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**FORMULATION OF A CANDIDATE GLASS FOR USE AS
AN ACCEPTANCE TEST STANDARD MATERIAL**

by

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Chemical Technology Division

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FORMULATION OF A CANDIDATE GLASS FOR USE AS AN ACCEPTANCE TEST STANDARD MATERIAL

W. L. Ebert, D. M. Strachan, and S. F. Wolf

ABSTRACT

In this report, we discuss the formulation of a glass that will be used in a laboratory testing program designed to measure the precision of test methods identified in the privatization contracts for the immobilization of Hanford low-activity wastes. Tests will be conducted with that glass to measure the reproducibility of tests and analyses that must be performed by glass producers as a part of the product acceptance procedure. Test results will be used to determine if the contractually required tests and analyses are adequate for evaluating the acceptability of likely immobilized low-activity waste (ILAW) products. They will also be used to evaluate if the glass designed for use in these tests can be used as an analytical standard test material for verifying results reported by vendors for tests with ILAW products. The results of those tests and analyses will be presented in a separate report. The purpose of this report is to document the strategy used to formulate the glass to be used in the testing program. The low-activity waste reference glass LRM that will be used in the testing program was formulated to be compositionally similar to ILAW products to be made with wastes from Hanford. Since the ILAW product compositions have not been disclosed by the vendors participating in the Hanford privatization project, the composition of LRM was formulated based on simulated Hanford waste stream and amounts of added glass forming chemicals typical for vitrified waste forms. The major components are 54 mass % SiO_2 , 20 mass % Na_2O , 10 mass % Al_2O_3 , 8 mass % B_2O_3 , and 1.5 mass % K_2O . Small amounts of other chemicals not present in Hanford wastes were also included in the glass, since they may be included as chemical additives in ILAW products. This was done so that the use of LRM as a composition standard could be evaluated. Radionuclides were not included in LRM because a nonradioactive material was desired. Surrogates for radionuclides were not included because different analytical techniques are used to measure the concentrations of the surrogates and the actual radionuclides, so that the inclusion of surrogates would serve no purpose.

1. INTRODUCTION AND BACKGROUND

The purpose of this report is to document the formulation and composition of the glass that will be used in a testing program to evaluate the adequacy of tests identified for use in the acceptance of immobilized low-activity waste (ILAW) products made with wastes currently stored at the U.S. Department of Energy (DOE) Hanford site. The glass will be evaluated for possible use as an analytical test standard material. The report includes three sections. The first section provides an introduction to the test program in which the glass will be used and the technical need that the testing program will address. In the second section, we report the composition of the glass and discuss the rationale of the formulation, and report the results of scoping tests that were conducted to verify that a homogeneous glass can be made having the formulated composition and determine processing conditions. In the third section, we summarize the results of tests with other glasses having compositions similar to the formulated glass that provided insight into the effects of composition on the glass response in tests similar to those to be conducted in the testing program.

1.1 Technical Need

A testing program has been initiated at Argonne National Laboratory (ANL) to provide a validated test method and a certified standard material that can be used in the acceptance process for ILAW products. The program is being conducted under the auspices of the DOE Tanks Focus Area (TFA), whose mission is to achieve tank waste remediation across the DOE complex. While the immediate application of this work is for Hanford tank wastes, the results are meant to be applicable to the immobilization of waste at other DOE sites as well. Treatment and immobilization of Hanford tank wastes will be performed by private contractors who will be provided wastes by DOE and will return final ILAW products to DOE for storage and disposal [PC-1996a,b]. Waste packages will be subject to DOE inspection to verify that they meet acceptance requirements. The ANL testing program will address the method used to measure the dissolution rate of ILAW products and other test methods that must be conducted by the glass producer for product acceptance. In the Phase I privatization contracts, it is specified that a 7-day test similar to the product consistency test (PCT) [ASTM-1994] that is used for high-level waste forms be conducted at 20°C to measure the average dissolution rate of the waste product, or that the response in a test conducted at a temperature between 20 and 90°C be empirically related to the response at 20°C.

Three issues need to be addressed with regard to the specification in the contracts that the PCT be used for ILAW product acceptance. The first issue arises from the fact that two versions of the PCT exist: PCT Method A and PCT Method B. The PCT Method A is identified for use in the qualification of high-level waste forms. Method A specifies the values of all test parameters and conditions to be used, one specification being that the test must be conducted at $90 \pm 2^\circ\text{C}$. The PCT Method B does not specify values for any of the test parameters, although acceptable ranges are given for some parameters. The values of test parameters such as temperature, size fraction of the crushed sample, leachant solution composition, glass/leachant mass ratio, and test vessel are optional in Method B. While the contracts specify the test temperature and duration, they do not specify the leachant to be used, the glass/leachant mass ratio, or other test variables that significantly affect the test results. Thus, the values of several test parameters must be identified before PCT Method B can be used as an acceptance test for ILAW products.

The second issue is that ILAW products will likely be sufficiently durable that tests conducted at 20°C will generate leachates with low concentrations of dissolved glass components. The PCT requires that analytes used to monitor glass corrosion be present at concentrations that are at least ten times their background concentrations. This criterion may not be met in tests with some waste forms at 20°C. Tests conducted at temperatures greater than 20°C may be required for sufficiently high concentrations of analytes to be generated for accurate analysis. Alternatively, higher solution concentrations can be generated by conducting tests at higher glass/leachant mass ratios or for longer durations.

A third issue is that the PCT Method A used for qualifying high-level radioactive waste glasses only requires that the measured solution concentrations of key glass components be less than the concentrations measured in tests with a benchmark glass, namely, the Environmental Assessment (EA) glass. The contract specifications for ILAW products for Hanford wastes require that the corrosion rate of the product be calculated from the test result for silicon. Thus, the absolute accuracy of the tests applied to ILAW must be verified, while only the relative accuracy of tests applied to products (i.e., relative to tests with the EA glass) must be verified for high-level waste products.

1.2 Technical Approach

To address the issues described above, we have designed a test matrix to measure the precision of test performance and solution analysis for different test conditions for a glass that is similar to the anticipated ILAW products made with Hanford tank wastes. Tests based on the PCT methodology will be conducted to measure the effects of temperature, test duration, and glass/water mass ratio on the mean response and standard deviation of replicate tests. Test parameters will be evaluated on the basis of the measured response and precision obtained under different test conditions and issues related to performance of the test and analyses. Some aspects of the test remain constant in all tests. For example, demineralized water that meets ASTM Type I water requirements, a Type 304L stainless steel vessel, and crushed sample in the size fraction of -100 +200 mesh will be used in all tests. These conditions were selected for consistency between the test used for low-activity waste forms and the PCT Method A that is used for high-level waste glasses.

A glass formulated to be similar in composition to anticipated ILAW products for Hanford tank wastes will be made for use in this test program. (The formulation of that glass is the subject of this report.) It is important that the glass be similar to expected waste forms so that the solution concentrations of dissolved components used to select the test parameters with the test glass are similar to those generated in tests with waste products. The relevance of the test method to the performance of waste products in the disposal site is also enhanced if the test glass and waste products corrode by similar mechanisms under the test conditions. The PCT Method A only provides a measure of the consistency of the waste products. Neither do we claim that the behavior of a waste product in product acceptance test will necessarily be related to its behavior in a disposal system. Likewise, the relevance of the response of a waste form in the PCT Method A to its likely performance in a disposal system has not been determined.

We will evaluate the suitability of the test glass for use as a standard test material with regard to homogeneity, microstructure, and several properties that are identified in the contracts that must be measured for borosilicate waste glasses, such as density, compressive strength, and the leachability index of sodium. While the glass used in these tests is not meant to be a performance standard, we will evaluate its behavior in these tests to further demonstrate that it is representative of possible waste products.

A supply of the standard test material will be procured for use in waste vitrification programs. We will conduct a round robin testing program to measure the interlaboratory reproducibility of tests conducted with the standard test material to establish an acceptable range of responses for the test glass under the selected test conditions. In its capacity as a standard test material, the test glass would be subjected to tests conducted in parallel with tests with the waste product. A measured response of the standard test material within the acceptable range provides added confidence to the results of tests and analyses performed with the waste product.

