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by J. K. Bates, N. R. Brown, E. C. Buck,
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**ANL TECHNICAL SUPPORT PROGRAM FOR DOE ENVIRONMENTAL
RESTORATION AND WASTE MANAGEMENT**

**ANNUAL REPORT
OCTOBER 1993 - SEPTEMBER 1994**

by

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Chemical Technology Division

June 1995

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ABSTRACT

A program was established for DOE Environmental Restoration and Waste Management (EM) to evaluate factors that are anticipated to affect waste glass reaction during repository disposal, especially in an unsaturated environment typical of what may be expected for the proposed Yucca Mountain repository site. This report covers progress in FY 1994 on the following tasks:

1. Critical Reviews of important parameters that affect the reactivity of glass in an unsaturated environment are being prepared. The parameters include radiation, glass surface area-to-liquid volume (SA/V) ratio, and glass weathering. A Critical Review was published on modeling of waste glass performance. Data Reports are also being prepared to cover the experimental work ongoing in the program.
2. A series of tests is ongoing to evaluate the reactivity of fully radioactive glasses in a high-level waste repository environment and compare it to the reactivity of synthetic, nonradioactive glasses of similar composition. These tests have now been in progress for over four years.
3. The effect of radiation upon the durability of waste glasses at a high SA/V ratio and a high gas-to-liquid volume ratio has been assessed. Tests addressing both vapor conditions and liquid conditions at high SA/V ratios have been completed, and the data have been compiled into both a Critical Review and a Data Report.
4. A series of tests is being performed to compare the extent of reaction of nuclear waste glasses at various SA/V ratios. Such differences in the SA/V ratio may significantly affect glass durability. At long-term periods and high SA/V ratios, acceleration in glass reaction has been observed. Both a Critical Review and a Data Report have been prepared for this Task.

5. Tests were initiated on West Valley Reference 6 (WV6) glass and on the Environmental Assessment (EA) glass. The tests being performed are static batch tests under high SA/V conditions known to accelerate glass reaction. The WV6 glass has reached near saturation conditions and the reaction rate has slowed considerably from its initial value. The EA glass has reached the reaction stage where secondary phases have formed and the rate of reaction has increased.
6. Tests with the actinide-doped West Valley glass ATM-10 have been in progress for over seven years as a part of work for the Yucca Mountain Site Characterization Project (YMP). During the first year of testing, eight tests were terminated, but the glass and metal components of the tests were never analyzed, so a full correlation between solution and component analysis could not be made. We have analyzed the glasses from these tests and found that the actinide-bearing phase, brockite, which was previously found in solution, actually forms as part of the reacted glass.
7. Analytical electron microscopy (AEM) is being used to assess the glass/water reaction pathway by identifying intermediate phases that appear on the reacting glass. Also, colloids from the leach solutions are being studied using AEM.

EXECUTIVE SUMMARY

This report is an overview of the progress during FY 1994 for the Technical Support Program that is part of the ANL Technology Support Activity for DOE Environmental Restoration and Waste Management (EM). The purpose is to evaluate, before hot start-up of the Defense Waste Processing Facility (DWPF) and the West Valley Demonstration Project (WVDP), factors that are anticipated to affect glass reaction in an unsaturated environment typical of what may be expected for the candidate Yucca Mountain repository site. Specific goals for the testing program include the following:

- reviewing and evaluating available data on parameters that will be important in establishing the long-term performance of glass in a repository environment
- performing tests to further quantify the effects of important variables where there are deficiencies in the available data
- initiating long-term tests to determine glass performance under a range of conditions applicable to repository disposal

The progress made in FY 1994 on each of the technical tasks is summarized below.

Critical Review of Parameters Affecting Glass Reaction in an Unsaturated Environment

The repository environment at Yucca Mountain has been predicted by the Yucca Mountain Site Characterization Project (YMP) to be hydrologically unsaturated and to have possible air exchange with the neighboring biospheres. We have identified several environmental conditions that can affect the durability of waste emplaced in such an unsaturated environment over repository-relevant time periods. To date, much of the information regarding what is known about these conditions has not been compiled for use within the waste glass research community. While the document "High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics" discusses some of the effects of unsaturated conditions on glass performance, we identified the need for a critical review of important parameters that would affect the reactivity of glass in an unsaturated environment. This task is currently underway.

The Critical Review reports provide more detail than the Compendium, contain more subjective judgments on the literature data than presented in the Compendium, and contain experimental data, either as part of the Review or as a separate Data Report, collected during this program that address each parameter studied.

This year, two Critical Review reports ("Effects of Radionuclide Decay on Waste Glass Behavior - A Critical Review" and "Critical Review of Glass Performance Modeling") were published. Reports related to glass composition, effects of glass surface area-to-liquid volume (SA/V), the reaction of fully radioactive glass, and the effect of unsaturated conditions on glass reaction are in preparation.

Long-Term Testing of Fully Radioactive Glass

Three types of tests are ongoing to evaluate the long-term performance of glass made from tank sludge from the Defense Waste Processing Facility (DWPF). These include (1) batch tests done under static conditions and a range of SA/V values, (2) drip tests done with as-cast glass and with glass aged by reaction with water vapor, and (3) laboratory analogue tests

wherein the glass is encased in a tuff core to closely simulate reactions that may occur in an unsaturated environment.

Batch tests are being performed to compare the reactivity of radioactive glasses and glasses with the same composition, but without the radionuclides. The radioactive glasses are designated R, and the simulated glasses, S. The batch tests with R and S glasses have been in progress for more than 208 weeks (four years). In only one case, out of all the glass compositions and SA/V ratios used, did the R and S glasses react differently. This was the 200 frit-based composition tested at $20,000 \text{ m}^{-1}$. Under those conditions, the R glass showed the accelerated glass reaction associated with the formation of stable secondary phases. When the secondary phases nucleate, glass reaction is favored because they act as a silicon sink. The amount of reacted 200S glass increased sharply after about one year, after which there was little further change because most of the glass had already reacted. Under the same conditions, the 200R glass reaction did not accelerate, primarily because of the radiation, which lowered the solution pH, thereby creating conditions unfavorable to the formation of the stable secondary phases required to increase glass reaction.

The drip tests have been in progress for 195 weeks and a significant disparity in the total release of elements can be observed between as-cast and aged glass. The as-cast glass showed fairly continuous reaction over the entire time period and low reaction rates. The release of radionuclides from the glass was dominated by reacted layers spalling from the glass surface. The aged glass initially showed about a 1000-fold greater release of B and Li compared to the as-cast glass, but the release continually decreased with time such that, after 195 weeks, the B and Li releases were only about 30-fold greater. The anionic content of the solution followed the trend observed for B and Li, in that the concentrations of SO_4^{2-} , Cl^- , and HPO_4^{2-} were initially large but decreased with time. However, the solution pH observed for the two test glasses has remained fairly constant at about 8 for the as-cast glasses and about 11.3 for the aged glasses. These tests are continuing so as to observe further trends in glass reactivity and to correlate the release of radionuclides with glass reaction.

The laboratory analogue tests have been in progress for several years, and the effluent that passes through the tuff is continually collected. The tuff is an outcrop type, and perhaps more highly fractured than the tuff that may exist at the repository horizon. No detectable radioactivity has been found in the test solution to date; thus, while it is not known to what extent the glass is being contacted by groundwater, because the system is closed, any radioactivity that has been released from the glass has not escaped through the rock.

Effect of Radiation on Glass Reaction at High SA/V

Ionizing radiation may affect the performance of glass in an unsaturated repository site by interacting with air, water vapor, or liquid water to produce a variety of radiolytic products. Tests were conducted to examine the effects of radiolysis under high gas/liquid ratios. Results indicate that nitrate is the predominant radiolytic product formed under both gamma and alpha radiation exposure, with lesser amounts of nitrite and carboxylic acids. The formation of nitrogen acids during exposure to long-lived, alpha-particle-emitting transuranic elements indicates that these acids may play a role in influencing nuclear waste form reactions in a long-term disposal scenario.

Experiments were also conducted with samples that simulate the composition of Savannah River Plant nuclear waste glasses. Radiolytic product formation in batch tests (340 m^{-1} , 90°C) caused small increases in the release rates of most glass components, although silicon and uranium release rates were slightly reduced, indicating an overall beneficial effect of radiation on waste form stability. The reduction in silicon release results from decreased silicic acid activity with decreasing pH, whereas the uranium decrease may be related to a corres-

ponding increase in the stability of the host silicate glass matrix, as well as decreased stability of uranyl carbonate complexes. By contrast, radiation exposure in the vapor hydration tests (150-200°C) resulted in a four- to ten-fold increase in alteration layer thickness relative to samples reacted without radiation exposure. These increases result from concentration of radiolytic acids in the thin film of water contacting the glass surface.

The paragenetic sequence of alteration minerals formed on the irradiated glass samples matches closely those developed during volcanic glass alteration in naturally occurring saline-alkaline lake systems. This similarity arises because the thin film of water present on the simulated waste glass samples is transformed into a saline-alkaline fluid by the release of glass components. Thus, it appears that the high temperatures used in these tests have not changed the underlying glass reaction mechanism relative to that which controls glass reactions under ambient surficial conditions.

Relationship between High SA/V Experiments and MCC-1

Static leach tests are being conducted to assess how the glass surface area/leachant volume ratio (SA/V) affects the rate and mechanism of glass corrosion. Test results available to date show that the predominant effect of SA/V is the extent to which released glass components are diluted: higher solution pH values and higher concentrations of released glass components occur in tests at higher SA/V. The solution chemistry in turn affects the glass corrosion and the behavior of radionuclides. High pH decreases the rates of ion exchange reactions and dealkalization, but increases the rate of hydrolysis reactions; higher silicic acid concentrations decrease the glass corrosion rate, and higher anion concentrations increase the solubilities of released radionuclides. The formation of secondary phases from concentrated leachates also affects the solution chemistry (particularly the silicic acid concentration) and the glass corrosion rate. Formation of critical secondary phases leads to an increase in the corrosion rate under some test conditions. Analysis of the corroded glass revealed that smectite clay was formed in tests at all SA/V tested and at all reaction times. Other phases were found in tests showing the higher final corrosion rate, including the uranium-bearing phases weeksite and boltwoodite, chabazite and heulandite group zeolites, clinoptilolite, and nagelschmidtite. A noncrystalline feature bearing uranium and titanium was also identified within the clay phase or between the clay layer and the underlying glass.

Laboratory Testing of West Valley Reference 6 and SRL EA Glasses

A laboratory testing program was initiated to characterize the corrosion behavior of a nonradioactive homologue of the high-level waste glasses to be produced by the West Valley Demonstration Project (WVDP). Tests are being conducted according to the MCC-1, Product Consistency Test (PCT), and vapor hydration test protocols to measure the corrosion rates under various conditions. Product Consistency Tests are also being conducted using the SRL EA glass. The results available to date indicate that the WV6 glass is as durable as other reference glasses under MCC-1 and PCT conditions. Corrosion of the WV6 glass in vapor hydration tests show that WV6 glass forms a wide variety of secondary phases as it corrodes, including zeolites, phosphates, and uranium silicate phases. Formation of these phases increases the glass corrosion rate, though they may contain radioactive elements when formed during the corrosion of radioactive glasses. Similar phases are expected to form in PCT tests after long reaction times. Indeed, PCT tests conducted with the less durable SRL EA glass showed formation of zeolite secondary phases within a few weeks.

