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## LABORATORY TESTING OF WEST VALLEY REFERENCE 6 GLASS

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### ABSTRACT

A series of laboratory tests is being conducted to characterize the corrosion of West Valley reference 6 glass (WV6) and to provide parametric values for modeling its long-term durability. Models require measurement of the corrosion rate in the absence of corrosion products and in fluids that are "saturated" with corrosion products, and the identification of alteration phases. Corrosion rates in dilute and saturated conditions were measured using MCC-1 and PCT tests, respectively. Vapor hydration tests were performed to generate secondary phases. The PCT tests show the WV6 glass to be more durable than SRL EA, SRL 202, and HW-39-1 glasses. Vapor hydration tests show weavite (a uranyl silicate), a potassium-bearing zeolite, analcime, potassium feldspar, a calcium silicate phase, and lithium phosphate to form as WV6 glass corrodes. Test results are presented and their relevance to long-term performance discussed.

### INTRODUCTION

The West Valley Demonstration Project (WVDP) will produce high-level waste glass from wastes generated during the reprocessing of nuclear fuels. A target composition for glass to be produced from high-level sludge has been identified by the WVDP. Argonne National Laboratory (ANL) is conducting laboratory tests using a nonradioactive homologue of this target glass. (The fully radioactive glass will be tested at ANL when that glass becomes available.) The glass being tested is referred to as West Valley Reference 6 (WV6) glass. The results of tests performed with WV6 glass will provide valuable insight regarding the corrosion behavior of the fully radioactive glass, since a more complete analysis of the corrosion behavior of nonradioactive WV6 glass will be possible. These tests are being performed under a range of conditions to demonstrate the performance of the glass produced by WVDP for disposal in a federal repository.

The long-term durability of vitrified waste forms emplaced in a repository can only be projected based on a mechanistic understanding of the corrosion process, which must be deduced from the results of short-term laboratory tests. Previous studies have shown that glass corrosion occurs in three stages, which depend on the solution chemistry. Stage I occurs under conditions in which solution concentrations of dissolved glass components are very low and the glass reacts at a characteristic forward rate that is unique to the glass composition, temperature, and solution pH. Stage II occurs as the concentrations of glass components in the

contacting fluid increase, and the glass corrosion slows to a rate that may become immeasurably low. Stage III occurs as secondary mineral phases precipitate from the fluid and lower the activities of species which affect the glass corrosion rate. Depending on which secondary phases form, glass corrosion may proceed at a rate similar to the low rate attained in Stage II or may be accelerated to a rate similar to that observed during Stage I. The rate of glass corrosion in Stage III will be controlled primarily by the chemistry of the solution in equilibrium with the assemblage of secondary phases that form.

The assemblage of these secondary phases depends in large part on the composition of the glass because corrosion of the glass supplies material to the fluid from which the secondary phases precipitate. For that reason and because specific phases that nucleate cannot be predicted *a priori*, laboratory tests are needed to determine which phases form and how the formation of these phases affects the glass corrosion rate. Completely describing glass stability requires that the corrosion behavior of a glass be characterized by tests that access the three different corrosion stages. Once the corrosion behavior of the glass is known, it can be related to anticipated storage conditions.

## EXPERIMENTAL

Laboratory tests were conducted to provide information regarding the corrosion behavior of WV6 glass at all stages of the corrosion process, i.e., when the rate is controlled by the intrinsic durability of the glass, the accumulation of glass corrosion products in solution, or secondary phases. Tests were conducted under conditions that highlighted the corrosion behavior in the three different corrosion stages: short-term MCC-1 tests [1] to maintain dilute solutions, long-term PCT-type tests [2] to generate highly concentrated solutions, and vapor hydration tests [3] to promote secondary phase formation. The test matrix is summarized in Table 1. The PCT tests were conducted in deionized water for 7 days to compare the durability of WV6 glass to other reference glasses. All other tests were conducted to characterize glass corrosion behavior, most in duplicate. Tests at 20,000 m-1 were conducted using two size fractions of crushed glass. The extent of corrosion in the MCC-1 and PCT tests is quantified by using the normalized mass loss (NL) of the glass based on soluble glass components.