The purpose of this report is to identify the composition of the glass that will be used in the tests and the rationale for its formulation. We emphasize that the glass developed in this program is intended for use only as a test standard to monitor the execution of tests with waste products and the solution analysis. The response of the test standard in the acceptance test is not meant to be a benchmark for the response of the actual waste product in the test. For ILAW products for Hanford, the required response of the waste product will be determined on the basis of the fractional amounts of key radionuclides that are immobilized. The role of the test standard is to demonstrate that a laboratory can reproduce its response in the test within an acceptable test uncertainty. That uncertainty will be determined by the round robin testing program that will be conducted with the standard material that is procured for use in acceptance testing. Demonstration of acceptable reproducibility in tests with the standard material will lend confidence to the results of tests with the waste product that are conducted at the same time.

2. FORMULATION OF GLASS COMPOSITION FOR TEST STANDARD

Formulation of the composition of the glass to be tested in this program was based on anticipated compositions of ILAW products for Hanford and other DOE low-activity waste (LAW) streams, available test results for relevant glass compositions, and discussions with personnel familiar with glass formulations for LAW from Hanford and elsewhere. A workshop was held in the TFA offices in Richland, WA, on May 14, 1997, to discuss the desired use of the test and standard materials in the privatization efforts, possible leveraging of work in this program for other DOE needs at Hanford and other sites, and "lessons learned" from other programs regarding the effects of glass composition on glass corrosion behavior.

Formulation of the glass composition for use in these tests and as a possible standard material was based largely on the anticipated compositions of ILAW forms for Hanford tank wastes. Because Contractors have not formally submitted target product compositions to DOE for approval, we have based our formulation on simulations of a representative waste stream for Hanford tanks and glasses used previously to study the immobilization that waste stream by vitrification [DARAB-1996].

2.1 Hanford Low-Activity Waste Stream

Glasses that have been developed and studied for vitrification of Hanford LAW differ from high-level waste glasses primarily in their high Na_2O content and the lower concentrations of transition metals. The chemistry of the LAW stream expected to be generated during remediation of Hanford tank wastes will be dominated by sodium (about 10 M Na) and will contain only small amounts of iron, which is a major constituent in high-level wastes. Table 1 lists the concentrations of components in a Hanford double-shell simulated feed (DSSF) that has been used during the development of glass compositions [DARAB-1996]. Other key components besides sodium in the waste stream include $\text{Al}(\text{OH})_4^-$, K^+ , F^- , and Cl^- , which are present in the DSSF at concentrations of 1.0, 0.5, 0.25, and 0.16 M , respectively. The desired waste loading will require the ILAW forms to contain about 20 mass % Na_2O . The DSSF was formulated so that the concentrations of some minor components are significantly higher than those anticipated in the waste streams or those that will be allowed in the ILAW products. This was done, in part, to facilitate detection of those components in laboratory tests.

2.2 Formulation of Glass for Testing and Analysis

The glass composition formulated for use in this testing program is listed in Table 2 on an oxide basis. The glass is referred to as the low-activity waste reference material, or LRM. Brief comments regarding each component are included in Table 2. The contents of key components are discussed in more detail later in this report. A large amount of LRM glass will be made for testing and analysis from a mixture of dried reagent grade oxides, carbonates, chlorides, fluorides, iodates, and sulfates. The target composition for batching the reagents is listed in Table 3. The actual composition of the glass made for testing will be determined by chemical analysis. We anticipate that the concentrations of some components may be less than their target values due to volatility. For example, the concentrations of mercury and iodine are expected to be significantly lower than the as-batched concentrations. Some of the chloride, fluoride, and sulfur may also be lost to volatilization. These elements were included to take into account their possible effect on the vitrification of other components and the homogeneity of the resulting glass.

The composition of LRM glass was formulated to (1) be relevant to the anticipated ILAW produced during the remediation of Hanford tanks, (2) be relevant to ILAW products for other DOE sites, and (3) include glass-making components that may be used in ILAW products. The third criterion was included because it was desired that the test standard also serve as a composition standard for waste products. Some components that are present in trace quantities in Hanford wastes were included in the LRM at higher concentrations than what is anticipated for ILAW products to facilitate their analysis for evaluation of LRM as a composition standard. These components include Ba, Cd, Fe, Mn, Mo, Ni, and Pb. Small amounts of Ca, Fe, Mg, Ti, and Zr were included because they may be present as added chemicals in pretreatment steps or ILAW formulations. The concentrations of these components are high enough that they can be analyzed reliably if LRM glass is used as a composition standard, but low enough that the glass composition and response of the glass in the acceptance test remain similar to ILAW products for Hanford tank wastes. The addition of Fe and Zr is expected to improve the durability of the glass slightly [ELLISON-1994]. The addition of Ca and perhaps also Mg is expected to degrade the long-term durability of the glass.

The concentrations of Cl, F, K, and Na were selected to match waste loading requirements. Slightly higher amounts of Cl and F were added to account for partial volatilization during melting. (We recognize that the extent of volatilization in the crucible melts that will be used to prepare LRM for testing may differ from that in melters used for waste vitrification.) All of the B and Si and about one-half of the Al represent chemicals added to the waste to make a glass. The amounts of glass formers added to LRM glass are typical of those used previously in Hanford glasses [FENG-1995].

Also included in the glass formulation were Ba, Cd, Cr, Hg, and Pb, which are regulated under the Resource Conservation and Recovery Act (RCRA) as toxicity characteristic constituents. These are included in LRM glass to facilitate use of the glass as a composition standard and demonstration that the glass is not hazardous per the Toxicity Characteristic Leaching Procedure (TCLP).

Neither radionuclides nor surrogates for radionuclides were included in the LRM glass. A glass with nonradioactive surrogates is not a useful composition standard for radioactive glasses because different analytical techniques will be used for the radionuclides than will be used for the other components. A standard containing the actual radionuclides of interest is needed to verify the results of analyses of ILAW products that are required to show that radionuclide limits for Class C waste are met. A radioactive composition standard may be developed at a later time. The presence of radionuclides in the actual ILAW products is not expected to affect the chemical durability of the glass due to structural, chemical, or radiolytic effects.

2.3 Scoping Tests with Low-Activity Reference Material

Scoping tests were conducted to verify that homogeneous batches of glass could be prepared with the composition in Table 2 and to determine the temperature at which the glass will be melted. Two batches of glass were prepared by the following procedure. Reagent chemicals were manually ground under acetone with a mortar and pestle, dried in an oven, and then ground again. Aliquots of about 10-30 g of the batched chemicals were placed in platinum crucibles and heated to various temperatures between 1100°C and 1350°C. The mixtures were heated slowly to facilitate outgassing. The melts were held at the maximum temperature for about 2 h. The melts were briefly swirled while at the melting temperature to facilitate mixing of the melt in the crucible. The viscosity of each melt was visually assessed by tilting the crucible immediately after removing it from the oven. The glasses were quenched in the crucibles by placing the bottom of the crucibles in

a water bath. The cooled glass was then knocked out of the crucible and visually inspected. Samples of some of the product glasses were examined with a scanning electron microscope to characterize the homogeneity of the glass. Small amounts of some glasses were dissolved and chemically analyzed. One sample that had been melted at 1150°C and then quenched to room temperature was remelted at 1150°C for 2 h to determine if remelting affected the composition. Analyses showed that

- Precipitated phases did not form within the glass;
- The glass was physically and chemically homogeneous;
- All the mercury and most of the iodine were volatilized from all melts; and
- Glass viscosity increased with increased time of heating, probably due to the loss of volatiles.

The loss of some components by volatilization can be taken into account by adding excess material to the mixture that is melted and by melting at the lowest possible temperature for the shortest duration that will provide a homogeneous glass. However, the loss of volatile components from the glass will not affect use of the glass to determine the test conditions for the acceptance test or the test standard glass. Therefore, efforts to retain mercury and iodine will not be pursued when making glass for testing and analysis.

Based on the results of these scoping tests, LRM glass will be prepared for use in the testing and analysis program by the following method. Glass will be made by melting reagent chemicals in a platinum/rhodium crucible in a laboratory furnace at 1250°C. Chemicals will be combined manually in the proportions given in Table 3 to provide a large supply of stock mixture that will be used to make several batches of precursor glass. Those batches of precursor glass will be crushed, manually mixed, and then remelted to make the glass for testing. Some of the glass made in the second melting will be annealed and used to prepare monolithic samples for testing with the American Nuclear Society ANS 16.1 and vapor hydration test procedures. The compressive strength and density of the annealed glass will also be measured. The rest of the glass made in the second melting will be crushed, mixed, and sieved for use in the PCT-type tests and TCLPs. Samples of the annealed glass and glass that was not annealed will be analyzed with a scanning electron microscope to ensure that the annealing step did not affect the microstructure. Samples of the glass that was not annealed will be dissolved and compositionally analyzed, since this glass is used in tests to measure the durability.