Components from Drip Tests with ATM-10 Glass

Components of actinide-doped West Valley ATM-10 reference glass and sensitized 304L stainless steel were reacted with liquid groundwater using the Unsaturated Test Method.

Surface corrosion and reaction products, resulting from tests of up to one year on these components, were analyzed. These tests, initiated in 1987 and still ongoing for several other samples, were designed to determine the suitability of glass waste forms for the proposed high-level repository at the Yucca Mountain Site. While elemental release rates to solution have been reported for these tests, an analysis of reaction products and surface corrosion of the waste form components is important for a more complete understanding of reaction mechanisms and dynamics. Together, these data will provide constraints on long-term geochemical modeling of waste form performance in the repository.

Analyses of the components included optical microscopy, scanning electron microscopy, and analytical transmission electron microscopy (AEM). These combined techniques led to the identification of secondary phases, dominated by smectite clays, iron-silicates, thorium-calcium-phosphate (brockite), and an amorphous thorium titanate. Disposition of released matter from the waste form onto the surrounding stainless steel waste form holder was assessed by optical and scanning electron microscopy; these components were then acid-stripped to determine actinide sorption by high-resolution alpha spectroscopy and inductively coupled plasma-mass spectrometry (ICP-MS). An ANL Topical Report on these findings is forthcoming, as are a presentation and an open literature publication for the American Ceramic Society in May of this year.

Analytical Electron Microscopy Support

The Analytical Support staff collaborates with other members of the Technical Support Program to investigate and identify reaction products produced from corrosion of nuclear waste forms during simulations of expected environmental conditions. These structural studies provide information necessary to understand the reaction processes. This information will contribute to the development of the models needed for prediction of glass behavior. Analysis of samples from the Long Term Testing and Effects of SA/V tasks was performed this year. New samples from the SRL-EA and WV6 Glass Testing task were also examined by AEM.

In addition to the reaction layers, colloidal particles present in the leachate, some of which may carry radionuclides, were examined. Examination of colloids present in the leachate has permitted not only identification of colloidal phases, but also a picture of colloidal particle formation in the leachate.

This year presentations were made by members of the AEM Group to the Annual America Ceramic Society Meeting in Indianapolis, IN, the Fall National Meeting of the American Chemical Society in Washington DC., Scanning '94 held in Toronto, the Annual Meeting of the American Physical Society in Pittsburgh, PA, and the Microscopy Society of America Annual Meeting in New Orleans, LA, where the Group's work on analysis and ultramicrotomy of waste glass was awarded a prize in the Poster Exhibition.

I. INTRODUCTION

The High-Level Nuclear Waste Technical Support Program at Argonne National Laboratory (ANL) is part of a continuing activity performed for the U.S. Department of Energy (DOE) as part of their Environmental Restoration and Waste Management (EM). The purpose of the program is to evaluate factors likely to affect glass reaction in an unsaturated environment before hot start-up of the Defense Waste Processing Facility (DWPF) and the West Valley Demonstration Project (WVDP), and to provide input that may prove useful in developing glass compositions as part of the Tank Waste Remediation System (TWRS) at Hanford. Past progress is given in the annual reports for FY 1990 through FY 1993 [1-4]. The program is based on determining the long-term glass performance under conditions that may simulate an unsaturated repository environment and studying the release of radionuclides from a glass waste package. Such tasks will not be completed until the application for a repository license occurs, which will be several years after the production of waste for storage and disposal begins. The Technical Support Program at ANL also recognizes that the modeling and performance assessment programs must have a firm basis that (1) accounts for important physical parameters that will affect glass reaction in an unsaturated environment and (2) relates the mechanistic basis of glass reaction to conditions that will exist in an unsaturated environment.

The goals of the ANL Technical Support Program are to (1) review parameters that will be important in evaluating glass performance, (2) perform testing to further quantify the effects of important variables, (3) perform long-term testing that will examine glass performance under a range of conditions that may be important to storage of waste in an unsaturated environment, and that can be used to validate models generated to predict long-term performance, and (4) identify mechanisms that control glass reaction thereby providing input to models that predict glass performance. The information developed in this program, when combined with data generated by the glass waste producers and by the Yucca Mountain Site Characterization Project (YMP), will form the basis for a well-founded program that will ultimately qualify vitrified high-level waste for repository disposal.

The parameters that are important for controlling glass reaction in an unsaturated environment include (1) glass composition, (2) radiation, (3) temperature, and (4) surface area of glass/volume of liquid (SA/V). Also being studied are the effects of unsaturated conditions (weathering) on glass reaction and modeling of glass performance. Prior to hot facility start-up, these items will be critically evaluated such that their role in glass performance will be established. Results will be presented in Critical Reviews and Data Reports.

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II. BACKGROUND

Work in each area is governed by a Task Plan, which enables the work to be planned according to the quality guidelines of the ANL Technical Support Program and allows all program activities to be coordinated. The Task Plans outline work to be done in an activity, but they do not restrict the flexibility to make adjustments based on knowledge gained as the test results are evaluated. Plans are in place for the following tasks:

- (1) Critical Review of Parameters Affecting Glass Reaction in an Unsaturated Environment,
- (2) Long-Term Testing of Fully Radioactive Glass,
- (3) Effect of Radiation on Glass Reaction at Large SA/V,
- (4) Relationship between High SA/V Experiments and MCC-1,
- (5) WV6/EA Glass Testing, and
- (6) ATM-10 Components Analysis.

While these Task Plans are not formally published documents, copies of them are available upon request. Ongoing work in each of these tasks is described in latter sections of this report.

An integral part of the testing program was the identification and preparation of glasses to be used. Several factors were considered in choosing glass compositions, including the following: (1) the composition of "fully" radioactive glasses* available for testing; (2) the need to test a range of compositions based on glass durability, which may be a function of the test conditions; (3) the desire to use compositions similar to those already in use so that a comparative data base can be developed; (4) the necessity to test both radioactive and nonradioactive compositions (for comparative and technique-development purposes); and (5) minimization of testing time and cost.

The compositions of fully radioactive glasses are set by glass availability and include (1) 165 sludge-only-based glass, designated 165/42 (the glass frit is 165 type and the sludge is from tank 42); (2) 131 sludge-only-based glass, designated 131/11 (the glass frit is 131 type and the sludge is from tank 11); and (3) 200 frit-based glass, 200R (the glass frit is 200 type, the sludge is from tanks 8 and 12, and the precipitate hydrolysis aqueous [PHA] feed is simulated). These glasses were produced by Westinghouse Savannah River Co. (WSRC) over the past several years and represent glasses developed as the process engineering matured. The base frits used in these glasses (131, 200, and 165) represent the expected durability range from least to most durable based on hydration theory [5]. The sludge from tanks 11 and 42 is rich in aluminum, and the final compositions of the 131/11 and 165/42 glasses do not represent glasses expected to be produced by the DWPF. However, the composition of 200R glass was expected to be similar to that of the blend identified in the Waste Compliance Plan (WCP) [6] and, therefore, similar to a production glass. However, the composition of the test glass differed

*The term "fully radioactive glass" is used to designate glasses made containing actual waste taken from the waste storage tanks at the Westinghouse Savannah River Site. The glass may not contain the complete complement of radionuclides anticipated to exist in the final DWPF product because the glass contains only radionuclides contained in the sludge component of the waste.

from that of the WCP blend and was close to a bounding composition. Bounding in this context means that the calculated free energy of hydration of the glass is near the limit of acceptability for the DWPF, and the bounding composition is predicted to be more reactive than the blend composition.

The extent to which a glass composition falls within the range of production compositions influences the use of the glass in testing. The 131/11 and 165/42 compositions, although they may not be produced, are useful for comparative testing with a simulated nonradioactive glass of the same composition to demonstrate whether any differences in reactivity exist between production and simulated glasses. The 200R glass is also useful for comparative testing, but because its composition is closer to that of the production glass, it is used in a more extensive test matrix to assess glass performance under unsaturated conditions. (See Sec. IV for details of testing these glasses.) For each of these fully radioactive glasses, simulated glasses were produced with the same composition. Simulated glasses are designated as "S" glasses (e.g., 131/11S).

Because none of the fully radioactive glasses are exact representations of glasses identified in the WCP, we felt that another set of glasses should be produced for testing done in other tasks in this program and in other testing performed by the YMP. Concurrence of glass compositions to be tested was obtained from Lawrence Livermore National Laboratory, the agency responsible for the YMP Glass Task. The compositions chosen are 131-, 165-, and 202-based DWPF glasses, WV6 reference glass identified by the WVDP, and the environmental assessment (EA) glass used by all U.S. vitrification facilities. The actual compositions are based on the use of manufactured bulk frits as starting frits modified to match WCP glasses as closely as possible. Thus, the "base 131 frit" is 131 frit produced in the semiworks at WSRC, the "base 165 frit" is 165 blank frit manufactured by Ferro Corp., the base 202 frit is based on DWPF start-up frit, WV6 glass was produced by The Catholic University, and the EA glass was produced by the Corning Glass Works. Each base frit is modified, if required, by the addition of chemical additives, including zeolite and actinide elements, to produce the glasses used in testing. If a glass contains uranium but no transuranic elements, it is designated U (e.g., 131U). If a glass contains transuranic elements, it is designated A (e.g., 131A).

At this time, testing has been initiated on all of the fully radioactive (R) and simulated (S) glasses. The starting glasses have been analyzed several times over the past few years to obtain the most reliable values to be used in data assimilation. The compositions are shown in Table 1 and may vary slightly from compositions given in previous annual reports [1-4]. This is especially true for the radionuclide content of the glasses which were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) and alpha counting combined with electroplating. The data presented in the subsequent sections of this report are based on the values in Table 1. A standard leachate, which is based on the equilibration of well water J-13 with tuff rock, was used throughout the testing program. The resulting water is termed "EJ-13 water," and its general composition is listed in Table 2. The composition of EJ-13 water varies slightly between batches, and the composition used in more recent tests has a slightly higher pH.

Table 1a. Composition of Nonradioactive Glasses Used in Testing.^a
 Compositions are reported in units of oxide wt %.

Element	131/11S	165/42S	200S	EA ^b	WV 6 ^c
Al	9.1	9.2	5.4	3.6	6.0
B	9.3	7.9	9.5	11.1	12.9
Ba	0.05	0.36	0.03	N.D. ^d	0.16
Ca	2.9	0.31	0.86	1.2	0.48
Ce	N.D.	N.D.	N.D.	N.D.	0.16
Cr	0.69	0.50	0.28	N.D.	0.14
Cu	0.04	0.02	0.18	N.D.	0.03
Fe	5.2	6.51	9.1	9.1	12.0
K	0.16	0.05	3.2	0.04	5.0
La	N.D.	N.D.	0.02	0.28	0.04
Li	3.2	4.7	3.3	4.2	3.7
Mg	1.6	0.96	1.7	1.8	0.89
Mn	1.7	1.7	1.5	1.4	1.0
Mo	N.D.	N.D.	0.02	N.D.	0.04
Na	17.5	10.0	15.3	16.8	8.0
Nd	N.D.	N.D.	N.D.	N.D.	0.14
Ni	0.56	0.70	0.91	0.53	0.25
Pb	0.13	N.D.	0.43	N.D.	N.D.
Rh	N.D.	N.D.	N.D.	N.D.	N.D.
Ru	N.D.	N.D.	N.D.	N.D.	N.D.
Si	45.8	55.4	46.1	48.6	41.0
Sr	0.02	0.01	0.02	N.D.	0.02
Th	N.D.	N.D.	0.01	N.D.	N.D.
Ti	1.7	0.07	0.13	0.65	0.80
U	0.26	0.13	1.9	N.D.	0.59
Zn	0.05	0.02	0.04	0.26	0.02
Zr	0.12	1.4	0.09	0.48	1.32

^aResults were obtained by analyzing dissolved, cleaned, 100-200 mesh glass. Values are typically mean values from multiple analyses. Analyses were performed using ICP-AES and ICP-MS.