The vapor hydration tests were conducted following a procedure developed at Argonne National Laboratory. Tests were conducted at 200°C to accelerate the corrosion. While glass will not be exposed to water vapor at 200°C in the repository, glass corrosion in VHT tests at high temperatures has been shown to simulate corrosion at lower temperatures.

The WV6 glass used in testing was supplied by Catholic University of America; the composition is given in Table 2. Deionized water was used as the leachant in 7-day PCT and vapor hydration tests. All other tests employed a leachant prepared by reacting crushed Topopah Springs tuff with water from well J-13 of the Nevada Test Site for 28 days at 90°C. The composition and pH of the resulting solution (referred to as EJ-13 water) are given in Table 3.

Table I. Summary of Test Matrix

Test Type	S/V <sup>a</sup>	Temp °C	Sample	Leachant	Reaction Times, days
MCC-1	10	90	monolith	EJ-13	3, 7, 14, 91, 182, 367
PCT	2000	90	-100+200 <sup>b</sup>	DIW	7
PCT	2000	90	-100+200	EJ-13	7, 30, 70, TBD <sup>c</sup>
PCT	20,000	90	-100+200	EJ-13	56, 98, 182, 367, TBD
PCT	20,000	90	-200+325	EJ-13	56, 98, 182, 367, TBD
Vapor Hydration		200	monolith	DIW	7, 12, 14, 21, 28, 35, 55, 63

<sup>a</sup> Glass surface area/solution volume, in m<sup>-1</sup>.

<sup>b</sup> Mesh size fraction of crushed glass.

<sup>c</sup> TBD = Reaction Time "to be Determined," tests in progress.

Table II. Composition of WV6 Glass<sup>a</sup>, in Oxide wt%

Oxide	wt%	Oxide	wt%	Oxide	wt%
Al <sub>2</sub> O <sub>3</sub>	6.00	Li <sub>2</sub> O	3.71	SO <sub>3</sub>	0.23
B <sub>2</sub> O <sub>3</sub>	12.89	MgO	0.89	SiO <sub>2</sub>	40.98
BaO	0.16	MnO <sub>2</sub>	1.01	Sm <sub>2</sub> O <sub>3</sub>	0.03
CaO	0.48	MoO <sub>3</sub>	0.04	SrO	0.02
CeO <sub>2</sub>	0.16	Na <sub>2</sub> O	8.00	ThO <sub>2</sub>	3.56
CoO	0.02	Nd <sub>2</sub> O <sub>3</sub>	0.14	TiO <sub>2</sub>	0.80
Cr <sub>2</sub> O <sub>3</sub>	0.14	NiO	0.25	UO <sub>2</sub>	0.59
Cs <sub>2</sub> O	0.08	P <sub>2</sub> O <sub>5</sub>	1.20	Y <sub>2</sub> O <sub>3</sub>	0.02
CuO	0.03	PdO	0.03	ZnO	0.02
Fe <sub>2</sub> O <sub>3</sub>	12.02	Pr <sub>6</sub> O <sub>11</sub>	0.04	ZrO <sub>2</sub>	1.32
K <sub>2</sub> O	5.00	RhO <sub>2</sub>	0.02		
La <sub>2</sub> O <sub>3</sub>	0.04	RuO <sub>2</sub>	0.08	Total	100.00

<sup>a</sup>Glass composition as provided by The Catholic University of America

Table III. Analyzed Composition of EJ-13 Water, in ppm.

Al	1.41	K	5.88	Na	47.5
B	0.23	Li	0.057	Si	41.1
Ca	3.2	Mg	0.035		
Fe	0.137	Mn	0.1	pH	9.2

Analysis of unreacted polished disk samples revealed the presence of primary phases containing Ru and Fe, or Fe, Cr, Mn, and Ni. Iron spinels and ruthenium oxide have been observed to be present in a similar glass [4].

