass is usually monitored by measuring the release of soluble glass components into the solution. Changes in the solution composition that occur during a static leach test include changes due to corrosion of the reaction vessel and alteration of the gas phase present in the test vessel, as well as those due to the glass reaction. Most static leach tests are performed in either stainless steel vessels or in PFA (perfluoroalkoxy) Teflon vessels. Neither vessel is inert with respect to the solution composition. The steel surface may adsorb components released from the glass or may corrode to release metal ions into solution [1]. Teflon may release hydrofluoric acid (HF) into solution [2], which may accelerate the glass corrosion and acidify the leachate. Teflon is also permeable to carbon dioxide, which may affect the solution pH [3]. It is important to account for effects related to vessel interactions to accurately measure the extent of glass reaction. Because the glass reaction is known to be strongly influenced by the solution chemistry [4-7], both the effects of the initial leachant composition and changes to the leachate chemistry due to interactions other than glass corrosion must be understood to assess the extent and nature of the glass reaction.

Static leach tests were performed to assess the effects of the initial leachant composition and reaction vessel material on the measured extent of reaction using SRL 202 glass, which is representative of the glass to be produced at the Defense Waste Processing Facility (DWPF). Tests were performed using both monolith samples and crushed glass and followed slight modifications of the MCC-1 [8] or PCT [9] protocols at glass surface area/leachant volume ratios (SA/V) of 340 and 2000 m^{-1} . Either deionized water (DIW) or a J-13 groundwater solution was used as

the leachant, and tests were performed in either 304L stainless steel or Teflon vessels at 90°C. These tests were conducted as part of a larger experimental matrix designed to characterize the effects of the SAV used in a static leach test on the glass reaction [10].

EXPERIMENTAL

Glass received from the Westinghouse Savannah River Site was doped with ^{238}U , or with ^{99}Tc , ^{237}Np , ^{238}U , ^{239}Pu , and ^{241}Am to produce what are referred to as SRL 202U or SRL 202A glasses. The glasses were cast into bars and then cored and sectioned to generate monolith disks for tests performed at 340 m^{-1} . The remaining glass was then crushed and the size fraction between 74 and 149 μm (-100+200 mesh) was used in the tests performed at 2000 m^{-1} . The glass composition is given elsewhere [10]. Both the monoliths and crushed glass were washed prior to use and representative samples were analyzed using a scanning electron microscope (SEM) to verify acceptability. The leachant was prepared by equilibrating J-13 groundwater, which is a reference groundwater of the Yucca Mountain Project, with crushed Topopah Spring tuff at 90°C [11]. The solution was then allowed to cool to room temperature, then filtered using 0.1 μm filters and is referred to here as EJ-13. The EJ-13 leachant composition is given in Table I. Other tests were performed in DIW. Four monolith disks, each with a geometric surface area of about 1.6 cm^2 , were placed on a Teflon support and submerged in about 2 mL of leachant to achieve an SAV of about 340 m^{-1} . The support assured that the bottom face of the sample was fully exposed to the leachate. Tests with crushed glass were performed by adding 1 g of glass to 10 g leachant to achieve an SAV of about 2000 m^{-1} . (The surface area of the crushed glass is assumed to be $2\text{E-}2\text{ m}^2/\text{g}$, based on cubic particle geometry.)

Tests with actinide-doped glass (SRL 202A) were performed in steel vessels with EJ-13 at 2000 m^{-1} and tests with uranium-doped glass (SRL 202U) were performed in Teflon vessels with DIW or EJ 13 at 340 m^{-1} and with DIW at 2000 m^{-1} . Blank tests with DIW or EJ-13 were run in both steel and Teflon vessels to determine background values for tests with glass. All tests were run in duplicate. Tests using Teflon vessels were run in a constant temperature water bath to minimize water loss while tests in steel vessels were run in a dry air oven, both at $90 \pm 2^\circ\text{C}$.