^bCompositions reported are from C. M. Jantzen, et al. WSRC-TR-92-346, Rev. 1 (1993). Values have been normalized to 100% oxide wt %.

^cThe compositions reported are from Catholic University of America (CUA). Values have been normalized to 100% oxide wt %.

^dDesignation N.D. means no data exist for that element.

Table 1b. Composition of Radioactive Glasses Used in Testing.^a
 Compositions are reported in units of oxide wt %.

Element	131/11R	131U/A	165/42R	165U/A	200R	202U/A
Al	9.9	3.3	11.1	4.5	6.3	3.9
B	10.5	9.8	9.9	6.7	10.7	8.0
Ba	0.02	0.02	0.05	0.03	0.02	0.21
Ca	3.8	0.94	0.40	1.6	0.92	1.3
Ce	0.05	0.06	0.06	<0.01	0.04	<0.01
Cr	0.34	0.13	0.33	0.02	0.30	0.12
Cu	0.02	0.02	0.03	N.D. ^b	0.10	0.41
Fe	5.9	12.8	6.3	12.2	9.1	11.9
K	0.18	3.9	0.05	0.20	3.4	3.7
La	0.01	0.02	0.03	<0.01	0.05	0.11
Li	3.1	3.0	4.7	4.5	3.1	4.4
Mg	1.3	1.3	0.99	0.73	1.4	1.4
Mn	1.8	2.5	2.2	2.8	1.7	2.2
Mo	0.01	<0.01	<0.01	0.01	0.01	0.05
Na	15.8	12.2	11.1	11.4	14.1	7.8
Nd	0.04	0.09	0.09	N.D.	0.07	<0.01
Ni	0.51	1.2	0.69	0.85	1.0	0.85
Pb	0.01	<0.01	0.04	0.01	0.02	0.01
Rh	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ru	<0.01	<0.01	0.02	0.01	<0.01	<0.01
Si	44.3	44.3	50.4	52.4	45.7	50.2
Sr	0.02	0.01	0.04	0.11	0.01	0.03
Th	0.40	0.01	0.50	N.D.	0.03	0.28
Ti	1.5	0.66	0.12	0.15	0.08	0.93
U	0.21	3.0	0.13	1.1	1.7	2.0
Zn	0.03	0.02	0.02	0.02	0.02	0.29
Zr	0.07	0.22	0.72	0.70	0.04	0.06
²⁴¹ Am	9.1E-5	4.5E-4	8.1E-5	1.8E-4	2.8E-4	4.4E-4
⁶⁰ Co	4.1E-8	N.D.	1.9E-7	N.D.	3.6E-7	N.D.
²⁴⁴ Cm	1.2E-6	N.D.	2.1E-6	N.D.	2.1E-5	N.D.
¹³⁷ Cs	6.6E-4	N.D.	9.9E-5	N.D.	6.5E-5	N.D.
¹⁵⁴ Eu	8.5E-6	N.D.	1.3E-5	N.D.	3.8E-6	N.D.
¹⁵⁵ Eu	1.1E-6	N.D.	1.5E-6	N.D.	1.2E-6	N.D.
²³⁷ Np	5.6E-4	1.3E-2	8.0E-4	1.4E-2	2.1E-4	1.4E-2
²³⁸ Pu	5.7E-4	N.D.	2.7E-4	N.D.	2.8E-4	N.D.
²³⁹ Pu	1.6E-3	1.2E-2	1.5E-3	8.7E-3	2.0E-3	1.3E-2
²⁴⁰ Pu	3.1E-5	N.D.	1.7E-4	N.D.	2.7E-4	N.D.
¹²⁵ Sb	7.5E-8	N.D.	1.0E-7	N.D.	1.0E-7	N.D.
⁹⁹ Tc	2.9E-4	3.5E-3	1.6E-5	1.5E-3	3.3E-5	3.0E-3

^aResults were obtained by analyzing dissolved, cleaned, 100-200 mesh glass. Values are typically mean values from multiple analyses. Stable element analyses were performed using ICP-AES and ICP-MS. Radionuclide content was measured using a combination of ICP-MS, gamma spectrometry.

^bDesignation N.D. means no data exist for that element.

Table 2. Composition of EJ-13
Leachate at a pH of 8.1

Component	mg/L
Al	1.1
B	0.17
Ca	5.4
Li	0.050
Mg	0.4
Na	53.9
Si	46.4
K	7.3
NO ₃ ⁻	11
F ⁻	2.3
HCO ₃ ⁻	100
Cl ⁻	8.4

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III. CRITICAL REVIEW OF PARAMETERS AFFECTING GLASS REACTION IN AN UNSATURATED ENVIRONMENT

A. Introduction and Background

The repository environment at Yucca Mountain has been predicted by the YMP as being hydrologically unsaturated and having possible air exchange with the neighboring biosphere. Emplacement scenarios for the waste include both thermally "hot" and "cold" modes, which will affect the length of time the container remains dry, but which should not affect the ultimate waste/water contact modes. We have identified several environmental conditions that can affect the durability of waste emplaced in such an environment over repository-relevant time periods. To date, much of what is known about these conditions has not been compiled for use by waste glass researchers, and we identified the need for such a critical review. That task is now underway.

During the projected repository lifetime, large amounts of liquid water are not expected to come into contact the waste; however, water vapor or small volumes of transient water may contact the waste at any time during the emplacement. We have identified the amount of water contacting the glass waste to be a primary parameter affecting waste glass durability. Other identified primary parameters include the waste temperature, radiation fields, glass composition, and weathering of the glass to form alteration phases. Detailed critical reviews of how each of these parameters affects waste glasses are part of this task, as is a review of models for evaluating waste performance.

B. Objectives

The purpose of the Critical Review Task is to review the existing literature in order to evaluate the state of knowledge regarding the influence of each of the identified critical parameters on glass reaction. Each review will be issued as a stand-alone document; they already have been integrated into a summary document, *High-Level Nuclear Waste Borosilicate Glass: A Compendium of Corrosion Characteristics* [7] that was published in FY 1994. The results from this Task will be used to support start-up of the DWPF and WVDP, and provide input to the development of high-level waste forms for the TWRS program and for wastes at the Idaho National Engineering Laboratory (INEL).

C. Technical Approach

The technical approach for this task has been to assemble all known and pertinent sources of scientific literature on how each critical parameter affects nuclear waste glass reaction and to objectively and critically consider the current state of knowledge. We have included reviews and discussions on materials other than nuclear waste glasses when we considered it useful to relate waste glass reaction to the parameter being reviewed.

D. Results and Discussion

A preliminary critical review has already been performed to provide a foundation for subsequent detailed reviews of each parameter [8]. The first detailed report, which reviews the effects of temperature on waste glass performance, has been issued [9].

The parameters reviewed during FY 1994 were predictive glass reaction models, the effect of glass composition on durability, the role that SA/V plays in controlling glass reaction and solution chemistry, and the effects of radiation on glass reaction.

The report on glass performance modeling [10] described the use of mechanistic chemical models to predict the rate at which radionuclides will be released from the glass under repository conditions. The most successful and useful of these models link reaction path geochemical modeling programs with a glass dissolution rate law that is consistent with transition state theory. These models have been used to simulate several types of short-term laboratory tests of glass dissolution and to predict the long-term performance of the glass in a repository. Although mechanistically based, the current models are limited by a lack of unambiguous experimental support for some of their assumptions; notable is the lack of an experimental validation of the mechanism that controls long-term glass dissolution rates. Thus, models need to be improved by performing carefully designed, long-term experiments, and using the results to validate the rate-controlling mechanisms implicit in the models. The mechanistic basis of the models should be explored by using modern molecular simulations, such as molecular orbital and molecular dynamics, to investigate both the glass structure and its dissolution process.

The review of radiation effects on waste glass behavior [11] recognized that the collisions and ionizations caused by radiation can damage solid glass materials through bond alterations and atomic displacements. This type of damage was shown to induce minor volume changes in the glass, increase fracture toughness, induce phase separations, and increase the release rates of glass components up to four-fold during subsequent corrosion tests. Solid-phase radiation damage may also enhance the release of intermediate decay-series daughter radionuclides from damage tracks in the glass. Under actual disposal conditions, however, glass annealing processes may negate most of the solid radiation damage effects.

The release of glass components, including radionuclides, into solution may be changed by the presence of radiolytically produced nitric acid, carboxylic acid, and transient water dissociation products, such as $\bullet\text{OH}$ and O_2^- . In batch tests, gamma and alpha irradiation increased glass corrosion a maximum of three- to fivefold over controls, while in other studies, the presence of radiolytic products actually decreased the release rates of some glass components. Bicarbonate in groundwaters will buffer against pH decreases, and the resultant corrosion rate increases, arising from the formation of radiolytic acids. Under the high SA/V conditions characteristic of an unsaturated repository setting, however, the bicarbonate buffering reservoir may be rapidly overwhelmed by radiolytic acids that are concentrated in the thin films of water contacting the samples. Glass reaction rates have been shown to increase 10- to 15-fold under these conditions because of radiation exposure.

Areas where more information is needed on radiation effects include: (1) the extent of selective release of intermediate decay-series radionuclides along damage tracks, (2) repository-relevant testing of glass annealing, (3) radiation-induced phase separation, (4) mechanistic understanding of radiolysis product interaction in glass corrosion, (5) repository-relevant testing of glass under high SA/V conditions, (6) the influence of alteration phases on glass dissolution and radionuclide migration, (7) alpha radiation effects on solution composition, and (8) comparisons between simulated and fully radioactive glass reactions.

The review of glass composition effects [12] on durability centered on the role of composition in determining the progression of glass corrosion.

The path of glass corrosion is divided into three distinct stages: (1) the short-term stage, in which the solution is still dilute with respect to glass corrosion products; (2) the intermediate stage, in which the concentration of glass components is relatively high; and (3) the long-term stage, in which the concentrations of most glass components are so high that crystalline phases precipitate from solution. Note that corrosion will follow this path regardless of whether or not the glass in question is an alkali borosilicate glass, though the details of the corrosion path depend on the identities and concentrations of components released into solution.

The interactions between glass and solution, and between glass, solution, and secondary crystalline phases, have characteristic effects on the rate of glass corrosion. These effects are depicted schematically in Fig. 1. In the short-term stage, the chemical potential gradient between the glass components in the glass and the solution is steep; therefore, glass components are released to solution at a comparatively high rate. In particular, components that are highly soluble in water, such as alkalis and boron, are generally released to solution at a disproportionately high rate compared to less soluble components, such as zirconium. This results in the formation of a layer on the glass surface that is depleted in soluble components relative to the bulk glass. As the concentration of components approaches the saturation concentration of crystalline phases, the chemical potential gradient between glass and solution flattens, and the rate of glass reaction slows. In static tests of the reaction of alkali borosilicate glasses with aqueous solution, this stage is characterized by relatively high solution pH, which increases the solubility and rate of reaction of the SiO_2 component of the glass. In the long-term stage, crystalline phases act as "sinks" for less soluble glass components. The chemical potential gradient between glass and the crystalline phase assemblage is steeper than that between the crystal and solution, and thus the rate of glass corrosion will change. Whether this change is large or small depends on the identity, distribution, and surface area of the secondary crystalline phases, but in general the result will be an increase in the corrosion rate. Moreover, the first phase assemblage to form is unlikely to be the final phase assemblage because the solution will continue to evolve and the crystals may end up in reaction relationships with one another. Therefore, the long-term stage is unlikely to be characterized by a single reaction rate, but rather a variable rate that accelerates or decelerates with changes in the phase assemblage.