3. SUMMARY OF TESTS WITH OTHER RELEVANT GLASSES

In this chapter, we summarize the results of tests with other glasses relevant to ILAW products for Hanford wastes. The results of those tests provided valuable insight into the effect of the composition of a glass on its dissolution rate that was used in formulating LRM glass. Results of tests conducted with some of these glasses are summarized here. Because the amount of sodium that can be immobilized will probably limit the waste loading in ILAW products for Hanford wastes, glasses have been formulated and studied to understand the impact of high Na₂O contents on glass corrosion behavior.

3.1 Glasses for Hanford Low-Activity Waste

A suite of glasses was formulated at Pacific Northwest National Laboratory (PNNL) to study the immobilization of the DSSF simulated waste stream for Hanford LAW. Several glasses were formulated to contain 20 mass % soda, which was assumed to represent the required waste loading. The glass composition designated LD6-5412 has probably been used in more tests than any other LAW glass. Its composition, which is given in Table 4, simulates the mixing of 26.7 mass % DSSF and 73.3 mass % chemical additives. The LD6-5412 glass contains a significant amount of added Al, in addition to the Al present in the waste stream, and added Ca. It also includes added B and Si as glass formers.

The compositions of LD6-5412 as well as three other PNNL glasses are listed in Table 5. These glasses were formulated to study the effects of the Al, B, Ca, and Si contents on several properties of the glass melt and the glass. The composition of the EA glass, which is used as a benchmark for high-level radioactive waste glasses, is included for comparison. The EA glass contains less Na₂O than the glasses for LAW, but the total alkali oxide contents are about 22 mass % for all glasses. The EA glass has much less Al₂O₃ and more Fe₂O₃ than the LAW glasses; it also contains several components that are not contained in the LAW glasses, including La₂O₃, Li₂O, TiO₂, and ZrO₂.

The results of tests conducted with LD4-9012, LD6-5412, and EA glasses provide insight into the corrosion behavior of glasses with high soda contents. The average results of 28-day MCC-1 tests and of 7-day PCTs conducted at 90°C with these three glasses in terms of the normalized mass losses based on B, Na, and Si are summarized in Table 6. The normalized mass loss (NL) values give the mass of glass that dissolved based on the measured solution concentrations of a given glass component. The NL values based on element *i* that are given in Table 6 were calculated by the equation

$$NL(i) = [i] / [(S/V) \cdot f_i] \quad (1)$$

where $[i]$ is the concentration of *i* in solution, in g/L (less the background concentration), S/V is the glass surface area/solution volume ratio, in m⁻¹, and f_i is the mass fraction of elemental *i* in the glass. The LD6-5412 glass is found to be more reactive than the LD4-9012 glass in the MCC-1 tests, but less reactive in the PCTs, based on NL(B) and NL(Si). Both glasses are about 20 times less reactive than the EA glass in the PCTs. The MCC-1 tests provide a better measure of the intrinsic durability of the glass than the PCTs because the influence of the solution chemistry on the glass dissolution rate is much less in the MCC-1 tests than in the PCTs. The results in Table 6 indicate that LD6-5412 glass is intrinsically more reactive than LD4-9012 glass, but that the dissolution of LD6-5412 glass is more sensitive to changes in the solution chemistry than is LD4-9012 glass; that is, the buildup of dissolved glass components has a greater effect on the dissolution of LD6-5412 glass.

3.2 Product Consistency Tests with Glasses Having Various Soda Contents

A series of tests with borosilicate glasses having soda contents between 14 and 25 mass % was conducted to determine if a PCT-based test could be used as an acceptance test for vitrified LAW waste forms and to assess how the soda content affected the dissolution rate. A modified PCT procedure was used to maintain more dilute solutions than the standard PCT in some tests. Tests were conducted with demineralized water and crushed glass within the -100 +200 mesh size fraction (75-150 μm) at glass/water mass ratios of 0.3:15, 0.75:15, and 1.50:15. These mass ratios yield S/V ratios of about 400, 1000, and 2000 m^{-1} , respectively. Tests were conducted to determine the effects of temperature (20 and 40°C) and the reaction time (1, 3, and 7 days) on the measured corrosion rate.

The six alkali borosilicate glasses that were tested at ANL included the standard glass SRM 662 and five glasses developed at PNNL (Table 7). The various glasses contained between about 14 and 25 wt % Na_2O . The SSHTM-3 glass was prepared using the LD6-5412 formulation as a basis. Tests were conducted at all three S/V ratios for 3 and 7 days at 20 and 40°C and, in addition, for 1 day at 20°C and $\text{S/V} = 400 \text{ m}^{-1}$. Tests with L8-3 and SSHTM glasses were also conducted for 1 day at 20 and 40°C and for 7 days at 20°C using a pH 12 buffer solution instead of demineralized water; those tests were conducted to characterize the effect of high pH values on the corrosion rate without the buildup of glass corrosion products that occurs after longer reaction times. The leachate solutions were analyzed for B, Na, and Si. Blank tests were also conducted with demineralized water and the pH 12 solution. These showed the background concentrations of all monitored components to be negligible compared to the measured concentrations. The normalized glass dissolution rate based on element i is calculated as:

$$\text{NR}(i) = [i] / [(S/V) \cdot f_i \cdot t] \quad (2)$$

where t is the reaction time in days. The rate has units of $\text{g}/(\text{m}^2 \cdot \text{d})$.

The normalized mass losses and dissolution rates for the PCT tests with LD6-5412 glass SSHTM-3 are summarized in Tables 8 and 9. The mass fractions of Na, Si, and B calculated from the compositions are also included in Table 8. The results indicate that dissolution of the glass is nonstoichiometric in all tests in demineralized water, with Na being released between about 2 and 10 times faster than B and Si, respectively, depending on the test conditions. However, the dissolution rates based on B, Na, and Si are nearly equal in tests conducted in the pH 12 solution.

Results for tests conducted at a glass/water mass ratio of 1:10 are plotted in Fig. 1 as the normalized mass loss based on the silicon concentration in solution against the mass % Na_2O in the glass. There is a general increase in the values of $\text{NL}(\text{Si})$ with increasing soda content for tests conducted under the same conditions. However, the SRM 622 glass does not follow this trend, probably because of differences in two important components: the SRM 622 does not contain boron and has a much higher calcium content than the other glasses. Boron stabilizes some of the sodium in the glass, and the high calcium content may have adversely affected the durability of the glass [ELLISON-1994].

For waste forms having a particular geometry and technetium content, calculations indicate that an average glass dissolution rate of less than $1 \times 10^{-3} \text{ g}/(\text{m}^2 \cdot \text{d})$ at about 20°C was needed to meet containment requirements for Hanford ILAW. This requirement has been included in the Hanford Privatization Contracts [PC-1996]; the value of $\text{NL}(\text{Si})$ in a 7-day test is to be used to calculate the rate. From the results shown in Fig. 1, the rates measured in 7-day tests at 20°C with L7-15, LD4-9012, and L8-3 glasses are at or slightly

below that level. The rates measured in tests with other glasses, including SSHTM-3 glass, were greater than $1 \times 10^{-3} \text{ g}/(\text{m}^2 \cdot \text{d})$. None of the glasses had dissolution rates below $1 \times 10^{-3} \text{ g}/(\text{m}^2 \cdot \text{d})$ in 3-day tests. In addition to the average dissolution rate decreasing with increasing test duration, after a specific reaction time, the rate increases as the S/V ratio decreases and as the pH increases.

3.3 Vapor Hydration Tests with Different Glasses Having the Same Soda Content

Vapor hydration tests (VHTs) were conducted as screening tests to measure the tendencies of several glasses to form alteration phases and the effects of phase formation on the glass dissolution rate. These test results are included in this report because they demonstrate the possible detrimental effect of calcium on glass durability. The VHT is conducted by sealing a monolithic sample with a small amount of water in a vessel and heating the vessel to a high temperature, during which the sample is exposed to saturated water vapor. Corrosion occurs in a thin film of water that condenses on the sample. This film becomes saturated after very little glass has dissolved, and alteration phases nucleate on the glass surface. At the end of the test, the alteration phases can be examined while still attached to the monolith (e.g., with optical and scanning electron microscopy) or removed for analysis (e.g., with analytical transmission electron microscopy, X-ray diffraction, dissolution for chemical analysis).