The Teflon vessels were carefully cleaned prior to use. The cleaning procedure included filling the vessels with a 5% NaOH solution to preleach HF from the Teflon then rinsing with dilute HNO_3 and DIW until rinse volumes from representative vessels had measured pH values near that of fresh DIW (typically within 0.2 pH units). Several vessels were then filled with DIW and leached at 90°C for up to 4 weeks. The leachates were then analyzed for pH and fluoride using a pH or ion selective electrode. The vessels were considered clean when the pH was that of fresh DIW (± 0.2 pH units) and the fluoride level was below 0.05 ppm. The steel vessels were cleaned using a nitric acid wash followed by several DIW rinses. Blank tests were performed for times up to one year parallel to tests with glass to monitor long-term vessel interactions.

Prior to opening the Teflon vessels, they were removed from the water bath and placed in the dry air oven for about 1 hour to dry the outer surface of the vessel so the mass change could be measured. Upon opening the vessels, aliquots of the leachate were removed for carbon and transuranic analyses. The leachate was then removed from the vessel while still near the reaction temperature using a pre-heated

Table I
Composition of EJ-13 Leachant and Leachates from
182-Day Blank Tests, in ppm

Element	EJ-13	EJ-13/Teflon	EJ-13/Steel
Al	1.1	1.1	0.56
B	0.16	2.1	0.15
Ca	5.1	2.6	4.6
K	7.3	7.4	7.0
Li	0.05	<0.1	0.05
Na	54	55	51
Si	46	44	45
F ⁻	2	2	3
Cl ⁻	8.4	8	9.7
NO ₃ ⁻	11	10	11
SO ₄ ⁼	22	22	24
Total Carbon	20	30	21
Organic Carbon	2	10	5
pH	8.2	9.2	8.6

pipette tip. Leachate from tests with crushed glass was immediately filtered using pre-heated 0.45 µm polycarbonate filters. Aliquots of the leachates from tests with monolith samples and of the filtrates from tests with crushed glass were then analyzed for pH, anions, and cations. Aliquots of the leachates from some tests were further filtered through approximately 6 nm filters and these filtrates analyzed for cations. Cations were analyzed using inductively coupled atomic emission spectroscopy or fluorescence, carbon by infra-red, and anions by ion chromatography or an ion-selective electrode.

RESULTS

Blank Tests

The leachate pH values of blank tests with DIW or EJ-13 in Teflon vessels and EJ-13 in steel vessels are plotted in Figure 1 against the reaction time. Tests with DIW in Teflon became acidified relative to the initial solution pH (about 5.6) at most times. Tests with EJ-13 in Teflon vessels had more basic leachates than the initial EJ-13 solution (about 8.2) at all times.

The fluoride concentration of the initial EJ-13 leachant was measured to be about 2 to 3 ppm. Figure 1b shows the fluoride concentrations measured in the blank tests. Tests with DIW in Teflon had about 1 ppm fluoride in the leachate at all times tested. The measured fluoride values, which include the fluoride in the initial EJ-13 solution, are plotted in the figure. Tests in Teflon vessels show an increase of about 10 ppm fluoride due to vessel reaction, while no fluoride is released from the steel vessels.

The total carbon and organic carbon levels in blank tests with DIW were both between 0.5 and 3 ppm at all reaction times. The organic and inorganic carbon contents of the blank tests with EJ-13 in Teflon vessels are shown in Figure 1c. Analysis of the EJ-13 leachant gave a total carbon concentration of about 20 ppm