Fig. 1. Generalization of the Reaction Pathway Followed by Glass. Test methods are shown that can be used to reach each stage in the reaction progress. (See reference [12] for a full discussion of the test methods.)

The report reviewed the known effects of waste glass composition on durability, as well as the tests that have been developed to determine the durability of glasses. It was shown that the tests that most accurately probe the resistance of a glass to chemical attack by water are those in which the glass components released to solution remain extremely dilute. (Otherwise, the buildup of corrosion products results in feedback between the evolving solution and the glass. The response of the glass to changes in solution chemistry will, in turn, cause further evolution of the solution, etc.) These "solution-dominated" conditions are best obtained in tests that use low-surface-area samples in a large volume of solution, such as short-term MCC-1 tests. Even better are Soxhlet or flow-through tests, conducted at moderately high flow rates. By the same token, short-term tests designed to verify product consistency, such as the PCT, may not be appropriate for determining the compositional dependence of waste glass corrosion.

Because the results obtained in "glass-dominated" tests depend on the details of the experimental setup, the relationship between glass performance and composition is not necessarily revealed in such tests. On the other hand, glass-dominated tests such as long-term MCC-1, PCT, and vapor hydration tests provide important information about the response of the glass to changes in solution chemistry that are produced by the buildup of corrosion products in the solution. This information is needed as input to long-term modeling of waste glass performance. It is particularly important to determine the identity, order of appearance, and quantity of secondary mineral phases produced when the solution becomes saturated in their components, because certain secondary crystalline phases are known to have an adverse effect on waste glass corrosion rate. Also, the rates of release of radionuclides and RCRA metals are needed, to verify that release rates in the long term will meet current regulatory limits.

On an atomic level, the aqueous corrosion of a glass requires the destruction of cation-anion bonding arrangements in the glass and the formation of new bonding arrangements, either in an altered layer or in the solution. This suggests that a limiting factor in glass corrosion is the strength of local cation-anion bonds. Local atomic arrangements in borosilicate and aluminosilicate glasses were reviewed to identify the components that form the strongest cation-anion bonds in these glasses, and to show how sharing of oxygen atoms in the glass by different cations may enhance cation-anion bond strength. The strongest bonds are between those oxygen and silicon atoms; less strong are those between oxygen atoms and small trivalent cations, which share the oxygens with low-valence alkali or alkaline earth cations; and weakest are bonds between oxygen atoms and combinations of high-valence and low-valence cations that share the same oxygen atoms. When bond strengths depend on the presence of two or more different cations, small changes in glass composition may produce a very large change in durability, as measured in solution-dominated durability tests, or may cause variations in the rheologic properties of the melt from which the glass is formed.

This local-atomic-arrangement approach to the description of glass corrosion can predict the response of glasses to aqueous attack in solution-dominated tests. Simple glasses, containing components involved in mutual bonding interactions, tend to be more durable than those containing a smaller number of components that are not involved in such interactions. Especially important are the interactions between alkali cations and aluminum or boron, and between alkali cations and large, high-valence cations, such as zirconium. Experimental observations of corrosion in simple glasses have directly influenced the interpretation of results of short-term, solution-dominated tests of candidate waste glasses. In particular, the addition of components whose chemistry is strongly coupled with the chemistry of alkali cations markedly enhanced waste glass durability.

This background information and a large database of solution-dominated test results for multi-component glasses were used to evaluate the merits of four models that purport to explain the compositional dependence of glass durability. It was shown that thermodynamic approaches that rely on estimates of the free energy of dissolution (the free-energy-of-hydration model) of a

glass, or on estimates of the average strength of cation-anion bonds (the structural-bond-strength model), are strongly correlated with measures of the release of glass components to solution; however, these models predict the rate of corrosion for individual glasses poorly. A structural model that treats alkali cations as the only components that decrease glass durability (the valence-oxygen model) was shown to describe the overall compositional dependence of glass corrosion at least as well as the thermodynamic approach, but this model is also a poor predictor of the performance of individual glasses. Finally, a very simple model of glass chemistry that estimates the number of nonbridging oxygen atoms in a glass (the nonbridging-oxygen model) was shown to be a poor predictor of the compositional dependence of glass corrosion because it does not take into account the true complexity of bonding interactions in the glass.

The use of these and other models for predicting the long-term performance of waste glasses in repositories was also discussed. Short-term durability test results are generally incorporated into long-term corrosion models as measures of the forward rate of the corrosion process. Models that accurately predict forward corrosion rates might potentially be of use in these long-term models. Most long-term corrosion models require empirical observations as input, such as the saturation concentrations of secondary crystalline phases, and, therefore, the sensitivity of their predictions to knowledge of the forward rate has not been established.

The most important conclusions from this review are as follows:

1. More experimental work is needed to isolate the roles of various cation and anion combinations in determining the response of glasses to aqueous attack. It is very important to (a) establish whether the addition to a glass of components that have low solubilities in aqueous solution will invariably increase glass durability, and (b) identify which cations are most likely to form dependent relationships in their bonding interactions with oxygen atoms in glasses and waste glasses.
2. Thermodynamic and structural models of the compositional dependence of glass and waste glass durability should be modified to take better advantage of the known bonding arrangements in glasses. For example, the free-energy-of-hydration model would benefit from a more realistic set of glass components, and the structural-bond-strength model would benefit from use of glass components rather than simple oxides. Use of more realistic components would more accurately reflect the true bonding interactions in the glass and would reduce the magnitude of highly nonlinear thermodynamic mixing terms.
3. The predictive capabilities of the models reviewed in this study are probably not sufficient for predicting the long-term performance of waste glasses.

E. Future Progress

Reports were also written to evaluate the effects of SA/V and unsaturated conditions on glass reaction. These reports are undergoing review and revision and will be published in FY 1995.

In addition to critically reviewing the literature on selected parameters, we compiled Data Reports to present all of the data generated from the testing tasks of this program. These Data Reports may be included with the Critical Review reports or may be issued as stand-alone documents. Data reports are being written on the testing of radioactive glasses and on radiation effects on glass reaction. These reports will be published in FY 1995.

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IV. LONG-TERM TESTING OF FULLY RADIOACTIVE GLASS

A. Introduction and Background

The source term for the release of radionuclides from a nuclear waste repository is the waste form. Evaluation of the performance of the repository and the engineered barrier system (EBS) against regulations established by the Nuclear Regulatory Commission and the Environmental Protection Agency requires that (1) factors be assumed regarding the reaction of waste form (glass) and radionuclide release, and bounding limits placed on the role of the source term in calculating release from the EBS and the boundary of the repository; or (2) a predictive model be developed, based on a mechanistic interpretation of the radionuclide release as a function of reaction progress, and validated by using tests done under a variety of different potential reaction conditions.

The problem with the first approach is that there is little experience to draw upon when evaluating glass waste form reaction under unsaturated conditions, such that the error in applying expert judgment to the problem may be unacceptably large. The alternative approach, testing and modeling the glass reaction progress, is a more defensible means of providing input to the prediction of radionuclide release and performance of the repository, because information related to the source term has a technical basis and will provide an essential starting point to make more reasonable assumptions regarding the remainder of the EBS and repository performance. Keys to obtaining the necessary input are in establishing and understanding the reaction progress, that is, the corrosion rate as a function of time and reaction conditions and the manner in which the radionuclides are released to solution.

Most performance evaluation of high-level waste glass used simulated, nonradioactive analogs of the same nominal composition as the radioactive glass. To apply the knowledge gained in those studies to the assessment of the performance of the fully radioactive production glass, it must be demonstrated that experiments with simulated glasses are an adequate representation of the reaction that will occur with the actual production glasses. Also, to obtain information regarding the performance of radionuclides, tests must be done with radioactive glasses. To fully assess glass performance it is necessary to address the following:

1. Do both the radioactive and simulated glasses react through the same controlling mechanism, thereby producing the same secondary phases in the same sequence?
2. Is there an effect due to the radioactivity, which is not adequately simulated when using the nonradioactive glass?
3. What is the relevance to the actual production process of using glass that may not contain all the nonradioactive components present in the sludge, supernate, and frit feeds? (Simulated glasses are generally produced with pure starting materials and the minor components are ignored.)
4. Is there a difference in reactivity between the two glass types?

Comparison studies on the performance of fully radioactive and simulated nuclear waste glasses [13-19] assessed these questions. Most of the studies [13-16] were performed at low to intermediate SA/V ($\leq 1100 \text{ m}^{-1}$) in static batch test for periods of less than one year. The general conclusion from these studies is that there is little difference in the reactivity between the two glass types. The comparison study reported here reinvestigated that conclusion by evaluating glass performance under conditions that are more applicable to the prediction of long-term performance, and which built on previous testing of radioactive glasses by WSRC [20-24]. The studies reported

here were done in the batch mode for longer time periods at higher SA/V values, such that the reaction process was accelerated, and also in a dripping water mode to evaluate conditions that are more relevant to an unsaturated repository.

B. Objectives

The objective of this task is to evaluate the performance of fully radioactive glasses, similar to those that will be produced by the DWPF, in meeting the performance objectives for glass storage in a high-level waste repository, with emphasis on conditions that may be encountered in an unsaturated horizon. Specifically, long-term data will be generated such that (1) reaction of fully radioactive glass can be compared with that of nonradioactive glass with a similar nominal composition; (2) interactions between waste package components that must be accounted for in independent reaction path models are identified; and (3) the long-term behavior of glass is established under anticipated disposal conditions, such that glass performance models can be validated.

To meet the above objectives we evaluated (1) how the glass reaction progressed along its long-term reaction progress as predicted by models of glass reaction (Fig. 1), and (2) the release of radionuclides from the glass. To evaluate radionuclide release, we measured the amount of an isotope released from the glass, and determined its distribution between dissolution, suspension in solution as colloidal material, and sorption onto metal components of the test. The fractional components together make up the total release of radioactivity and can be used as input to evaluate the performance of glass under a repository setting.

C. Technical Approach

To provide information that can be fully used in evaluating the performance of glass throughout its reaction progress, tests must cover a range of conditions and times. The goal is to provide information regarding the "final" portion of the reaction progress, since that information is most relevant to long-term performance, and to evaluate factors that can be used as source term input for EBS design and repository assessment. An unsaturated environment presents a challenge in performing long-term testing because the conditions, in particular the amount of water available to react with the glass and to transport radionuclides, are expected to change, perhaps significantly, over the duration of storage.