All of the glasses tested contained 20 mass % Na_2O . Tests were conducted at 150°C for 7, 14, and 28 days. The primary differences in the compositions were the amounts of B_2O_3 , CaO , and Al_2O_3 , as shown in Table 10. The test results are also given in Table 10 in terms of the thickness of the crust of alteration phases on the outer surface and whether or not zeolite alteration phases and a calcium-bearing phase or phases formed. The results indicate two responses in the tests. Glasses that do not contain CaO and have at least 6 mass % B_2O_3 are not corroded in the VHTs. Glasses that do contain Ca and have less than 6 mass % B_2O_3 are highly corroded in the VHTs; most are completely altered within 28 days. These results are interesting in that neither Ca nor B is incorporated into the zeolites, which are assumed to be the phases that lead to the increase in the reaction in Stage III. Variations in the amounts of Na , Al , and Si in the glasses had no obvious effect on the formation of the zeolites.

3.4 Replicate PCTs with SSHTM-3 Glass

We have conducted replicate 7-day PCT-type dissolution tests with SSHTM-3 glass at 20 and 40°C to measure the reproducibility of the test method. These tests were conducted to determine the uncertainty range associated with the PCT-type tests at low temperatures, and can be viewed as scoping tests for the product acceptance test under development. The tests were conducted with -100 +200 mesh crushed glass and demineralized water in Teflon test vessels. The crushed glass was either washed following the PCT procedure to remove fines or left unwashed. Nine tests were conducted at 20 and 40°C each with washed glass, and two tests were conducted at each temperature with unwashed glass. One aspect that these tests address is the relative importance of the individual masses of glass and water used in the test and their mass ratio. Most of the tests were conducted with between 0.91 and 0.96 g of crushed glass. All tests were conducted with an amount of demineralized water that was exactly 10 times the mass of glass (to the nearest 0.01 g), so all tests had the same glass/water mass ratio of 1:10. The test solutions were analyzed for pH and Al , B , Na , and Si concentrations. Each solution was analyzed for pH once. Analyses were performed with inductively coupled plasma mass spectrometry (ICP-MS) on three separate days to measure the reproducibility of both the test execution and the solution analysis. That is, the mean and variation of the solution

concentrations of replicate tests were determined from the results of analyses conducted on one day and compared to the means measured on two other days. This method allowed us to distinguish the reproducibility of the test execution from the reproducibility of the solution analysis by evaluating the within-day variability and between-day variability.

The complete test results for the replicate tests are summarized in Table 11. The results indicate that dissolution of fines in tests with unwashed glass increases the concentrations of soluble components relative to tests with washed glass by about four times at 20°C and about three times at 40°C. The effect of fines is smaller in tests at higher temperature because the fines represent a smaller fraction of the total volume of glass that reacts in a test; that is, glass fines provide a very high surface area but little volume. Therefore, the relative effect of the dissolution of fines will decrease significantly as more glass dissolves. Although only two tests were conducted at each temperature with unwashed glass, the difference in the replicate tests is similar to that measured in the nine tests with the washed glass. This finding indicates that similar amounts of fines were present in both of the tests with unwashed glass. Only tests with washed glass are considered further in this report.

Figures 2a and b show the measured concentrations of B, Na, and Si as functions of the mass of glass in tests with washed glass conducted at 20 and 40°C, respectively. The results of the first analyses with ICP-MS are plotted. The variation in the concentration with the mass of glass used was similar in subsequent ICP-MS analyses, although the measured concentrations differed slightly, as discussed below. These data were assessed to determine if the specific masses of glass and water used in a test affect the final solution concentrations, or if only the glass:water mass ratio is important. As can be seen in Figs. 2a and b, the concentrations are not correlated with the amount of glass in the tests conducted at either temperature. Therefore, the measured solution concentrations were used directly to determine the reproducibility of the test. Note in Fig. 2a that the B and Si concentrations measured in two tests conducted at 20°C with 0.92 g glass differed slightly, but that the Na concentrations were the same in both tests. Likewise, the B and Si concentrations in the tests conducted at 40°C with 0.93 g glass differed more than the Na concentration. These differences reflect the greater uncertainty in the analyses of the B and Si concentrations compared to the Na concentration. The B values have greater uncertainty because of the lower absolute concentrations, and the Si values have greater uncertainty because of isobaric interference in the ICP-MS analysis.

The averages of the B, Na, and Si concentrations of replicate 7-day tests are summarized in Table 12. For each set of tests, the mean, standard deviation (s.d.), and percent relative standard deviation (rsd) for the analysis of B, Na, and Si are given for the analyses conducted on three different days. The values in the rows labeled 1, 2, and 3 are for the nine replicate tests analyzed on separate days. The overall mean, standard deviation, and percent relative standard deviation of the three analyses of solutions from the replicate tests are given in the rows labeled "avg." These results show that, based on the percent relative standard deviation values, the uncertainty in the measured Si concentration is significantly higher than the uncertainties in the measured B and Na concentrations at both temperatures. Based on the variation in the ICP-MS results of replicate analyses of the same solutions, the day on which the ICP-MS analyses were performed appears to have a significant effect on the measured concentrations and test precision in tests at 20°C, but not in tests at 40°C. For tests at 40°C, the percent relative standard deviation for each set of ICP-MS analysis of nine replicate tests is not significantly different from the overall percent relative standard deviation of all 27 analyses.

This method of replicate tests and analyses will be used in the evaluation of the effects of test parameter values on the response of LRM glass. A detailed statistical

evaluation of the analytical results will be performed with that data to determine if the analytical uncertainties are statistically significant.

The normalized mass losses and normalized dissolution rates were calculated by using the overall average concentrations and assuming an S/V ratio of 2000 m^{-1} . The S/V ratio was estimated on the basis of the sieve size fraction and the density of the glass, which is about 2500 kg/m^3 . The results are summarized in Table 13. The preferential release of sodium observed in these tests is known to persist through at least two years at both temperatures [BAKEL-1995].

In conclusion, the results of replicate 7-day tests at 20°C and at 40°C show that the test reproducibility is within the analytical uncertainty of the ICP-MS analysis. Washing the glass has a significant effect on the test results, and this effect is more significant at 20°C than at 40°C . The dissolution rate calculated for tests with unwashed glass is about four times as high as that calculated for tests with washed glass. The dissolution rates at 40°C are about twice those at 20°C . The effect of temperature on the dissolution rate in these tests is less than that in MCC-1 tests. This is probably because the effect that the buildup of silicic acid has on the rate is greater in tests conducted at 40°C than in tests at 20°C . The test precision is greater at 40°C than at 20°C , probably due to the higher concentrations and the smaller influence of the particle shapes and fines in tests at 40°C . The uncertainty in the reproducibility due to test execution is less than the analytical uncertainty at both temperatures.

3.5 Other Laboratory Tests Conducted with LD6-5412 Glass

During the last four years, the LD6-5412 glass has been subjected to different test methods to study its corrosion mechanism and to measure the kinetics of its dissolution under conditions relevant to near-surface disposal. This glass was selected for detailed testing because its performance in short-term tests, such as the 28-day MCC-1 and 7-day PCT (both at 90°C), was representative of a large number of LAW glass formulations. Summaries of the test methods and the results are given below.

3.5.1 Single-Pass Flow Through (SPFT) Tests

Single-pass flow-through (SPFT) tests with LD6-5412 glass were conducted at PNNL to measure the effect of temperature, pH, and flow on the dissolution rate. Some SPFT tests were also conducted at ANL. Test conditions are such that these tests measure the rate in Stage I, in which dissolved glass components do not significantly affect the dissolution rate. Tests were conducted at 20, 40, 70, and 90°C in solutions having pH values between about 6 and 12 [McGRAIL-1997a]. The results of these tests indicate that the intrinsic dissolution rate of the glass has pH and temperature dependencies that are similar to those measured for other alkali borosilicate glasses. The rate increases with increasing pH by a factor of $10^{0.4 \cdot \text{pH}}$ and increases with temperature following Arrhenius behavior, with an activation energy of about 78 kJ/mol. The measured rate increases slightly with the solution flow rate. This effect occurs because the steady-state concentrations of glass components that affect the dissolution rate, such as $\text{SiO}_2(\text{aq})$, decrease as the flow rate increases.