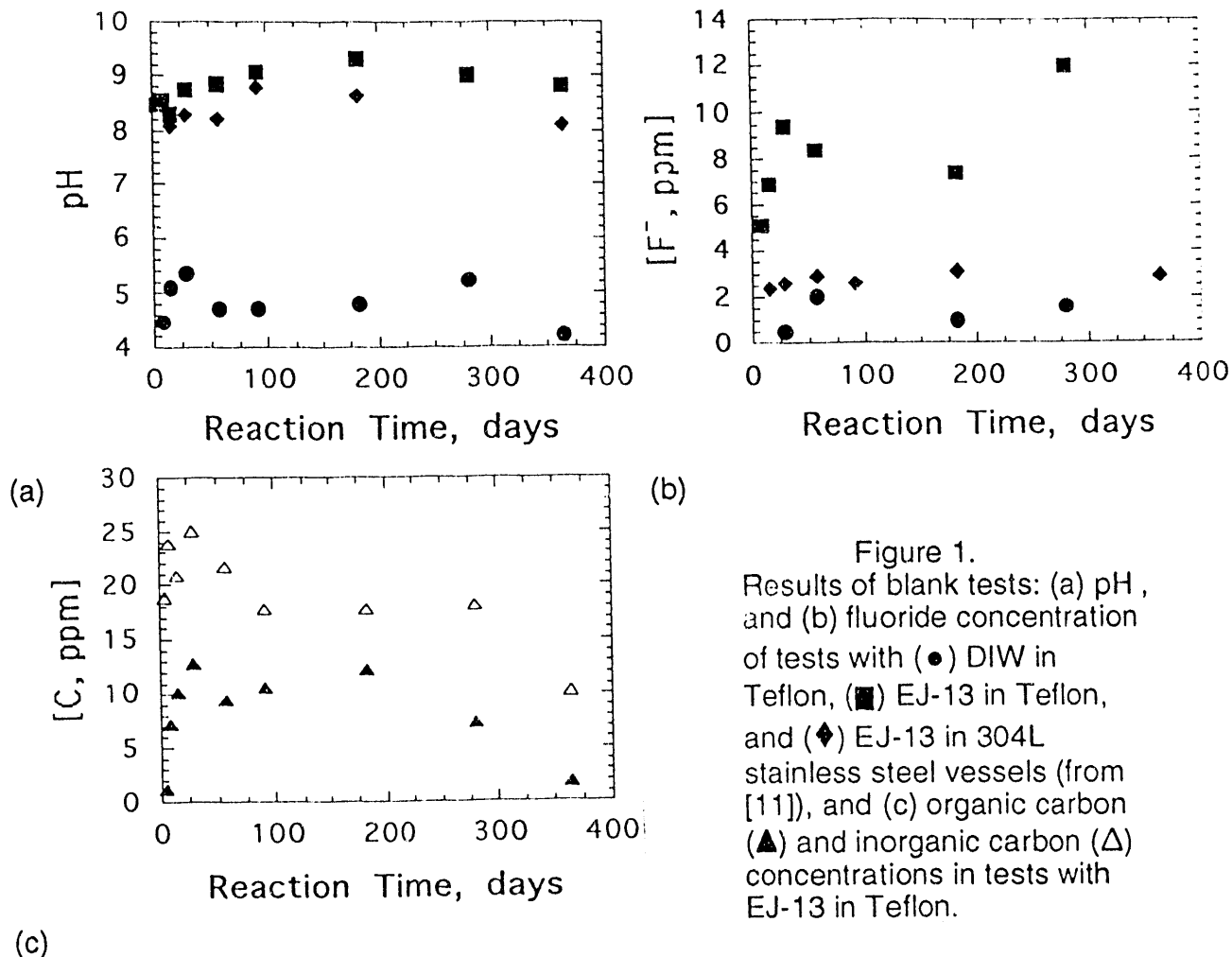
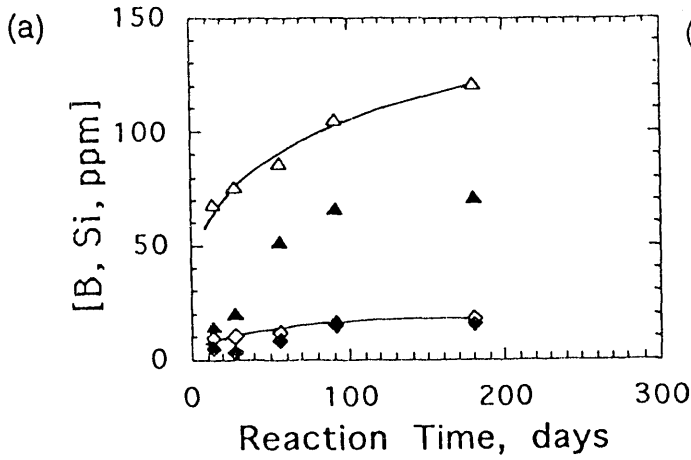
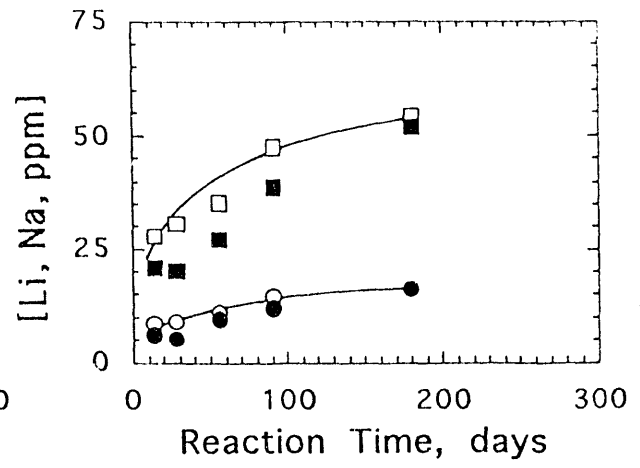
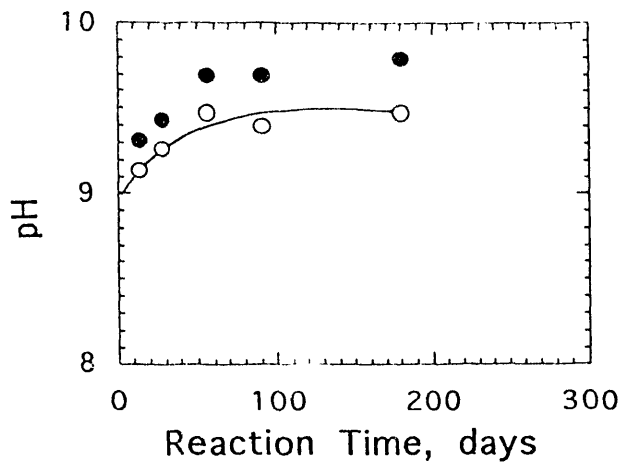