Tests to evaluate the performance of glass in an unsaturated environment must address the unique features of such an environment and must be performed for time periods long enough so that the stage is reached where secondary phase formation (as opposed to supersaturated solution concentrations) controls the glass reaction. Relevant tests include static and intermittent-flow tests performed at high SA/V ratios to simulate the waste package environment. The information obtained from these tests must include the solution composition as a function of time, combined with a description of the glass alteration. To meet these goals, three types of tests are being performed:

- (1) Long-term static tests (i.e., no water flow) at high SA/V with monoliths and powders. These tests provide temporal solution trends, plus easy identification of secondary phases combined with the distribution of radionuclides in the reacted glass layers.
- (2) Long-term intermittent flow tests at high SA/V following a modified version of the Unsaturated Test Procedure [25] as applied to "aged" and fresh glass monoliths.
- (3) Long-term repository environment tests following the laboratory analog procedure as applied to "aged" and fresh glass monoliths [26].

The tests are being performed with the three different general groups of glass compositions: 165-, 200-, and 131-frit based glasses (Table 1). The tests in each test category, including status and results/discussion, are described below.

D. Results and Discussion

1. Long-Term Static Tests

To date, 160 of the planned 212 long-term tests have been terminated. The longest tests have been in progress for more than 55 months. For a complete test matrix and the status of the tests, refer to Table 3. The solution analyses of all the terminated tests, which include analyses on leachate pH values, cations, selected anions, total carbon, and actinides, are about 95% complete. The surface analyses on the terminated samples are also nearly complete and include optical microscopy (OM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS), and transmission electron microscopy with associated analytical equipment (AEM).

a. Blank Tests

A series of static blank tests are in progress to monitor the concentration changes in EJ-13 water (see Table 2) with time. These background cation concentrations associated with the test water are subtracted from the total cation concentration in the leachant. Over time several trends have been observed regarding the major cations in the EJ-13 water. The elemental concentrations of Na, K, B, and Li remain constant with time, those of Si, Ca, and Al decrease slightly, and the concentrations of Fe, Ni, Cr, and Cu increase because of interaction with the stainless steel test vessel.

b. Tests with SRL 200 Glasses

Tests were performed at SA/V values of 340, 2000 and 20,000 m^{-1} to cover the reaction progress of glass (see Fig. 1). The tests at 340 m^{-1} , provide information regarding the initial stage of the reaction progress, tests at 2000 m^{-1} , the interim stage, and tests at 20,000 m^{-1} , the final stage. The test durations are now sufficient that meaningful insight can be provided into each stage of glass reaction.

Elemental releases normalized to SA and elemental concentration, $(\text{NL})_i$, for Li, Na, B, and Si, and solution pH values are given in Figs. 2, 4, and 6, for SA/V values of 340, 2000, and 20,000 m^{-1} , respectively. Figure 2 shows the results for the R and S glasses at 340 m^{-1} . These tests have been completed through the 728-day period and show that the release from the 200R glass is slightly less than that from the 200S glass. The largest difference in $(\text{NL})_i$ is about 30%. This is consistent with the observation that the pH in the tests with the R glasses is about 0.5 pH unit lower than in the S glass tests. The pH difference is probably due to the radiation field present with the R glasses, which, because of the small volume of water in the tests (2 mL of water with four glass monoliths), results in radiolysis of the air in the test vessel and subsequent dissolution of the products. Small changes were measured in the anionic content of the leachate, which confirms this hypothesis.

The reaction of the SRL 200 glasses at 340 m^{-1} demonstrated the behavior expected for stages 1 and 2 of the reaction progress. Initially, the reaction was rapid as the solution concentration of silicic acid increased, but after about 200 days the reaction rate had slowed and became nearly constant as the reaction reached stage 2. Analysis of the reacted surface of these glasses (Fig. 3) showed that a clay layer had formed, but no other secondary phases

Table 3. Test Matrix^a for Long-Term Static Tests at High SA/V Ratios (duration in days)

Reaction Progress, ^b day•m ⁻¹	131 Glass Type ^c				200 Glass Type ^d						165 Glass Type ^d				Blank ^c
	131/11R		131/11S		200R			200S			165/42R		165/42S		
	340	2000	340	2000	340	2000	20,000	340	2000	20,000	340	2000	340	2000	
1,020															3
2,380															7
4,760					14 ^e			14							14
6,000						3			3						28
9,520	28		28								28		28		56
14,000															70
19,040					56			56							91
28,000						14			14						98
30,940	91		91								91		91		140
60,000		30		30								30		30	182
61,880					182			182							238
123,760	364		364		364			364			364		364		280
140,000		70		70		70			70			70		70	364
247,520	728		728		728			728			728		728		546
280,000		140		140			15			15		140		140	728
495,000	1456		1456		1456			1456			1456		1456		980
560,000		280		280		280			280			280		280	1456
990,080	2912		2912		2912			2912			2912		2912		1820
1,120,000		560		560		560	56		560	56		560		560	2912
1,960,000		980		980		980	98		980	98		980		980	TBD
3,649,000		1820		1820		1820	182		1820	182		1820		1820	TBD
7,280,000							364			364					TBD
10,920,000							546			546					TBD
14,560,000							728			728					
					TBD ^f	TBD	TBD	TBD	TBD	TBD ^g	TBD	TBD	TBD	TBD	
					TBD	TBD	TBD	TBD	TBD	TBD					

^aThe tests done at 340 m⁻¹ used monoliths, the tests done at 2000 and 20,000 m⁻¹ used powder.

^bReaction Progress in terms of SA/V•t (units of day•m⁻¹). No significance is implied to the use of this reaction progress indicator.

^cTests are single tests.

^dTests are duplicate.

^eThe underlined tests are terminated.

^fTBD represents to be determined.

^gTBDs were terminated on 330, 390, and 1095 days.

Fig. 2. Normalized Release of (a) Li and Si and (b) Na and B from both 200R and 200S Glasses Reacted at 90°C and 340 m^{-1} . In (c) the solution pH is shown.

Fig. 3. Photomicrographs of Cross Sections of 200R Glasses Reacted for 728 Days at 90°C and 340 m⁻¹. The micrographs were obtained using transmission electron microscopy (TEM).

typical of stage 3 of the reaction progress. Thus, in 720 days the reaction of 200 R and S glasses progressed to stage 2, but, based on the pH values (<10), stage 3 will not be reached for a long time.

The reaction progress at 2000 m^{-1} is shown in Fig. 4. Results were similar to those of the 340 m^{-1} tests in that the R glass always corroded less than the S glasses throughout the 560 days. The largest differences observed were about 30%. This difference in reactivity is considered small, especially in light of the minor differences in the glass compositions, and, when the similarity in reacted layer morphology is taken into account, these glasses can be considered to have very similar corrosion behavior. The leachate pH from the 200S glass was always higher than that of the 200R glass by as much as 0.5 pH unit. The reacted surfaces of the R and S glasses, shown for 980 days in Fig. 5, were similar and also resembled the 340 m^{-1} samples. A clay layer had formed, but there was no evidence of other secondary phases forming.

In the tests at 2000 m^{-1} , the reaction reached stage 2 and proceeded further toward stage 3 than in the tests at 340 m^{-1} , as indicated by the pH of the leachates which have reached 11 (R) and 11.5 (S) after 300 days. It is not until the pH reaches values higher than about 11.7 that secondary phase formation begins, resulting in the onset of stage 3 of the reaction progress (see discussion of $20,000\text{ m}^{-1}$ test, below).

The reaction at $20,000\text{ m}^{-1}$ is shown in Fig. 6. The general observation that the R glasses react at a slower rate than the S glasses still holds for this test, and the difference is magnified in that the S glass reached stage 3 in the reaction progress while the R glass was still in stage 2. Evidence for this conclusion is that (1) the reaction rate for the 200S glass increased between 182 and 546 days such that $(\text{NL})_B$ was about 40 gm/m^2 at 364 days, (approximately 40 times higher than the release for the R glass); (2) the leachate pH for the S glass reached 12.12 (0.61 units higher than the R glass for the same time period); and (3) the S glass transformed into an assemblage of secondary phases, with very little unreacted glass remaining. Because of this transformation, the actual $(\text{NL})_i$ values need to be adjusted to the decreasing SA available for reaction. This adjustment has not yet been made because of uncertainty as to the exact onset of the accelerated reaction. The virtual completion of the glass reaction, and the accompanying decrease in available SA, resulted in very small increases in the normalized release values after 364 days.

The onset of stage 3 of the 200S glass reaction is attributed to the nucleation of secondary phases that decrease the concentration of Si in solution, thereby increasing the propensity of the glass to react. The solution chemistry, as measured by the pH, and the concentration of major mineral-forming elements cause the phases to become stable and nucleate. The lower pH of the R test leachate implies that conditions were not reached for the R glass to support secondary phase formation and the onset of stage 3 reaction. The major source of the radiation field in the R glass is gamma and beta radiation from the decay of ^{137}Cs and ^{90}Sr , and the alpha field generated by the transuranic elements. The gamma and beta radiation are able to penetrate the leachant in the present test configuration, but the alpha particles cannot. Thus, it is likely that, in the absence of these short-lived radionuclides, the R and S glasses would both reach stage 3 in the current test setup. In an unsaturated repository environment it is unlikely that the glass in the pour canister will be crushed to create a high SA/V condition, but this condition will prevail, due to a decrease in the solution volume. With a small solution volume, it may be possible for the alpha radiation to penetrate the water, and the resulting radiation effect may slow the onset of the stage 3 reaction.

Fig. 4. Normalized Release of (a) Li and Si and (b) Na and B from both 200R and 200S Glasses Reacted at 90°C and 2000 m⁻¹. In (c) the solution pH is shown.

(a)

(b)

Fig. 5. Photomicrographs of Cross Sections of (a) 200S and (b) 200R Glass Reacted for 980 Days at 90°C and 2000 m^{-1} . The micrographs were obtained using TEM.

Fig. 6. Normalized Release of (a) Li and Si and (b) Na and B from both 200R and 200S Glasses Reacted at 90°C and 20,000 m⁻¹. In (c) the solution pH is shown.

c. Tests with SRL 165/42 Glasses

The corrosion behavior of 165/42 R and S glasses is shown in Figs. 7 and 8, for SA/V ratios of 340 and 2000 m⁻¹, respectively. (No tests at 20,000 m⁻¹ were performed with this glass since the composition is not one that is anticipated for production at the DWPF.) These tests were designed to evaluate the difference in reactivity of R and S glasses. At 340 m⁻¹ the leachate pH was slightly higher for the S glass than the R glass, but the (NL)_i values for the major glass elements were similar. These results, coupled with analysis of the glass surfaces (not shown) demonstrate similar reactions for the R and S glasses under these test conditions up to 1456 days.

At 2000 m⁻¹, the releases from the R glass were faster than from the S glass (Fig. 8). The largest differences were factors of 2.25 and 1.35, for B and Na, respectively. These differences, over a time period of 980 days, are small and could easily be due to minor compositional differences between the R and S glasses. The leachate pH values were similar for the two glass types. Thus, there appears to be little difference in corrosion between the R and S glasses at 2000 m⁻¹.

d. Tests with SRL 131/11 Glasses

Figure 9 shows that reaction trends and (NL)_i values for B, Li, Na, and Si were similar for R and S glasses at 340 m⁻¹. There is an indication from the last data point of the 720-day time period that the S glass corroded faster than the R glass, but this will have to be confirmed with longer-term data (at this time only the 1456-day R glass test has been completed). The leachate pH values were also similar for both glasses, which reinforces the general conclusion that at 340 m⁻¹ there is little difference in reactivity between the R and S glasses over the test period.