## RESULTS AND DISCUSSION

### MCC-1 Tests in EJ-13

The MCC-1 tests were conducted with WV6 glass in EJ-13 water for periods of 3, 7, and 14 days. The leachate solution concentrations of key glass components were used to determine the initial corrosion rate. The concentrations of all glass components after 3, 7, and 14 days of corrosion were only slightly above their concentrations in the EJ-13 water. The normalized mass loss values based on boron, NL(B), after 3, 7, and 14 days were all about  $0.07 \text{ g/m}^2$ , corresponding to corrosion rates of about 0.02, 0.01, and  $0.005 \text{ g/m}^2/\text{d}$ , respectively. The MCC-1 test run for 91 days had NL(B) values of  $0.28 \text{ g/m}^2$  (overall corrosion rate of about  $0.003 \text{ g/m}^2/\text{d}$ ). For comparison, the WV-205 glass had a measured corrosion rate of about  $0.6 \text{ g/m}^2/\text{d}$  in deionized water over 28 days in an MCC-1 test [5]. These results suggest that silicic acid present in the EJ-13 or released as the glass corrodes slows the corrosion relative to similar tests in deionized water.

### PCT Tests in Deionized Water

The PCT test has been used to study a wide range of waste forms and compare the performance of glasses having different compositions. Replicate PCT tests conducted in deionized water for 7 days gave an average NL(B) value of about  $0.3 \text{ g/m}^2$  for WV6. For comparison, the reported NL(B) values in PCT tests are  $0.4 \text{ g/m}^2$  for SRL 202, a reference glass for the Defense Waste Processing Facility (DWPF) [6]; about  $5 \text{ g/m}^2$  for the DWPF Environmental Assessment glass [7]; and about  $0.4 \text{ g/m}^2$  for HW-39 glass, a reference glass for the Hanford Waste Vitrification Plant (HWVP) [8]. Thus, the WV6 glass has a slightly lower release after seven days than these reference glasses for the DWPF and the HWVP.

### PCT Tests in EJ-13

The solution concentrations of major glass components in tests conducted at S/V ratios of 2000 and  $20,000 \text{ m}^{-1}$  with crushed glass of the -100+200 and -200+325 mesh size fractions are presented in Fig. 1 as the normalized mass losses as a function of the reaction time. The results show alkali metals and boron to be released faster than silicon; uranium and silicon are released stoichiometrically. All solution concentrations increase with the reaction time; this indicates that the solutions have not become saturated. The similarity in the results of tests conducted at  $20,000 \text{ m}^{-1}$  with both size fractions of crushed glass indicates no significant effect of particle size. Curves drawn through the boron data show the trend with respect to reaction time, but do not represent regressed fits to the data. The build up of corrosion products in the solution slows the corrosion at all S/V.

In modeling glass durability, the silicic acid concentration is usually assumed to control the corrosion rate [9], and the maximum (or "saturation") silicic acid concentration is a key model parameter. The total silica concentrations measured in these tests are plotted in Fig. 2. Note that the silica concentration (1) increases with time except in tests at  $10 \text{ m}^{-1}$ , (2) increases with the S/V, (3) is the same in tests at  $20,000 \text{ m}^{-1}$  with -100+200 and -200+325 mesh glass, and (4) remains constant in tests at  $10 \text{ m}^{-1}$  at a concentration slightly above that in the EJ-13 water. The increase in the silica concentration with S/V is probably tied to the increase in the solution pH; the average pH values of the 367 day tests are 9.2, 10.3, and 10.4 for S/V ratios of 10, 2000, and (both size fractions)  $20,000 \text{ m}^{-1}$ . These data indicate that the pH 9.2 solutions in the tests at  $10 \text{ m}^{-1}$  are saturated but the pH 10.3 and 10.4 solutions in the tests at 2000 and  $20,000 \text{ m}^{-1}$  are not.

### Solids Analysis

Corrosion in PCT tests results in a slight alteration of the glass surface. Scanning electron microscopy of reacted glass particles showed the surface to attain a chain-mail appearance similar to that seen on other glasses during the formation of smectite clays. Analysis of cross-sectioned surfaces using analytical electron microscopy revealed the presence of thin strands of clay-like material that form the alteration layer, as shown in Fig. 3. The composition and lattice spacings are consistent with smectite clay.