3.5.2 Materials Characterization Center MCC-1 Tests

Workers at ANL conducted MCC-1 tests with LD6-5412 glass at 20, 40, and 90°C . These tests reveal the corrosion behavior in Stages I and II. The solution concentrations that are attained in short-term tests at low temperatures (e.g., 7 days at 40°C) are low

enough that they do not affect the dissolution rate, but the solution concentrations in tests at higher temperatures conducted for longer time periods (e.g., 14 days at 90°C) measurably affect the rate. The results of these tests are useful for verifying that the steady-state solutions attained in SPFT tests are not affecting the dissolution rate. Comparison of the MCC-1 and SPFT results indicates that the steady-state solution concentrations of silicon in tests conducted at 20, 40, and 70°C do not affect the dissolution rate significantly, but the concentrations in tests at 90°C may have a slight effect. Another key finding of the MCC-1 tests is that the release of boron is congruent with the release of sodium, and both are released faster than silicon. This finding indicates that, under these test conditions, ion exchange reactions to release sodium and hydrolysis reactions to release boron occur at nearly the same rate, and both occur faster than the hydrolysis reactions to release silicon. In contrast, the results of PCTs show that the release of B is slowed more than the release of Na as the solution becomes more concentrated, so the release of B and Na becomes nonstoichiometric as corrosion proceeds.

3.5.3 Long-Term Product Consistency Tests

A large number of PCTs with LD6-5412 glass were conducted at ANL at temperatures of 20, 40, 70, and 90°C for durations between 28 days and 2.5 years. Tests were conducted at glass/water mass ratios of 1:1 and 1:10. Depending on the temperature and duration, these tests reveal the corrosion behavior in Stages II or III. Tests at 20 and 40°C have not progressed to Stage III after about 2.5 years. The dissolution rates at both temperatures are extremely low. The solution concentrations in tests at a glass/water mass ratio of 1:1 conducted at 70 and 90°C have caused the reactions to enter Stage III after about 400 and 100 days, respectively. A significant increase in the glass dissolution rate occurred after the formation of phases that are compositionally and structurally very similar to analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) and gobbinsite ($\text{Na}_5\text{Al}_5\text{Si}_{11}\text{O}_{32} \cdot 11\text{H}_2\text{O}$). The dissolution rate at 90°C increased by about 1000 times in passing from Stage II to Stage III. The rate was measured to be $>0.5 \text{ g}/(\text{m}^2 \cdot \text{d})$ in Stage III. (Only a lower limit could be determined because it was uncertain exactly when the phases formed or when the glass was completely altered.) The measured pH remained at about 12 in both stages.

3.5.4 Vapor Hydration Tests

Vapor hydration tests were conducted with LD6-5412 glass at ANL at temperatures of 70, 120, 150, 175, and 200°C. The VHT was developed to promote the formation of alteration phases and access to Stage III. Analcime, gobbinsite, and a calcium-bearing phase formed in tests conducted at 150, 175, and 200°C within a few days and in tests conducted at 120°C after about 142 days. The rate at which the glass converted to alteration phases was measured by the thickness of the crust of alteration phases that formed on the surface of the glass. The corrosion rate as a function of temperature showed Arrhenius behavior and had an effective activation energy of about 81 kJ/mol, which is in excellent agreement with that measured in the SPFT tests. This agreement suggests that the same rate-limiting step controls dissolution in SPFT tests and alteration in VHTs. Extrapolation of the corrosion rate to 90°C gave a value of about $2 \text{ g}/(\text{m}^2 \cdot \text{d})$. This value is consistent with the rate of $>0.5 \text{ g}/(\text{m}^2 \cdot \text{d})$ measured with the PCTs at 90°C.

3.5.5 Accelerated Dissolution Tests

Determination of the dissolution rate in Stage III with the PCTs and VHTs is limited by the uncertainty of when the alteration phases form and Stage III begins, and also of when the glass is completely altered. Those tests only provide a lower bound to the rate. The accelerated dissolution test (ADT) was developed at ANL to measure the dissolution rate in Stage III without the uncertainty of when the alteration phases form. The test is

conducted by placing a fresh sample, a vapor-hydrated sample containing alteration phases, and a pre-saturated leachate solution in a vessel and tracking the mass loss of the fresh sample as it dissolves. The test results available to date indicate that an incubation period occurs before the glass dissolves at the Stage III rate. The delay may be due to the need for the system to equilibrate. The dissolution rate measured in replicate ADTs for LD6-5412 at 90°C and pH 12 is about 1.8 g/(m²•d). This rate is in excellent agreement with the Stage I rate estimated from the SPFT test results. This value indicates that the formation of alteration phases overcomes the effects of the dissolved glass components such that the dissolution rate in Stage III becomes similar to the rate in Stage I.

3.5.6 Pressurized Unsaturated Flow Tests

A new test apparatus is being developed at PNNL to measure the changes in the hydraulics of an unsaturated system as a glass corrodes. Basically, a column is packed with crushed glass, and water is forced through the column by a constant head pressure to attain a very low flow rate. In these pressurized unsaturated flow (PUF) tests, the mass of the column is measured to track the amount of water in the column, and the conductivity and pH of the effluent are measured continuously to track the reaction. The effluent is collected and chemically analyzed periodically. It was found in scoping tests conducted with LD6-5412 glass that the column became completely plugged after only a few weeks due to the formation of alteration phases [McGRAIL-1996]. Analysis of the solids in the column with X-ray diffraction revealed that zeolites similar to those formed in PCTs and VHTs had formed. The assemblage of phases formed in static tests and the PUF tests differ slightly because a lower solution pH is maintained in the PUF test than in the PCTs and VHTs due to solution flow. This test confirms that the behavior observed in PCTs and VHTs also occurs in a dynamic system.

4. SUMMARY

A glass has been formulated for use in a testing program to provide a data base for selection of test parameters for an acceptance test. The glass will also be evaluated as a possible reference material to monitor the execution of the acceptance test at different laboratories. The glass was formulated to be compositionally representative of anticipated waste forms for Hanford LAW. It also contains small amounts of other components that may be present in other DOE waste streams or added to the waste form. Formulation of the glass was based also on insight from tests conducted with glasses that were formulated previously for Hanford wastes.

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6. REFERENCES

ANDREWS-1993

M. K. Andrews and N. E. Bibler, "Radioactive Demonstration of DWPF Product Control Strategy," *Ceram. Trans., Environmental and Waste Management Issues in the Ceramics Industry* 39, 205-221 (1993).

ASTM-1994

Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT), Standard C1285-94, American Society for Testing and Materials, Philadelphia, PA.

BAKEL-1995

A. J. Bakel, W. L. Ebert, and J. S. Luo, "Long-Term Performance of Glasses for Hanford Low-Level Waste," *Ceram. Trans., Environmental and Waste Management Issues in the Ceramics Industry* 61, 515-522 (1995).

CUNNANE-1994

J. C. Cunnane (ed.) J. K. Bates, C. R. Bradley, E. C. Buck, J. C. Cunnane, W. L. Ebert, X. Feng, J. J. Mazer, D. J. Wronkiewicz, J. Sproull, W. L. Bourcier, B. P. McGrail, and M. K. Altenhofen, *High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics*, U. S. Department of Energy Office of Waste Management Report DOE-EM-0177 (1994).

DARAB-1996

J. G. Darab and P. A. Smith, "Chemistry of Technetium and Rhenium Species during Low-Level Radioactive Waste Vitrification," *Chem. Mater.* 8(5), 1004-1021 (1996).

ELLISON-1994

A. J. G. Ellison, J. J. Mazer, and W. L. Ebert, *The Effects of Composition on the Corrosion Behavior of High-Level Waste Glasses: A Critical Review*, Argonne National Laboratory Report ANL-94/28 (1994).

FENG-1995

X. Feng, P. R. Hrma, J. H. Westsik, Jr., M. J. Schweiger, H. Li, J. D. Vienna, G. Chen, G. F. Piepel, D. K. Peeler, D. E. Smith, B. P. McGrail, S. E. Palmer, D. Kim, Y. Peng, W. K. Hahn, A. J. Bakel, and W. L. Ebert, *Glass Optimization for Vitrification of Hanford Site Low-Level Tank Waste*, Pacific Northwest Laboratory Report PCTD-T3B-95-208 (1995).

HRMA-1994

P. R. Hrma, G. F. Piepel, et al. *Property/Composition Relationships for Hanford High-Level Waste Glasses Melting at 1150°C*, Pacific Northwest Laboratory Report PNL-10359 (1994).

KIM-1994

D. Kim, Pacific Northwest National Laboratory, personal communication, May 16, 1994.

McGRAIL-1995

B. P. McGrail and D. K. Peeler, *Evaluation of the Single-Pass Flow-Through Test to Support a Low-Activity Waste Specification*, Pacific Northwest Laboratory Report PNL-10746 (1995).