At 2000 m⁻¹, similar release trends were observed for Li and Si through 980 days of reaction (Fig. 10). However, the releases of B and Na from the S glasses were faster than from the R glasses by factors of 1.8 and 1.4, respectively. The corrosion behavior of the SRL 131/11 glasses at 2000 m⁻¹ was similar to the corrosion behavior of the SRL 200 glass in that the S glass corroded faster than the R glass, while the opposite is true for the SRL 165/42 glasses.

e. Radionuclide Release

Release of the radionuclides, ²⁴¹Am, ²⁴⁴Cm, ²³⁸Pu, ²³⁹Pu, ²³⁷Np, ¹³⁷Cs, ^{154,155}Eu, ⁶⁰Co, and ¹²⁵Sb, from the radioactive glasses was monitored. After a predetermined test duration, the test vessels were removed from the oven and opened. An aliquot of the leachate was removed directly from the vessel at test temperature, deposited on a planchet, and analyzed by alpha spectroscopy. Another aliquot was wicked through a "holey" carbon TEM grid to collect suspended material. The leachate was then filtered through a 0.45-μm cartridge filter at test temperature, and another aliquot, taken for analysis by alpha spectroscopy. After cooling, an aliquot of the leachate was filtered through an Amicon model CF50A filter, which has an effective filter size of about 6 nm. This aliquot was also analyzed by using alpha spectroscopy.

The remaining test solution was then submitted for detection of radionuclides by gamma counting and by ICP-MS. A portion of the ICP-MS solution was also used for electrodeposition followed by alpha spectroscopy. The test vessel was then soaked with dilute nitric acid overnight at 90°C to strip any elements that may have sorbed to the vessel walls. The strip solutions were analyzed using alpha and gamma spectroscopy and ICP-MS. By assaying the same radionuclides using different techniques, we determined their distribution between "truly dissolved," "suspended" and "colloidal," and "precipitated" material sorbed to the metal

Fig. 7. Normalized Release of (a) Li and Si and (b) Na and B from 165/42R and 165/42S Glasses Reacted at 90°C and 340 m⁻¹. In (c) the solution pH is shown.

Fig. 8. Normalized Release of (a) Li and Si and (b) Na and B from 165/42R and 165/42S Glasses Reacted at 90°C and 2000 m⁻¹. The solution pH is shown in (c).

Fig. 9. Normalized Release of (a) Li and Si and (b) Na and B from 131/11R and 131/11S Glasses Reacted at 90°C and 340 m⁻¹. The solution pH is shown in (c).

Fig. 10. Normalized Release of (a) Li and Si and (b) Na and B from 131/11R and 131/11S Glasses Reacted at 90°C and 2000 m⁻¹. The solution pH is shown in (c).

components of the test. The criteria used to assess the radionuclide fractions were: "suspended" — the leachate fraction that was directly collected from the test vessel or that passed through a 0.45- μm filter but not through a 6-nm filter; "dissolved" — the leachate fraction that passed through the 6-nm filter; and "precipitated" — the fraction fixed to the stainless steel vessels, which was measured from the acid strip solution. The total radionuclide release is the sum of dissolved, suspended, and precipitated fractions. Radionuclides not found in these fractions are assumed to remain associated with the altered glass (see retention factor discussion later). These analyses resulted in an extensive compilation of data, which will be presented in the Data Report for the Long-Term Testing of Fully Radioactive Glass Task. In this annual report, only preliminary results from some of the techniques are presented.

Cesium-137 is expected to form mainly soluble compounds and to be found in the dissolved fraction. Based on gamma counting of the solution fractions, this was true for all glasses at 340, 2000, and 20,000 m^{-1} for periods up to 728 days. At higher SA/V, such as 2000 and 20,000 m^{-1} , 10 to 100 times more ^{137}Cs was in the dissolved fraction than in the precipitated fraction, and about 1 to 10 times more at 340 m^{-1} . There are two data points for the 165/42R glass that show the opposite effect, i.e., there was more ^{137}Cs precipitated onto the stainless steel than in the dissolved fraction. These results will have to be verified.

Curium-244 was mainly fixed to the stainless steel vessels, and a small fraction was suspended material in the form of colloids. This was observed for all glass types. At 340 m^{-1} , the about 5 to 100 times more radioactivity was fixed to stainless steel than in colloidal form, and 10 to 100 times more was precipitated than in the dissolved fraction. At SA/V values of 2000 and 20,000 m^{-1} , the ^{244}Cm was more evenly distributed among the precipitated, colloidal, and dissolved fractions than at 340 m^{-1} .

About 2 to 100 times more ^{237}Np was counted in the colloidal fraction than in the dissolved fraction, but most was fixed to the stainless steel vessels. The SA/V affects ^{237}Np distribution in a similar fashion to that observed for other radionuclides, i.e., at 2000 and 20,000 m^{-1} the ^{237}Np was more evenly distributed among the dissolved, suspended, and precipitated fractions than at 340 m^{-1} .

The available data indicate that, except for ^{137}Cs , the radionuclides are preferentially fixed to the stainless steel vessels. It is possible that the radionuclides sorbed to the vessels may be mobilized as the metal corrodes or as the solution chemistry changes. The dissolved fraction is assumed to be fully mobile, whereas the mobility of the suspended fraction (colloids) will depend on the environment.

f. Future Progress

The data that have been generated to date are being compiled into a data report. This report, while not including all of the data to be generated during the finalization of the test matrix, will provide results through about 1456 days of testing, which is the longest period for which data is available on the reaction of fully radioactive glasses under a wide range of conditions. The report is scheduled for release in FY 1995.

The ongoing static tests will be continued, as tests are scheduled to be continued through eight years. Data generated from solution analyses will be combined with surface layer studies to compare more completely the reactivity of the radioactive and simulated waste glasses and to provide a data base for validation of glass performance models. Several tests of to-be-determined duration will be terminated to confirm the observed trends.

2. Long-Term Intermittent Flow Tests

The long-term intermittent flow tests are being conducted using a modified version of the Unsaturated Test, or drip test procedure developed by the YMP, to assess glass performance in an unsaturated environment [26,27]. The standard drip test matrix was modified to include effects of aging both the glass and metal components to make the results more relevant to an actual storage environment. The tests are being performed with 200R glass, and the objectives of the tests are to provide (1) data that describe the release of radionuclides from a specifically designed waste package under strictly controlled test conditions and (2) information concerning synergistic effects that may occur between waste package components. Radionuclide release is evaluated as both the amount dissolved in solution and the fraction associated with particles suspended in solution.

a. Status

The test matrix is shown in Table 4. There are two sets of five replicate tests and one blank test. The test periods have been modified from the matrix presented in the FY 1991 report [2] to collect more solution for analyses and to allow for more flexibility in hot-cell operations.

The first set of five tests (N4-1 to N4-5) is being done with aged components. The glass was aged by contact with water vapor at 200°C. This reaction accelerated hydration of the glass such that the outer surface of the glass was transformed into stable crystalline phases. Two degrees of hydration aging were obtained by reacting the glass samples for two and four weeks. Two tests (one batch and one continuous) are being done with the four-week hydrated glass, and three tests (one batch and two continuous) are being done with the two-week hydrated glass. The hydration of glass in a vapor environment is not only a process that can be used to age the glass in the laboratory, but also a process that likely will occur in the repository. Glass aging could occur in a steam environment if containment breach occurs before the temperature of the waste package cools below 95°C. However, the rate of aging is expected to be low under these conditions because, while the atmosphere is steam saturated, the relative humidity drops below 100% because the pressure remains at ambient. Glass reaction in vapor where the relative humidity is less than 80% is known to be quite slow.

Glass aging could also occur in a vapor environment if a breach occurs at a temperature below ~95°C prior to ingress of liquid water. The latter case is the expected environment for the unsaturated repository; thus, the present tests are being done to induce a degree of vapor hydration aging that likely will occur in the repository. However, a direct relationship between temperatures and the aging rate for 200R glass has not been established, so the relative aging imparted to the glass is now known with certainty. It is anticipated that the relationship between time, temperature, and extent of vapor hydration will be developed by the Yucca Mountain Site Characterization Project.

The second set of five tests (N4-6 to N4-10) is being performed with unaged or as-cast glass, and the results will be comparable with previous test series using the Unsaturated Test method [27]. These tests represent the scenario whereby the container and pour canister are breached at a time after liquid water has penetrated the waste package environment and liquid water immediately passes through one breach, contacts and reacts with the glass, and passes out through a second breach. This scenario is unlikely; nevertheless, it represents a bounding condition with fresh glass, and the results will form a basis for comparison with tests done with aged components.

Table 4. Test Matrix for Long-Term Intermittent Flow Tests at High SA/V Ratios

Test No.	Test Type ^a	Components ^{b,c}	Test Duration, weeks							
			0	18	55	85	114	143	169	195
N4-1	Batch	4-week-aged glass & 304L SS holder	_____							
-2	Continuous	4-week-aged glass & 304L SS holder	_____✓_____✓_____✓_____✓_____✓_____✓_____→							
-3	Batch	2-week-aged glass & 304L SS holder	_____							
-4	Continuous	2-week-aged glass & 304L SS holder	_____✓_____✓_____✓_____✓_____✓_____✓_____→							
-5	Continuous	2-week-aged glass & 304L SS holder	_____✓_____✓_____✓_____✓_____✓_____✓_____→							
-6	Batch	glass, 304L SS holder	_____							
-7	Batch	glass, 304L SS holder	_____							
-8	Continuous	glass, 304L SS holder	_____✓_____✓_____✓_____✓_____✓_____✓_____→							
-9	Continuous	glass, 304L SS holder	_____✓_____✓_____✓_____✓_____✓_____✓_____→							
-10	Continuous	glass, 304L SS holder	_____✓_____✓_____✓_____✓_____✓_____✓_____→							
-11	Continuous	blank	_____✓_____✓_____✓_____✓_____✓_____✓_____→							

^aThe continuous tests are sampled approximately every 30 weeks after the 55-week period.

^bIn tests 6-10, the 304L SS holder is partially sensitized; in tests 1-5, the 304L SS holder is partially sensitized and then subjected to an aging process along with the glass.

^cIn tests 6-10, the glass is unaged (as-prepared). In tests 1-5, the glass is aged as indicated in the text.

There has been some variance from the matrix in that sampling was done at the 85- and 114-week periods, and two tests (N4-3 and N4-7) were terminated at the 114-week period. The sampling periods were adjusted from the original matrix to allow more water to be collected for analysis. This was required because a series of solution filtrations was added to investigate particle size distribution in solution, and these filtrations required ideally 1-2 mL of solution. For reference, about 5 mL of solution is retained in the test vessel after a year of testing. Samplings are now done at 6-month intervals.

b. Results and Discussion

The tests were sampled at six-month intervals during FY 1994, in March and September. After the September sampling, the tests had been in progress for 169 weeks. At each sampling period, the solutions were analyzed for cations, anions, total and organic carbon, pH, and radioelements, and the distribution of radioelements between dissolved, suspended (colloidal), and precipitated (sorbed) fractions was evaluated. The size distribution of the colloids was obtained via a sequential filtering technique, whereby an aliquot of the test solution was passed through a relatively coarse filter (1 μm) and then through filters of decreasing pore size. The smallest size was usually about 0.01 μm . Any material that passed through the final filter was considered to be dissolved. While some colloidal material may pass through a 0.01- μm filter, this is used as the cutoff because filters with smaller pore size cannot easily be dissolved for autoradiography of the filtered particles. We aim to segregate the particles on these filters for additional analyses using autoradiography and AEM. To further evaluate the colloidal fraction, a small portion of the test solution was passed through a perforated carbon grid. The colloidal material retained on the grid can be studied using Transmission Electron Microscopy (TEM, see Section IX).