Figure 1. Results of blank tests: (a) pH, and (b) fluoride concentration of tests with (●) DIW in Teflon, (■) EJ-13 in Teflon, and (◆) EJ-13 in 304L stainless steel vessels (from [11]), and (c) organic carbon (▲) and inorganic carbon (Δ) concentrations in tests with EJ-13 in Teflon.

and an organic carbon concentration of about 2 ppm. The organic content increases at the shortest reaction times, but does not increase with the reaction time. The amount of inorganic carbon in solution decreases with the reaction time. The concentrations of other cations measured in blank tests run about 180 days are included in Table I to show changes in the EJ-13 composition due to testing in different vessels.

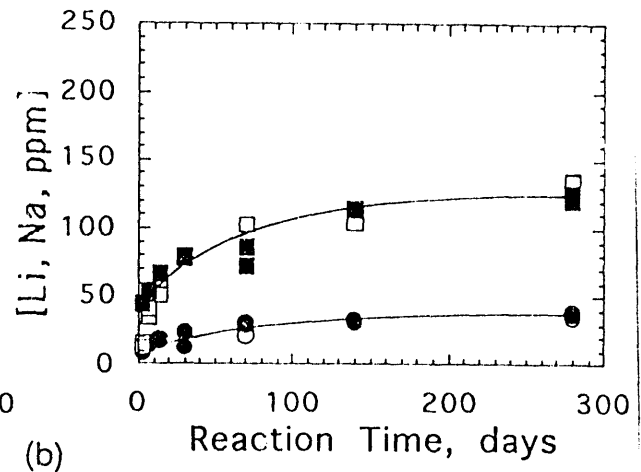
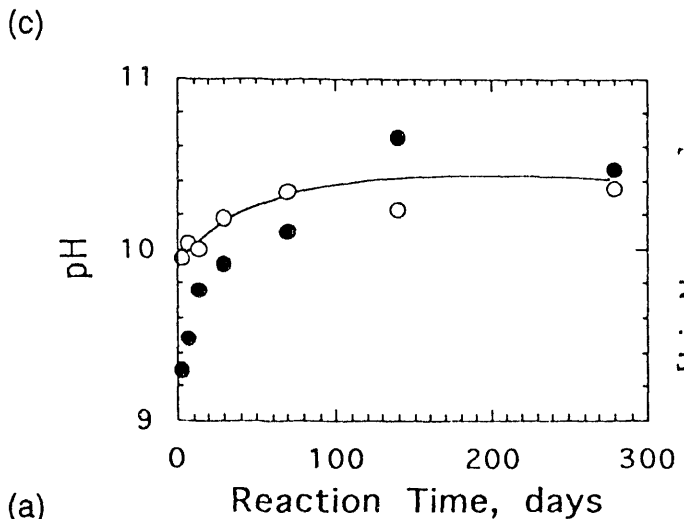
Tests with Glass