McGRAIL-1997a

B. P. McGrail, W. L. Ebert, A. J. Bakel, and D. K. Peeler, "Measurement of Kinetic Rate Law Parameters on a Na-Ca-Al Borosilicate Glass for Low-Activity Waste," *J. Nucl. Mater.* 249, 175-189 (1997).

McGRAIL-1997b

B. P. McGrail, C. W. Lindenmeier, P. F. Martin, and G. W. Gee, "The Pressurized Unsaturated Flow (PUF) Test: A New Method for Engineered-Barrier Materials Evaluation," *Ceramic Trans., Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries II* 72, 271-278 (1997).

McGRAIL-1997c

B. P. McGrail, P. F. Martin, and C. W. Lindenmeier, "Accelerated Testing of Waste Forms Using a Novel Pressurized Unsaturated Flow (PUF) Method," *Mater. Res. Soc. Symp. Proc.* 465, 253-260 (1997).

PC-1996a

U.S. Department of Energy, Tank Waste Remediation System (TWRS) Privatization Contract No. DE-AC06-RL13308 with BNFL, Inc. (1996).

PC-1996b

U.S. Department of Energy, Tank Waste Remediation System (TWRS) Privatization Contract No. DE-AC06-RL 13309 with Lockheed Martin Advanced Environmental Systems (1996).

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Table 1. Composition of Double-Shell Simulated Feed (DSSF),
from [DARAB-1996]

Species	Conc., <u>M</u>	Species	Conc., <u>M</u>
Al(OH)_4^-	1.0	Mg^{2+}	0.0010
Ca^{2+}	0.001	Mn^{2+}	0.00042
Cl^-	0.16	Mo(OH)_4^-	0.017 ^a
Cr(OH)_4^-	0.0087	Na^+	10.0
Cs^+	0.017 ^a	PO_4^{3-}	0.043
F^-	0.25	SO_4^{2-}	0.043
Fe^{3+}	0.00077	$^{90}\text{Sr}^{2+}$	0.017 ^a
I^-	0.017 ^a	$^{99}\text{TcO}_4^-$	0.017 ^a
K^+	0.5		

^aConcentration is higher than anticipated in ILAW products.

Table 2. Formulated Composition of LRM Glass on an Oxide Mass Percent Basis

Chemical	LRM, mass %	Comment
Al ₂ O ₃	10	Amount common to Hanford glasses studied previously; half from waste, half as added chemical
B ₂ O ₃	8	Added chemical, high content facilitates melting
BaO	0.005	Added as RCRA-regulated component
CaO	0.5	Higher than anticipated from waste; may be used as additive in some waste forms, although Ca has been observed to decrease long-term durability
CdO	0.2	Added as RCRA-regulated component
Cl	0.8	Twice the anticipated level for desired waste loading expect 50 % loss to volatilization
Cr ₂ O ₃	0.2	Near solubility limit in borosilicate glasses
F	1	Twice the anticipated for desired waste loading; expect 50 % loss to volatilization; added amount is near solubility limit of F in borosilicate glasses
Fe ₂ O ₃	1	Only trace amounts expected in waste stream; may be additive in pretreatment or ILAW products
HgO	0.002	Expected to be completely volatilized during vitrification
I	0.002	Expected to be completely volatilized during vitrification
K ₂ O	1.5	Anticipated for desired waste loading
La ₂ O ₃	0.009	Added for use as composition standard
Li ₂ O	0.1	Added for use as composition standard; may be additive in ILAW products
MgO	0.1	Higher than expected in waste forms to facilitate analysis; may be additive in ILAW products
MnO	0.1	Added for use as composition standard
MoO ₃	0.1	Added for use as composition standard
Na ₂ O	20	Target for desired waste loading
NiO	0.1	Added for use as composition standard
P ₂ O ₅	0.5	Near solubility limit in borosilicate glasses
PbO ₂	0.1	Added as RCRA-regulated component
SO ₃	0.2	Target for desired waste loading; expected to be partially volatilized during vitrification
SiO ₂	54.37	Typical concentration for waste ILAW glasses
TiO ₂	0.1	May be additive in ILAW products
ZrO ₂	1	May be additive in ILAW products

Table 3. Target Mixture of Chemical Reagents

Chemical	mass %	Chemical	mass %
Al ₂ O ₃	10.00	Li ₂ CO ₃	0.25
B ₂ O ₃	8.00	MgO	0.10
BaO	0.005	MnO	0.10
CaO	0.50	MoO ₃	0.10
CdO	0.20	Na ₂ CO ₃	29.95
NaCl	1.31	NiO	0.10
Cr ₂ O ₃	0.20	P ₂ O ₅	0.50
NaF	2.21	PbO ₂	0.10
Fe ₂ O ₃	1.00	Na ₂ SO ₄	0.35
HgCl ₂	0.0022	SiO ₂	54.37
KI	0.0026	TiO ₂	0.10
K ₂ CO ₃	1.50	ZrO ₂	1.00
La ₂ O ₃	0.009		

Table 4. Composition of LD6-5412 Glass, mass %, on oxide basis

Oxide	From DSSF	From Additives	LD6-5412
Al ₂ O ₃	12.56	11.82	12.00
B ₂ O ₃	-	6.82	5.00
CaO	0.01	5.46	4.00
Cl	1.36	-	0.35
Cr ₂ O ₃	0.15	-	0.04
Cs ₂ O	0.57	-	0.15
F	1.15	-	0.29
Fe ₂ O ₃	0.015	-	0.005
I	0.51	-	0.13
K ₂ O	5.67	-	1.51
MgO	0.008	-	0.003
MnO	0.007	-	0.002
MoO ₃	0.6	-	0.15
Na ₂ O	74.88	-	20.00
P ₂ O ₅	0.73	-	0.19
SO ₃	0.83	-	0.21
SiO ₂	-	75.91	55.65
SrO	0.43	-	0.11
TcO ₂	0.52	-	0.14
<i>% of Total</i>	<i>26.7 %</i>	<i>73.3 %</i>	<i>100 %</i>

Table 5. Compositions of Other Hanford LAW Glasses, Including Environmental Assessment (EA) Glass for Comparison

Oxide	LD6-5412	LD4-9012 ^a	LD6-5510	LD5-5314	EA
Al ₂ O ₃	12	12	10	14	3.6
B ₂ O ₃	5	9	5	5	11.16
CaO	4	-	5	3	1.23
Cl	0.35	0.35	0.35	0.35	-
Cr ₂ O ₃	0.04	0.04	0.04	0.04	-
Cs ₂ O	0.15	0.15	0.15	0.15	0.004
F	0.29	0.29	0.29	0.29	-
Fe ₂ O ₃ ^b	0.005	0.005	0.005	0.005	9.35
I	0.13	0.13	0.13	0.13	-
K ₂ O	1.51	1.51	1.51	1.51	0.04
La ₂ O ₃	-	-	-	-	0.29
Li ₂ O	-	-	-	-	4.21
MgO	0.003	0.003	0.003	0.003	1.79
MnO	0.002	0.002	0.002	0.002	1.36
MoO ₃	0.15	0.15	0.15	0.15	-
Na ₂ O	20	20	20	20	16.88
NiO					0.54
P ₂ O ₅	0.19	0.19	0.19	0.19	-
SO ₃	0.21	0.21	0.21	0.21	-
SiO ₂	55.65	55.91	56.91	54.91	48.76
SrO	0.11	0.11	0.11	0.11	-
TcO ₂	0.14	0.14	0.14	0.14	-
TiO ₂	-	-	-	-	0.65
ZrO ₂	-	-	-	-	0.48
T ^c	1323°C	1325°C	1296°C	1379°C	-

^aThe PNNL LD4-9012 glass is sometimes referred to as LD4-912. The values 9, 0, and 12 in the descriptor give the mass % of B₂O₃, CaO, and Al₂O₃ in the glass. We will refer to the glass as LD4-9012.

^bRepresents total iron.

^cTemperature at which measured viscosity is 10 Pa•s.