The results of the solution analyses are shown in Table 5. There was a significant difference in the reaction and subsequent solution composition for the aged and as-cast glass. The solution pH values for the aged glass were consistently in the 11.0 to 11.7 range, while the as-cast glass solutions had pHs of about 8. Differences in the anion, cation, carbon, and radioelement release to solutions were also significant.

Major glass cations (such as Li, B, Na, and Si) were initially detected in solution at levels several hundred times greater for the aged glass than for as-cast glass [2]. This probably reflects that not all of the major elements are incorporated into stable alteration products as the glass is aged and forms a hydrated layer; thus, they are readily rinsed from the surface during initial contact with liquid water. In fact, the amounts of the major elements in solution has been steadily decreasing throughout the duration of the test. The results for Li and B, two elements that are normally released most rapidly from glass, are shown as total elemental release in Tables 6 and 7.

While normalized release values could be calculated for the as-cast glass by employing the rationale used in analyzing the long-term test results of drip tests on SRL 165 [27], a normalized release from the hydrated glass was more difficult to determine because of the unknown surface area that contacts the test solutions. For the as-cast glass tests (N4#8 and N4#9), the release trends were similar in that the release was initially small and then increases by about an order of magnitude (B release) for several years. The release of Li was less than B, which is to be expected based on the compositions shown in Table 1; however, the ratio of the B/Li release suggests that Li may be incorporated to a small extent into a secondary phase. This phase is probably the clay phase that forms on the surface of the glass.

Table 5. Analyses of pH, Carbon, and Anions in Leachates from the Drip Tests

Test No.	Sampling Period ^a	pH	Carbon (ppm)		Anions (ppm)							
			Organic	Inorganic	F ⁻	CHO ₂ ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻	C ₂ O ₄ ²⁻
8	10/31/91	7.97	15	15	4.6	<0.5	7.5	5.2	3.3	<1	104	2.8
	7/16/92	8.26	8	25	7.6	b	14	15	2.5	<1	38	11
	2/11/93	6.73	13	5	2.0	14	1	3	2.1	<1	6	11
	9/2/93	7.40	9	4	4.0	13	29	1	3.5	<1	23	6
	3/24/94	7.80	3	10	41.0	18	10	24	9.1	<0.5	48	14
	9/22/94	7.75	2	11	12.0	19	8	11	7.2	<0.5	22	<1
	3/23/95	8.05										
9	10/31/91	8.12	10	20	9.3	<0.5	9.4	9.0	4.0	<1	10	<0.7
	7/16/92	7.94	13	13	8.5	b	20	23	4.3	<1	60	11
	2/11/93	5.61	10	3	1.2	b	1.5	2	2.8	1.0	13	11
	9/2/93	7.94	27	149	61	188	73	11	184	<1	294	332
	3/24/94	7.58	3	5	34	14	6	44	28	<0.5	28	8.8
	9/22/94	7.60	0	2	<0.2	<0.5	1.6	0.4	2.9	<0.5	3.3	<1
	3/23/95	8.29										
10	10/31/91	8.60	20	25								
	7/16/92	8.55	13	35	5.3	b	5.2	6.7	2.4	<1	18	10
	2/11/93	6.42	12	3	1.5	12	1.4	2.1	2.5	<1	11	9.2
	9/2/93	8.72	25	32	20	30	20	5.3	6.2	<1	31	2
	3/24/94	8.03	5	12	32	10	13	53	65	<0.5	39	5.2
	9/22/94	8.65	2	33	24	25	25	33	11	<0.5	62	<1
	3/23/95	8.16										
6	terminated	8.45	11	36	5.7	b	10	13	1.9	<1	81	7.8
7	terminated	9.14	32	33	4.4	4.6	11	3.1	4.3	<1	55	3.8

contd.

Table 5 (contd.)

Test No.	Sampling Period ^a	pH	Carbon (ppm)		Anions (ppm)							
			Organic	Inorganic	F ⁻	CHO ₂ ⁻	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻	C ₂ O ₄ ²⁻
2	11/4/91	11.28	145	20			167	<15	<25	193	5660	<50
	7/20/92	11.27	108	6	11	b	71	<15	42	169	781	56
	2/15/93	11.26	140	77	6	<1	7	30	8	135	171	61
	9/7/93	11.68	28	141	12	79	25	5.5	31	274	151	<30
	3/28/94	11.48	12	134	6	35	13	53	56	149	60	35
	9/26/94	11.50	7	135	20	<1	14	20	17	141	52	<1
	3/27/95	10.93										
4	11/4/91	11.37	21	4			211	<15	<25	397	9870	<50
	7/20/92	11.13	113	210	11	b	47	<15	40	168	815	60
	2/15/93	11.62	52	77	11	22	11	22	7	147	162	69
	9/7/93	11.48	29	90	16	74	31	3.4	20	150	175	<30
	3/28/94	11.48	7	93	19	<10	11	30	26	70	53	18
	9/26/94	11.50	6	107	17	<1	13	18	20	78	47	<1
	3/27/95	11.39										
5	11/4/91	11.33	35	0			256	<15	<25	334	8840	66
	7/20/92	11.43	96	6	13	b	36	<15	44	197	886	<50
	2/15/93	11.27	44	90	8	24	14	23	7	140	209	80
	9/7/93	11.38	33	79	12	86	31	3.7	20	78	137	<30
	3/28/94	11.19	12	108	11	<10	10	39	68	24	65	18
	9/26/94	11.34	10	144	12	<1	11	17	16	25	51	<1
	3/27/95	11.39										
1	terminated	11.09	125	15	29	b	58	<15	74	286	2376	59
3	terminated	11.11	212	11	12	117	38	5.4	9.3	138	87	<30

^aTests 6-10 were initiated on 6/23/91 and tests 1-5 on 7/1/91.

^bThe F⁻ and CHO₂⁻ peaks were not resolved; thus, the values reported for F⁻ include a factor due to CHO₂⁻. Because the starting concentration of F⁻ in the EJ-13 water is ~3 ppm, the contribution due to CHO₂⁻ is significant.

Table 6. Elemental Release

Test #	Sampling Period	Elemental Release, μg^a	
		B	Li
8	10/31/91	2	9
	07/16/92	33	17
	02/11/93	17	2
	09/02/93	18	2
	03/24/94	59	22
	09/22/94	15	6
9	10/31/91	3	6
	07/16/92	29	8
	02/11/93	24	3
	09/02/93	NR ^b	NR ^b
	03/24/94	65	19
	09/22/94	4	1
10	10/31/91	81	21
	07/16/92	60	28
	02/11/93	20	3
	09/02/93	17	17
	03/24/94	56	17
	09/22/94	16	4
6	07/16/92	46	52
7	09/07/93	139	66

^aAmount of each element detected in the leachate for the designated sampling period.

^bNo solution remained in the test vessel at the end of the sampling period. The vessel was rinsed and the rinse solution was analyzed but no data are reported.

Table 7. Elemental Release

Test #	Sampling Period	Elemental Release, mg ^a	
		B	Li
2	11/04/91	41.6	2.3
	07/20/92	22.1	1.6
	02/15/93	8.4	0.7
	09/07/93	0.4	0.7
	03/28/94	2.2	0.7
	09/26/94	0.5	0.3
4	11/04/91	39.4	2.2
	07/20/92	19.4	1.2
	02/15/93	7.7	0.5
	09/07/93	4.1	0.5
	03/28/94	1.5	0.3
	09/26/94	0.6	0.3
5	11/04/91	32.6	1.6
	07/20/92	24.8	1.4
	02/15/93	9.3	0.7
	09/07/93	4.2	0.5
	03/28/94	2.2	0.3
	09/26/94	0.8	0.2
1	07/20/92	53.6	3.4
3	09/07/93	6.3	0.3

^aAmount of each element detected in the leachate for the designated sampling period.

For test N4#10, the initial release was generally greater than that for subsequent time periods. The Li release again suggests incorporation of Li into a secondary phase. The overall release for tests N4#10 was slightly greater than from tests N4#8 and N4#9.

The releases from the tests with the vapor hydrated glasses were at least three orders of magnitude greater than from the as-cast glass (note that the values in Table 7 are in milligrams). The trend in all of these tests is for declining releases, essentially for the entire test period. The release of Li was significantly less than that of B, suggesting that during the hydration process Li was incorporated into a secondary phase and was not as readily rinsed from the hydrated glass as B.

Anion release provides perhaps the most striking and significant difference in the solution chemistries between the two test types. Anion concentrations in starting glasses are generally not reported because they are minor components (<0.1 wt %), are difficult to analyze, and are thought to have little effect on glass reactivity when present in low levels. However, the potential for anions to complex radionuclides [28] adds significance to their concentrations in the leachates. As is presented in Table 5, the concentrations of SO_4^{2-} , Cl^- , and HPO_4^{2-} in the leachates from the aged glass tests were initially in the 150 to 10,000 ppm range, which is significantly

larger than in the starting EJ-13 water or in the leachates from the as-cast glass tests. As the tests continued, the concentration of anions in solution decreased, suggesting that these elements are rapidly rinsed from the hydrated glass surface.

The measured amount of actinides in solution for the first two sampling periods was given previously [3]. As was mentioned then, the values presented were order of magnitude levels, provided to indicate differences between release from the two test types. Alpha spectroscopy and gamma spectroscopy on the original leachates were initially used to measure the levels; however, owing to the salt content in the aged samples, additional analytical methods have been employed. Over the past year, the radionuclide contents in the leachates and in the filtered samples have been analyzed by alpha spectroscopy combined with evaporated and electroplated methods, gamma spectroscopy, and ICP-MS. The results of all of these analyses are not yet correlated and thus will not yet be reported. There is a clear desire to report correct and consistent values for actinide release, and a combination of all techniques will be used to obtain the final values. A considerable amount of data is available from solutions that were sequentially filtered through filters of decreasing pore size, and both the filters and filtrates have been analyzed.

Some indication of the distribution of radionuclides and species in solution can be obtained by examining particles isolated on perforated carbon TEM grids. The solutions from tests N4-6 to N4-10 wicked easily through the grid and produced good samples for analysis. The solutions from the aged glass reaction contained a large salt content and were wicked with more difficulty through the grid. While the salt content disrupts the clear distinction of colloidal particles, some discrete colloids were identified. A full discussion of colloid examination from these tests is given in Section IX.

c. Future Progress

The ongoing drip tests will be sampled according to the schedule in Table 4. The components (glass and metal) from the terminated tests will be analyzed to determine the mass balance of the reaction progress. The data collected through the scheduled March 1995 sampling period will be compiled into an ANL topical report.

3. Long-Term Repository Environment Tests

The "laboratory analog" test [29] was developed to relate the performance of glass as observed in the Unsaturated Test with a more repository-relevant environment. In the laboratory analog test, the waste package assemblage (WPA), like that used in the Unsaturated Test, is placed within a bored-out cavity in a tuff core. The dimensions of the WPA and the cavity are similar to those used in the Unsaturated Test. A sketch of the apparatus can be found in the previous reports in this series [1-4]. The tuff core and WPA are assembled, and an unsaturated flow of water is forced through the core by using a vapor pressure slightly above ambient.