The results of tests performed with DIW or EJ-13 and SRL 202 glass at common SAV are compared to assess the effects of the leachant composition and vessel interaction on the glass reaction. Figures 2 and 3 show the leachate pH and the lithium, sodium, boron, and silicon concentration for tests at 340, and 2000 m⁻¹, respectively. The curves in the figures are drawn through the data for tests in DIW to distinguish the trend in the data of tests with DIW from that of tests in EJ-13, but do not represent analytical fits to the data. In Figure 2a, tests reacted with EJ-13 in Teflon vessels at 340 m⁻¹ have higher final leachate pH values than those reacted with DIW at all times tested. The pH increases above that of the initial leachant within 7 days, and increases slightly with longer reaction times. At 2000 m⁻¹, in Figure 3a, the pH values of tests with EJ-13 in steel vessels are slightly lower than those with DIW in Teflon vessels through 70 days, but the pH is higher in tests with EJ-13 in steel vessels after 70 days. The pH is similar in tests with DIW and EJ-13 after 280 days.



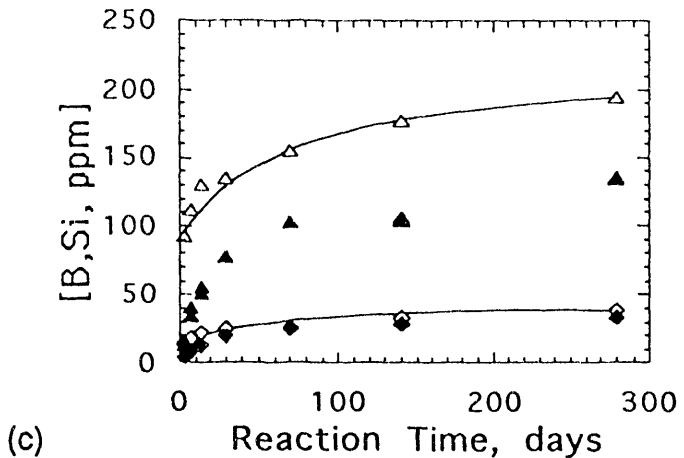
(b)

Figure 2.
Results of tests with SRL 202 glass at 340 m^{-1} : (a) pH, (b) lithium (\bullet) and sodium (\blacksquare) concentrations, and (c) boron (\blacklozenge) and silicon (\blacktriangle) concentrations. Open symbols represent tests with DIW in Teflon vessels and filled symbols tests with EJ-13 in Teflon vessels.



(a)

(b)



(c)

Figure 3.
Results of tests with SRL 202 glass at 2000 m^{-1} : (a) pH, (b) lithium (\bullet) and sodium (\blacksquare) concentrations, and (c) boron (\blacklozenge) and silicon (\blacktriangle) concentrations. Open symbols represent tests with DIW in Teflon vessels and filled symbols tests with EJ-13 in 304L stainless steel vessels.

The Li, Na, B, and Si concentrations measured in leachates of tests at 340 m⁻¹ and in the 0.45 μm filtrate solutions from tests at 2000 m⁻¹ are plotted in Figures 2b and c, and in 3b and c, respectively. The results from tests with EJ-13 solution have been corrected for background concentrations that were measured in blank tests with EJ-13 in steel or Teflon vessels (see Table I). The solution concentrations of lithium and boron are the same in all tests, within analytical error, regardless of the leachant or vessel used. The background-corrected concentration of sodium is also similar in tests in DIW and EJ-13 at 2000 m⁻¹, although the sodium concentration is consistently higher in tests with DIW than with EJ-13 at 340 m⁻¹. The silicon concentrations in tests with DIW are about 50 ppm higher than those in tests with EJ-13 at both 340 and 2000 m⁻¹ at all times tested, which is about equal to the amount of silicon that was subtracted as the background level of the initial EJ-13 leachant.