Table 6. Normalized Mass Loss (NL) and pH Results of 28-day MCC-1 Tests and 7-day PCTs at 90°C, in g/m²

	LD4-9012		LD6-5412		EA	
	28-d MCC-1	7-d PCT	28-d MCC-1	7-d PCT	28-d MCC-1	7-d PCT
NL(B)	5.06	0.35	7.94	0.11	91	8.5
NL(Na)	4.46	0.32	8.32	0.38	79	6.7
NL(Si)	3.11	0.13	7.87	0.10	48	2.0
pH	9.08	10.55	9.63	11.39	10.64	11.9
Ref.	[KIM-1995]	[KIM-1995]	[KIM-1995]	[KIM-1995]	[HRMA-1994]	[ANDREWS-1993]

Table 7. Nominal Compositions of Borosilicate Glasses, in oxide mass %

Oxide	SRM 662 ^a	L7-15	L8-3	SSHTM-3	L7-25	LD4-9012
Al ₂ O ₃	1.8	12.4	9	11.4	11.6	12
B ₂ O ₃	-	5.4	5	5.9	4.6	9
CaO	11.5	4.3	4	4.1	3.7	-
K ₂ O	0.04	-	-	1.1	-	0.3
Na ₂ O	14	15	20	21	25	20
SiO ₂	71.7	61.2	56.8	52.7	52.4	56.8
ZrO ₂	-	-	3	0.3	-	-
Others	0.55	1.7	2.2	3.6	2.7	1.9
Total	99.6	100	100	100.1	100	100

^aFrom the National Institute for Standards and Technology.

Table 8. Solution Concentrations and pH for PCTs with SSHTM-3 Glass

Test No.	Temp., °C	S/V, m ⁻¹	Time, d	pH	B, mg/L	Na, mg/L	Si, mg/L
1	20	400	1	9.22	0.03	1.93	0.261
2	20	400	3	7.93	0.08	3.28	0.38
3	20	400	7	9.5	0.11	2.84	2.74
4	40	400	3	9.22	0.21	4.05	2.95
5	40	400	7	9.78	0.39	6.2	5.57
6	20	1000	3	9.37	0.19	6.28	1.22
7	20	1000	7	9.93	0.23	6.74	2.13
8	40	1000	3	9.79	0.45	9.8	6.17
9	40	1000	7	10.07	0.58	11.8	8.41
10	20	2000	3	9.75	0.30	10.6	2.11
11	20	2000	7	10.28	0.44	13.5	3.78
12	40	2000	3	9.69	0.66	17.7	8.81
13	40	2000	7	10.48	0.85	20.8	11.8
14 ^a	20	400	7	12.46	1.23	11.5	18.5
15 ^a	20	1000	7	12.45	1.57	15.8	25.1
16 ^a	20	2000	7	12.44	1.85	23.2	29.5
17 ^a	20	400	1	11.87	0.23	2.37	2.43
18 ^a	40	400	1	12.04	1.26	9.84	17.2

^a Tests conducted in pH 12 solution.

Table 9. Normalized Dissolution Rates for Modified PCT with SSHTM-3 Glass

Test No.	Temp., °C	S/V, m ⁻¹	Time, d	NR(B), g/(m ² •d)	NR(Na), g/(m ² •d)	NR(Si), g/(m ² •d)
1	20	400	1	0.0041	0.031	0.0026
2	20	400	3	0.0037	0.018	0.0013
3	20	400	7	0.0022	0.0065	0.0014
4	40	400	3	0.0096	0.022	0.010
5	40	400	7	0.0077	0.013	0.0081
6	20	1000	3	0.0035	0.013	0.0017
7	20	1000	7	0.0018	0.0062	0.0012
8	40	1000	3	0.0082	0.021	0.0084
9	40	1000	7	0.0046	0.011	0.0049
10	20	2000	3	0.0027	0.011	0.0014
11	20	2000	7	0.0017	0.0062	0.0011
12	40	2000	3	0.0060	0.019	0.0060
13	40	2000	7	0.0033	0.0096	0.0034
14 ^a	20	400	7	0.024	0.026	0.027
15 ^a	20	1000	7	0.012	0.015	0.015
16 ^a	20	2000	7	0.0073	0.011	0.0086
17 ^a	20	400	1	0.032	0.038	0.025
18 ^a	40	400	1	0.17	0.16	0.17
mass fraction				0.0182	0.155	0.246

^a Tests conducted in pH 12 solution.

Table 10. Results of VHTs Conducted at 150°C with Several Glasses [BAKEL-1995]

Glass	Composition, mass %			Layer Thickness, μm			Did Zeolites Form?		
	B ₂ O ₃	CaO	Al ₂ O ₃	7-d	14-d	28-d	7-d	14-d	28-d
L4-906	9	0	6	0	- ^a	0	no	no	no
L4-909	9	0	9	0	0	0	no	no	no
L6-6012	6	0	12	0	0	- ^a	no	no	no
L4-9012	9	0	12	0	0	0	no	no	no
L4-12012	12	0	12	0	0	0	no	no	no
L5-096	0	9	6	30	100	300	yes	yes	yes
L5-912	0	9	12	40	50	>400 ^b	yes	yes	yes
L6-546	5	4	6	50	>400 ^b	>400 ^b	yes	yes	yes
L6-549	5	4	9	300	>400 ^b	>400 ^b	yes	yes	yes
L6-5412	5	4	12	0	400	>400 ^b	no	yes	yes
LD6-5412	5	4	12	0	200	>400 ^b	no	yes	yes

^a Hydration layer formed due to water diffusion into glass. No corrosion layer was formed.

^b Sample was completely corroded.

Table 11. Results of Replicate Tests with LD6-5412 Glass

Test No.	Mass, g	Glass	Water	pH	Analysis 1, mg/L				Analysis 2, mg/L				Analysis 3, mg/L			
					B	Na	Si	20°C with washed glass	B	Na	Si	B	Na	Si	B	Na
1	0.96	9.60	9.10	0.569	14.1	5.01	0.393	14.0	5.03	0.406	13.9	8.45				
2	0.92	9.20	8.60	0.559	15.3	4.19	0.375	14.3	3.88	0.389	13.1	6.40				
3	0.95	9.50	8.51	0.588	15.3	4.29	0.402	15.0	4.18	0.413	13.3	6.67				
4	0.92	9.20	9.66	0.658	14.3	6.68	0.440	13.8	6.62	0.465	12.6	10.7				
5	0.92	9.20	9.78	0.689	14.4	7.26	0.437	14.1	7.35	0.470	12.2	11.3				
6	0.94	9.40	9.66	0.683	14.7	7.41	0.458	14.0	7.15	0.473	12.5	11.2				
7	0.93	9.30	8.29	0.601	16.1	4.13	0.384	15.1	4.04	0.409	13.1	6.39				
8	0.91	9.10	8.01	0.635	16.5	4.26	0.412	15.7	4.27	0.437	14.9	7.19				
9	0.91	9.10	7.98	0.679	16.3	3.74	0.447	15.9	3.73	0.497	14.7	6.11				
mean				0.629	15.1	5.22	0.416	14.7	5.14	0.44	13.4	8.27				
s.d.				0.051	0.918	1.47	0.030	0.780	1.48	0.038	0.969	2.21				
rsd				8%	6%	28%	7%	5%	29%	9%	7%	27%				
-----40°C with washed glass-----																
10	0.93	9.30	9.88	1.303	28.6	14.8	1.08	28.7	15.6	1.21	26.7	15.5				
11	0.91	9.10	9.95	1.391	26.3	17.3	1.20	28.3	18.9	1.43	26.8	18.8				
12	0.92	9.20	9.81	1.375	30.0	19.3	1.25	28.7	19.0	1.34	26.8	18.8				
13	0.96	9.60	10.03	1.332	28.2	17.8	1.27	27.8	17.7	1.29	26.8	18.3				
14	0.93	9.30	9.51	1.258	29.8	14.5	1.20	28.4	14.1	1.20	26.3	13.8				
15	0.92	9.20	10.40	1.330	28.7	18.3	1.22	27.8	18.4	1.29	26.4	18.1				
16	0.95	9.50	9.09	1.326	30.6	12.9	1.27	29.8	13.0	1.29	29.4	13.3				
17	0.94	9.40	10.22	1.366	28.1	17.5	1.30	27.5	17.8	1.26	28.0	19.4				
18	0.93	9.30	8.58	1.739	32.0	8.06	1.20	31.3	8.21	1.22	29.9	8.26				
mean				1.380	29.2	15.6	1.22	28.7	15.9	1.28	27.5	16.0				
s.d.				0.140	1.66	3.51	0.065	1.21	3.58	0.071	1.36	3.69				
rsd				10%	6%	22%	5%	4%	23%	6%	5%	23%				

Table 11. Results of Replicate Tests with LD6-5412 Glass (cont.)