Corrosion in vapor hydration tests at  $200^\circ\text{C}$  generated an alkali-depleted surface layer that transforms into smectite clay. Also, a variety of secondary mineral phases precipitated from the fluid and condensed on the sample during the test. A photomicrograph of the thick layer formed on the surface of one of the samples reacted for 28 days is shown in Fig. 4. The dark region at the top of the photo is the mounting epoxy and the region at the bottom of the photo is the unreacted glass. The clay layer is approximately  $53 \mu\text{m}$  thick. Several secondary mineral phases can be seen at the outer surface of the layer. Iron and ruthenium-containing inclusion phases can be seen both in the unreacted glass and in the layer. The similarity of their distribution in the layer and the glass confirms that the clay layer is formed by *in situ* transformation of the alkali-depleted glass, while the observation that secondary minerals form on the outer surface indicates that they had precipitated from the fluid.

A key piece of information provided by the vapor hydration tests is identification of secondary phases that form as the glass corrodes. Several phases formed during corrosion of the WV6 glass. The morphology and compositions of most phases are identical to those formed on other WVDP reference glasses [9]. These include analcime, an unidentified zeolite orthoclase (potassium feldspar), lithium phosphate, and wecksite. Since the ability of the phases to sequester radionuclides will depend on their composition, identification of the secondary phases that form is important for projecting the disposition of released radionuclides. Photomicrographs of some secondary phases are shown in Fig 5.

## CONCLUSIONS

Laboratory tests are being used to measure corrosion characteristics of WV6 glass. Static leach tests at 90°C have been used to measure the corrosion rate in a tuff groundwater solutions under conditions where the solution either remains dilute or becomes concentrated with glass corrosion products. The highest measured rate under dilute conditions was about 0.02 g/m<sup>2</sup>/d. The rate decreased as the solutions became more concentrated with corrosion products. Vapor hydration tests at high temperatures (200°C) demonstrated that the glass will devitrify to generate various secondary phases. These phases will affect both the glass corrosion rate and the disposition of glass and waste components. Corrosion under PCT test conditions at high S/V should also reach Stage III, although the reaction time that is required for this to occur cannot be predicted.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste ASTM Standard C1220-92, American Society for Testing and Materials, Philadelphia PA (1992).
2. Standard Test Methods for Determining Chemical Durability of Nuclear Waste lasses: The Product Consistency Test (PCT) Standard C1285-94, American Society for Testing and Materials, Philadelphia PA (1994).
3. W.L. Ebert, J.K. Bates, and W.L. Bourcier, "The Hydration of Borosilicate Waste Glass in Liquid Water and Steam at 200°C," *Waste Management* **11**, 205-221 (1991).
4. D. McPherson, I. Joseph, A. Mathur, C. Capozzi, S. Armstron, and L.D. Pye, The Influence of Waste Variability on the Properties and Phase Stability of the West Valley Reference Glass, West Valley Nuclear Services Co., Inc., report DOE/NE/44139-29 (1987).
5. L.R. Eisenstatt, Description of the West Valley Demonstration Project Reference High-Level Waste Form and Canister, DOE/NE/44139-26 (1986).
6. C.M. Jantzen, N.E. Bibler, D.C. Beam, C.L. Crawford, and M.A. Pickett, Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material, Westinghouse Savannah River Company report WSRC-TR-92-346, Rev. 1 (1993).
7. W.L. Ebert and J.K. Bates, "A Comparison of Glass Reaction at High and Low Surface Area to Volume," *Nuclear Technol.* **104**(3) 372-384 (1993).
8. S.O. Bates, G.F. Piepel, and J.W. Johnston, Leach Testing of Simulated Hanford Waste Vitri-fication Plant Reference Glass HW-39, Pacific Northwest Laboratory report PNL-6884 (1989).
9. B. Grambow, "A General Rate Equation for Nuclear Waste Glass Corrosion," *Mat. Res. Soc. Symp. Proc.* **44**, 15-24 (1985).