DISCUSSION

These results show that the initial leachant composition does affect the releases of some glass components. The measured release of different glass components is related to their concentrations in the leachant. Lithium and boron have low concentrations in the leachant and the release of each from SRL 202 is the same in DIW and EJ-13. The EJ-13 leachant has a relatively high silicon concentration, and the amount of silicon released from the glass is lower in tests with EJ-13 than in tests with DIW. The difference is similar the amount of silicon in the initial leachant, and the total amount of silicon measured in solution is similar in tests with DIW and EJ-13. The EJ-13 leachant also has a high sodium content, but the amount of sodium released from the glass is only slightly lower in tests with EJ-13 than in tests with DIW. The measured extent of glass reaction is the same in EJ-13 and DIW based on boron release, but greater in DIW based on silicon release. High leachant silicon levels have been reported to reduce the boron release in other experiments [12], but the high silicon concentration in EJ-13 does not measurably reduce the boron release in the present tests over long time periods.

The leachate pH reflects the influence of several species released from the glass. The release of alkali metals via ion-exchange reactions leads to a pH increase during glass reaction while the released boric and silicic acids buffer the pH against excursions above about pH 9. Carbon dioxide dissolved in the solution will acidify the solution, and degassing the solution will increase the pH. Blank tests with DIW in Teflon showed the pH to decrease from the initial value near 5.6 to as low as 4 after one year. The decrease may be due to vessel interactions to release HF (see below). The low ionic strength of DIW makes pH measurements sensitive to additional CO₂ that may dissolve in the solution during the measurement, which will lower the pH. Blank tests with EJ-13 in Teflon vessels showed the pH to increase from the initial EJ-13 leachant pH of about 8.2 to about 9 after one year.. The rise is interpreted to be due to outgassing of the leachant solution and a net decrease in dissolved carbonic acid.

Tests with glass in DIW had higher pH values than tests in EJ-13 at 2000 m⁻¹, while tests run at 340 m⁻¹ with EJ-13 had higher pH values than those run with DIW. This suggests that the EJ-13 solution mitigated the pH rise due to the glass reaction while the DIW had little or no buffering capacity. The reaction at 340 m⁻¹ has apparently not progressed to the extent where the pH rise due to the glass reaction has reached the effective buffer pH of the EJ-13. Changes in the leachate chemistry due to the glass reaction dominate any changes due to vessel interaction in either Teflon or steel vessels.

The influence of the initial leachant composition on the amounts of Li, Na, B, and Si released from the glass is similar in Teflon and steel vessels. The vessel itself had little effect. The primary effects of Teflon vessels were reduced by (1) carefully cleaning the vessels prior to use to minimize the release of HF during the test, and (2) performing the tests in a water bath. While a water bath was used to minimize the water loss due to vessel leakage, use of the water bath also maintained a very low carbon dioxide partial pressure outside the vessels, which may have reduced the amount of carbon dioxide that diffused into the vessel. Indeed, the results of blank tests suggest that the CO₂ content of the Teflon vessels was actually reduced during the tests. The steel vessels formed an air-tight seal which prevented water loss and any infiltration or release of carbon dioxide.

The tests at 2000 m⁻¹ also show that the actinide-doped SRL 202A glass reacts the same as the uranium-doped SRL 202U glass. Key indicators of the glass reaction such as boron and lithium are released to equal extents from SRL 202A reacted with EJ-13 in steel vessels and from SRL 202U reacted with DIW in Teflon vessels. This is consistent with other tests performed at low SA/V with other actinide-doped glasses [11] and with glasses with actual waste [13]. Other tests with glasses containing actual waste do show radiation effects in tests at high SA/V [14]. Possible synergistic effects of radiation and the SA/V used in the tests need to be better understood.