Test No.	Mass, g		pH	Analysis 1, mg/L			Analysis 2, mg/L			Analysis 3, mg/L		
	Glass	Water		B	Na	Si	B	Na	Si	B	Na	Si
19	0.92	9.20	10.61	2.44	51.2	19.2	2.38	48.4	19.1	2.36	52.5	20.3
20	0.83	8.30	10.33	2.35	58.4	15.3	2.42	51.5	15.1	2.46	48.7	16.6
mean				2.40	54.8	17.3	2.40	50.0	17.1	2.41	50.6	18.2
s.d.				0.062	5.04	2.77	0.029	2.23	2.79	0.075	2.67	2.56
rsd				3 %	9 %	16 %	1 %	4 %	16 %	3 %	5 %	16 %

40°C with unwashed glass												
21			11.05	3.92	83.4	34.8	3.86	86.0	34.8	3.98	80.1	38.8
22			11.03	3.93	82.0	34.1	3.85	84.6	33.3	3.87	78.2	36.6
mean				3.93	82.7	34.5	3.85	85.3	34.0	3.93	79.2	37.7
s.d.				0.004	0.983	0.544	0.002	0.955	1.08	0.077	1.37	1.55
rsd				0 %	1 %	2 %	0 %	1 %	3 %	2 %	2 %	4 %

Table 12. Summary of Results of Replicate Tests and Analyses with Washed Glass

Analysis No.	B, mg/L			Na, mg/L			Si, mg/L		
	mean	s.d.	rsd	mean	s.d.	rsd	mean	s.d.	rsd
<i>9 tests at 20°C</i>									
1	0.629	0.051	8 %	15.2	0.918	6 %	5.22	1.47	28 %
2	0.416	0.030	7 %	14.6	0.780	5 %	5.14	1.48	29 %
3	0.440	0.038	9 %	13.4	0.969	7 %	8.27	2.21	27 %
avg.	0.495	0.104	21 %	14.4	1.16	8 %	6.21	2.25	36 %
<i>9 tests at 40°C</i>									
1	1.38	0.140	10 %	29.1	1.66	6 %	15.6	3.51	22 %
2	1.22	0.065	5 %	28.7	1.21	4 %	15.9	3.58	23 %
3	1.28	0.072	6 %	27.5	1.36	5 %	16.0	3.69	23 %
avg.	1.29	0.116	9 %	28.4	1.54	5 %	15.8	3.46	22 %

Table 13. Normalized Mass Loss NL(i) (with standard deviation) and Normalized Dissolution Rate NR(i) for Replicate Tests with SSHTM-3 Glass

T, °C	NL(i), g/m ²			NR(i), g/(m ² •d)		
	Na	B	Si	Na	B	Si
20	0.046±0.004	0.014±0.003	0.013±0.005	0.0066	0.0020	0.0019
40	0.091±0.005	0.035±0.003	0.032±0.007	0.0013	0.0050	0.0046

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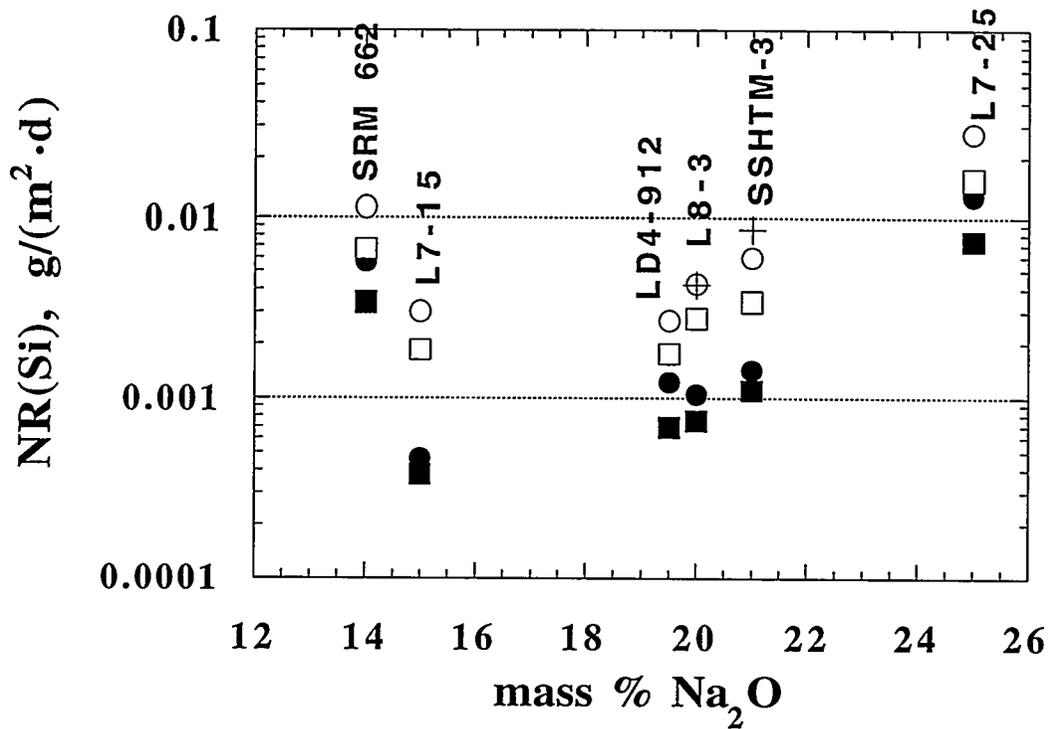
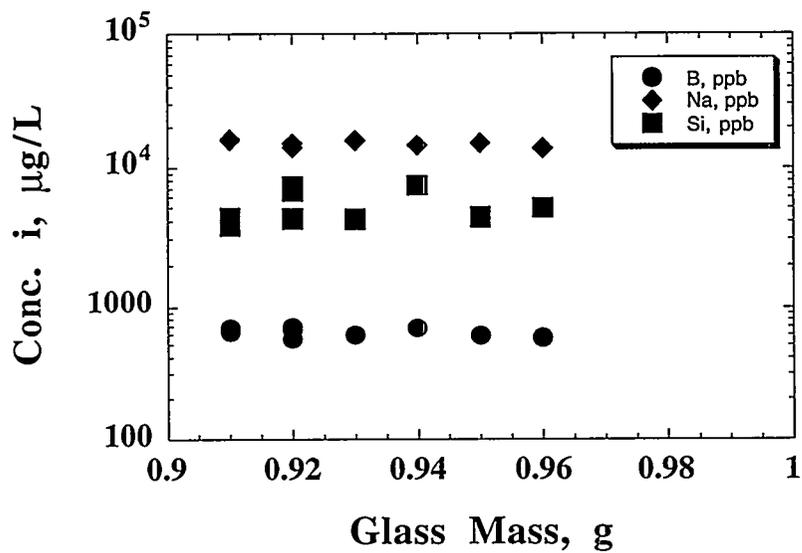
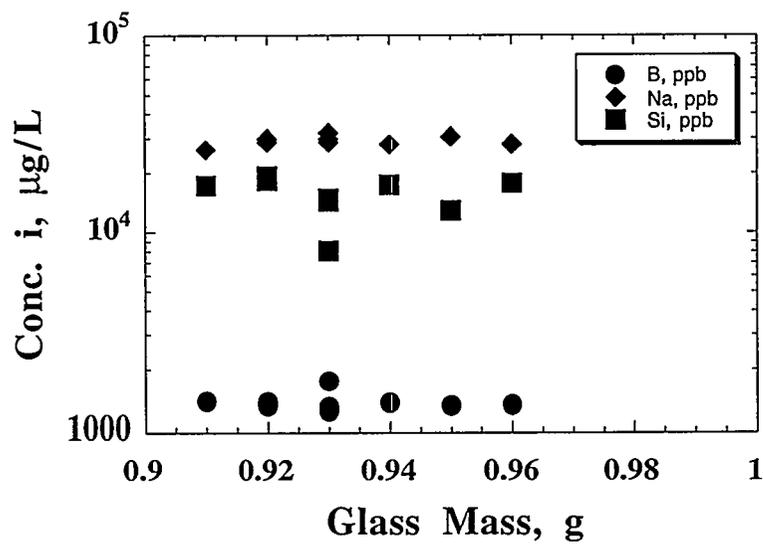


Figure 1. Measured NR(Si) for Glasses with Various Na_2O Contents in PCTs. Tests conducted at 2000 m^{-1} for (●) 3 days or (■) 7 days at 20°C , and (○) 3 days or (□) 7 days at 40°C in Demineralized Water or (+) 7 days at 20°C in pH 12 buffer solution.



a.



b.

Figure 2. Results of Nine Replicate Tests Conducted at (a) 20°C and (b) 40°C.

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