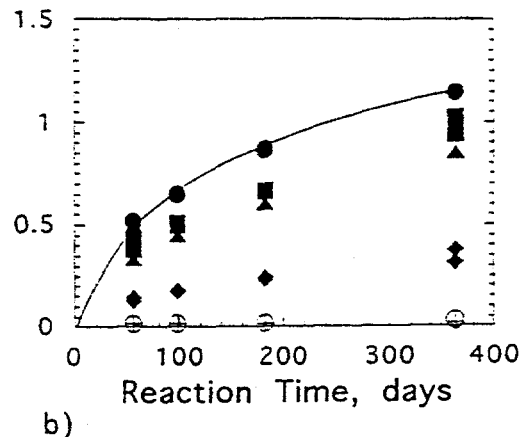
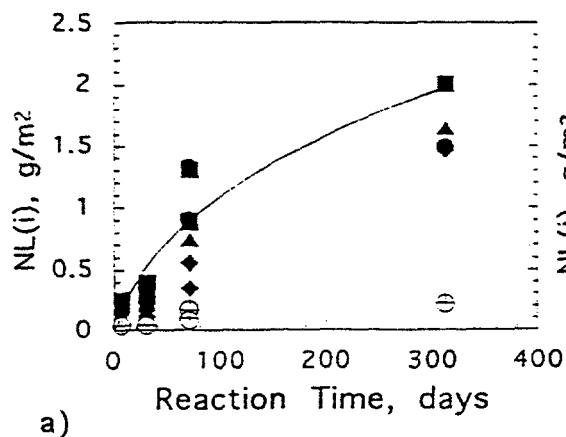


Figure 1. Normalized Mass Loss vs. Time for Tests at (a)  $2000\text{ m}^{-1}$ , (b)  $20,000\text{ m}^{-1}$  with  $-100+200$  mesh glass, and (c)  $20,000\text{ m}^{-1}$  with  $-200+325$  mesh glass. (●) B, (■) Li, (▲) Na, (◆) K, (○) Si, and (⊕) U. The results of duplicate tests are plotted.

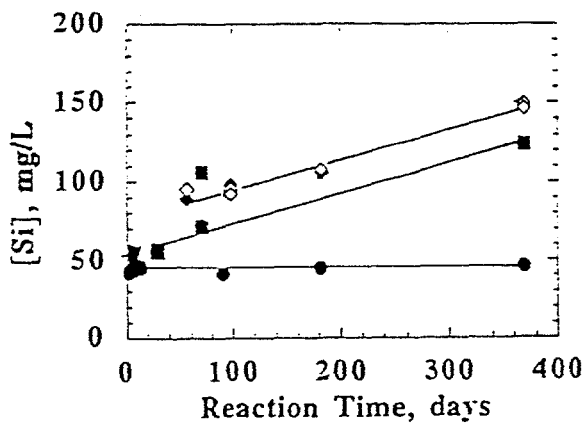
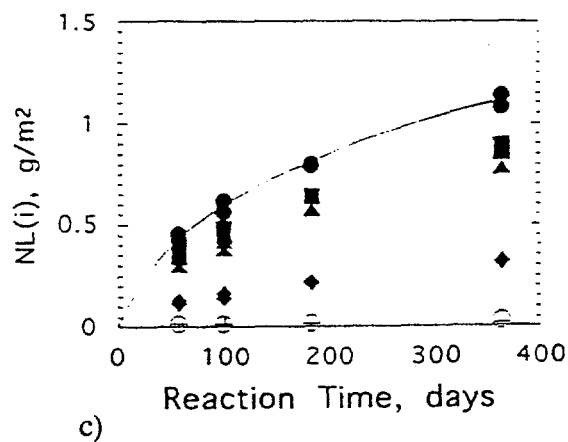


Figure 2. Silica Concentration vs. Time for Tests at (●)  $10\text{ m}^{-1}$ , (■)  $2000\text{ m}^{-1}$ , (◆)  $20,000\text{ m}^{-1}$  with  $-100+200$  mesh, and (◇)  $20,000\text{ m}^{-1}$  with  $-200+325$  mesh glass. The results of duplicate tests are plotted.

Figure 3. Photomicrograph of Sample from Test at 20,000 m<sup>-1</sup> with -100+200 Mesh Glass Reacted 182 days

Clay layer

Unreacted Glass



Precipitated phases

Clay layer

Unreacted Glass



Figure 4. Photomicrograph of Cross-section of Vapor Hydrated WV6 Glass (200°C for 28 days) Showing Alteration of Glass and Secondary Phases

Zeolite

Analcime



Ca-P phases

K-feldspar

Figure 5. Photomicrographs of Secondary Phases Formed on Vapor Hydrated WV6 Glass (200°C for 28 days)