CONCLUSIONS

Static leach tests at 340 and 2000 m⁻¹ performed with DIW and EJ-13 leachants in Teflon reaction vessels show a small effect of the leachant composition on the glass reaction but no effects of the vessel. A small amount of HF is released from the Teflon vessels even after thorough pre-leaching and cleaning, but the additional HF does not affect the glass reaction compared to identical tests performed in 304L stainless steel vessels. The initial leachant composition affects the releases of some glass components which are present in the initial leachant, such as silicon and sodium, but the release of other components that are commonly used as indicators of the extent of glass reaction, such as boron and lithium, are not affected by the leachant composition.

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REFERENCES

1. Bibler, N. E., "Leaching Fully Radioactive SRP Nuclear Waste Glass in Tuff Groundwater in Stainless Steel Vessels," Savannah River Laboratory Report DP-MS-85-141 (1986).
2. Strachan, D. M., "Effect of Gamma Irradiation on Simulated Waste Glass Leaching and on the Leach Vessel," J. Amer. Ceram. Soc. 66(9), C-158-C-160 (1983).
3. Barkatt, Aa., Al. Barkatt, P. E. Pehrsson, P. B. Macedo, and J. H. Simmons, "The Importance of CO₂ Buffering and of the Total Ionic Balance in Measurements on the Durability of Glasses," Nucl. Technol. 56, 271-277 (1982).

4. Grambow, B., and D. M. Strachan, "Leach Testing of Waste Glasses Under Near-Saturation Conditions," *Mat. Res. Soc. Symp. Proc.* 26, 623-634 (1984).
5. Chick, L. A., and L. R. Pederson, "The Relationship Between Reaction Layer Thickness and Leach Rate for Nuclear Waste Glasses," *Mat. Res. Soc. Symp. Proc.* 26, 635-642 (1984).
6. Bourcier, W. L., D. W. Peiffer, K. G. Knauss, K. D. McKeegan, and D. K. Smith, "A Kinetic Model for Borosilicate Glass Dissolution Based on the Dissolution Affinity of a Surface Alteration Layer," *Mat. Res. Soc. Symp. Proc.* 176, 209-216 (1990).
7. Bourcier, W. L., H. C. Weed, S. N. Nguyen, J. K. Nielsen, L. Morgan, L. Newton, and K. G. Knauss, "Solution Compositional Effects on the Dissolution Kinetics of Borosilicate Glass," *Symp. on Water Rock Interactions* (1992, in press).
8. DOE Nuclear Waste Materials Handbook DOE/TIC-11400 (1982).
9. Jantzen, C. M., and N. E. Bibler, "Product Consistency Test (PCT) to DWPF Glass: Part I. Test Development and Protocol," Savannah River Laboratory Report DPST-87-575 (1987).
10. Ebert, W. L., and J. K. Bates, "A Comparison of Glass Reaction at High and Low SA/V," *Proc. Third Internat. Conf. High-Level Radioactive Waste Mgmt.*, Vol. 1, Las Vegas, NV, 934-942 (1992).
11. Ebert, W. L., J. K. Bates, and T. J. Gerding, "The Reaction of Glass During Gamma Irradiation in a Saturated Tuff Environment, Part 4: SRL 165, ATM-1c, and ATM-8 Glasses at 1E3 R/h and 0 R/h," Argonne National Laboratory Report ANL-90/13 (1990).
12. Pederson, L. R., 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.* 15, 47-54 (1983).
13. Bibler, N. E., "Characterization of Borosilicate Glass-Containing Savannah River Plant Radioactive Waste, MCC-1 Tests and Durability in Geologic Repository Groundwaters," in Geochemical Behavior of Disposed Radioactive Waste, G. S. Barney, J. D. Navatil, and W. W. Schulz, eds., ASC Symposium Series 246, 359-372 (1984).
14. Feng, X., and J. K. Bates, "Initial Comparison of Leach Behavior Between Fully Radioactive and Simulated Nuclear Waste Glasses Through Long-Term Testing. Part 1. Solution Analysis," *Proc. of 3rd Internat. Conf. High-Level Radioactive Waste Mgmt.*, 925-933 (1992).

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