The objective of this test is to evaluate glass performance in an environment that closely matches that expected in the repository. Emphasis is placed on measuring glass reaction by examining the reacted glass and surrounding tuff rock at the test termination and by monitoring the radionuclide content of the groundwater as it is released from the test vessel. The tuff used in these tests is an outcrop sample taken from the same location as used for the large-scale block tests currently planned by the YMP. Thus, while not from the repository horizon, the tuff is similar to that expected for the repository site. The rock was conditioned by pouring water through it prior to testing in order to rinse out surface deposits; however, the focus of our analyses will be the radionuclide content of the effluent, not the chemical composition.

a. Status

On December 19, 1991, two analog tests were started using 200R glass. One test uses unaged glass and a sensitized 304L stainless steel retainer; the other uses three-week-aged glass and stainless steel. The tests have been ongoing for 156 weeks, and the water that passes through the cores is collected at selected intervals. The tests are being run at two different flow rates: the unaged glass has a flow rate of 0.02 mL/h, and the aged glass a flow rate of less than 0.005 mL/h. The effluent has been collected and periodically checked for gross radioactivity. To date, no indication of activity in the solution has been detected.

b. Results and Discussion

The tests are working as expected, in that water is passing through the cores, and no radioelements have been detected with gross counting methods. A more extensive analysis of the condensed solution will be needed to confirm this preliminary result.

c. Future Progress

The tests will continue, with periodic monitoring of the effluent, and the solutions will be subjected to extensive analysis.

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V. EFFECT OF RADIONUCLIDE DECAY ON GLASS REACTIONS

A. Introduction and Background

Radiation effects on high-level waste glasses are an important consideration for radionuclide immobilization. Radiation may affect the long-term performance of glass waste in an unsaturated repository environment by damaging solid materials and by interacting with air, water vapor, or liquid water to produce a variety of radiolytic products that may be reactive toward the glass.

Radiolysis effects on glass reactions are quite complex due to interaction between the dissolving glass components, radiolysis products, and the buffering capacity of silicate groundwater against radiolytically produced acids. Radiation damage to solid glass material, including the formation of alpha tracks, phase changes, and bubbles [30], may also increase the rate of glass alteration by providing access channels for water entry, thereby increasing the effective surface area of the solid. The influence of annealing processes in mitigating the cumulative radiation damage to solids also complicates interpretations of solid damage effects on glass alteration properties.

In tests conducted with borosilicate waste glass and gamma-irradiated aerated deionized water (DIW) systems, release rates of B, Al, Si, alkalis, and actinides were typically increased from three- to five-fold over nonirradiated tests, but they may vary for individual elements from less than one- to twelve-fold [31,32]. In tests conducted with alpha-emitting transuranic-doped glass that had no external gamma exposure, an increase in glass dissolution rates up to a factor of three was observed relative to nonirradiated tests [33,34]. Both the formation of nitric acid in the irradiated air above the aqueous solution and the formation of water dissociation products appear to have combined to accelerate glass reaction rates in these tests. Solid-phase alpha-decay damage may have also influenced glass reaction rates in transuranic-doped glass. Glass samples that were gamma-irradiated prior to being immersed in DIW generally do not display any increase in release rates, indicating that gamma irradiation of the glass does not have any measurable effect on glass dissolution rates.

Significant changes in the leachate pH and glass dissolution rates were not observed when glass samples were gamma-irradiated in the presence of groundwater equilibrated with tuff. Changes in solution pH of these systems were either buffered by bicarbonate in solution, and/or the radiogenic acids were diluted under the relatively low SA/V conditions of some of the tests [35-37]. In a few tests, glass dissolution rates were actually reduced, relative to nonirradiated tests, when the samples were exposed to irradiated solutions [38]. Van Iseghem et al. [39] observed a decrease in the glass reaction rate resulting from a decreasing pH of 8.5 to 7.5 for glasses reacted in the presence of clay at a temperature of 90°C and a SA/V ratio of 100 m⁻¹. The reduced pH led to a decrease in total silicon solubility and, consequently, to a reduction in the release rate of other glass matrix components.

Under the geologically unsaturated conditions expected at the proposed Yucca Mountain repository, the most likely scenario for water contact to occur with the waste glass in the event of container breaching is from small amounts of water condensing and/or dripping on the glass surface. In this environment, radiolytic products may rapidly concentrate, and the bicarbonate present in the small volume of water present may be quickly overwhelmed by nitric acid produced in radiolysis reactions [40]. Any nitric acid that subsequently condenses on the glass surface would accelerate the glass degradation process.

The small quantity of water expected to condense on the glass surface will also preclude any volumetric dilution of the radiolytic and glass dissolution products. Rapid increases in the concentration of glass dissolution products will cause the leachate to become saturated with respect to secondary alteration minerals, accelerating the eventual precipitation of these phases. Secondary phase formation may promote continued rapid dissolution of the glass, because the secondary phases sequester elements from the leachate and lower the activity of certain ions in solution, thereby promoting additional dissolution of the glass [41].

B. Objectives

The overall purpose of this task is to determine if radiation has any significant effect on glass durability under the high SA/V conditions that are expected for an unsaturated repository site. Exhaustive literature reviews were conducted in an effort to examine and tabulate previously published results concerning the effects of radionuclide decay on glass reactions. Results from these reviews were published elsewhere [11,42,43]. Several outstanding issues, which need to be addressed for full understanding of factors that may influence the stability of nuclear waste glass under disposal conditions, were identified [11]. Laboratory tests were performed to address three outstanding issues [11]. The first objective of these tests was to examine the effect of radiation on moist air systems in the absence of glass (blank experiments) and the distributions and concentrations of radiolytic products. Variables tested included radiation type (alpha vs. gamma), temperature, dose rate, and gas/liquid volume ratio (G/L). Results from this first set of tests indicated that both alpha and gamma radiation can produce nitrogen and carboxylic acids in a moist-air environment, with nitrogen acid production being inversely proportional to the reaction temperature [11,44]. The second test objective was to examine glass reaction rates under unsaturated conditions, utilizing a matrix of several glass compositions and SA/V ratios. Comparisons of alteration profiles from glasses reacted in irradiated vs. nonirradiated conditions were used to characterize the influence of irradiation on alteration rates. The final objective of these tests was to examine the influence of radiation on the stability and formation of secondary mineral phases. Detailed scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), analytical electron microscopy (AEM), and X-ray diffraction (XRD) examinations were used to provide a comparison between alteration assemblages developed on glass in irradiated vs. nonirradiated conditions.

C. Results

All experimental testing associated with this Task has been completed. Results from these tests were published elsewhere [11,45].

D. Future Progress

Remaining efforts will focus on the publication of the Data Report, which is currently under review, and close-out efforts for this Task.

VI. RELATIONSHIP BETWEEN HIGH SA/V EXPERIMENTS AND MCC-1

A. Introduction and Background

Static leach tests are being used to measure the durabilities and determine the corrosion mechanisms of borosilicate glasses. Results described in this Section represent glasses that may be produced by the vitrification of high-level waste during operation of the Defense Waste Processing Facility (DWPF), but the results are generally applicable to borosilicate glasses in general. The mechanism of glass corrosion and the release behavior of radionuclides must be known in order to project the long-term stability of high-level waste forms under anticipated storage conditions. This Task was initiated to clarify the effects of glass surface area/leachant volume ratio (SA/V), used in a static leach test, on the rate and mechanism of corrosion of the stabilizing glass matrix and the release of radionuclides from vitrified high-level waste forms. Variation of SA/V in static leach tests can be used to (1) simulate conditions in which the waste form is contacted by large or small volumes of groundwater during storage; (2) highlight different aspects of the corrosion process to determine the corrosion mechanism under different environmental conditions; and (3) based on an understanding of the corrosion mechanism, accelerate the corrosion process to provide insight regarding the durability of high-level waste forms over geologic time periods relevant to repository isolation.

Tests have shown the major effect of the SA/V on the glass reaction to be dilution of the corrosion products. Since the rate of glass reaction is known to depend on the solution chemistry (particularly the silicic acid concentration and the pH), differences in dilution of corrosion products in tests at different SA/V will affect the response of a particular glass. Both the rate controlling process and the measured rate of glass reaction change as the SA/V is varied. Under the dilute conditions in tests at low SA/V ratios, ion exchange reactions dominate the observed corrosion behavior, whereas under concentrated conditions, at high SA/V ratios, hydrolysis reactions dominate. To project the long-term glass durability, it is important to understand how the results of specific tests relate to the overall glass corrosion process.

To assess waste form and waste disposal system performance, not only must the effect of SA/V on the mechanism and rate of glass matrix corrosion be known, but also the effect on the behavior of individual radionuclides. While much is known about the chemistries of various radionuclides in aqueous solutions, little is known regarding the effects of glass corrosion on their disposition. Glass corrosion will affect the pH and Eh of the solution, will supply species that may complex actinide species and form solubility-controlling phases, and will generate colloids and secondary phases that may sorb actinides. The effects of glass corrosion on the disposition of radionuclides must be accounted for when assessing the long-term performance of high-level waste glasses during repository storage. Other studies characterized the disposition of radionuclides under very dilute conditions, where the buildup of glass corrosion products in the solution did not significantly affect the disposition. Tests in this Task directly compare the disposition of radionuclides under the dilute conditions maintained in tests at low SA/V ratios to that observed under the highly concentrated conditions attained in tests at high SA/V ratios. Tests measured the disposition of technetium, uranium, neptunium, plutonium, and americium between the glass, leachate, test components, and secondary phases, at different SA/V and at different stages of the corrosion process, by using glasses doped with these radionuclides. This report focuses on the disposition of these radionuclides observed in tests and analyses completed to date.

B. Objectives

The primary objective of this Task is to assess the effects of the SA/V used in a static leach test on the mechanism and rate of the glass reaction over both short test periods relevant to testing

product consistency and long test periods relevant to projecting long-term glass stabilities. Tests in this Task were designed to monitor changes in both the leachate composition and the reacted glass surface as a function of the SA/V, the reaction time, and the initial leachant solution composition. Tests were performed with glasses doped with radionuclides to monitor their disposition as the reaction proceeds. The results of these tests will provide insight into the relationship between tests performed at different SA/V, use of SA/V as an accelerating parameter for static leach tests, influence of SA/V on the assemblage of secondary phases that form, and the long-term glass reaction rate.

Another objective is to describe the corrosion mechanism of glass compositions relevant to the DWPF. These tests generate a large suite of corroded glass samples that show the glass alteration during the initial, intermediate, and long-term stages of the corrosion process (see Fig. 1). Detailed analysis of the reacted solids will provide a valuable description of the formation process of the alteration layers on the glass surface and their interaction with radionuclides.

C. Technical Approach

Glasses made from frits supplied by the Savannah River Technology Center were tested; the frits were modified to reflect waste loadings. The glasses tested were SRL 131 and SRL 202. The SRL 202 composition is the current reference composition for blended tank wastes at the Savannah River Site [46], and the SRL 131 composition was developed as a reference glass based on earlier estimates of tank waste compositions at the Savannah River Site. The SRL 131 glass is known to be less durable than the SRL 202 glass; thus, SRL 131 was tested to ensure that advanced stages of corrosion would be attained within the testing program. Both glasses were doped at ANL with Tc-99, U-238, Np-237, Pu-239, and Am-241, at levels of about 0.003, 2, 0.01, 0.01, and 0.0004 elemental wt %, respectively. Glasses doped with all five elements are referred to as SRL 131A and SRL 202A. Glass prepared with uranium as the only radioactive additive is referred to as SRL 202U. The glass compositions are presented in Table 1. (The SRL 202U composition is the same as the SRL 202A, except that it contains no Tc, Np, Pu, or Am.) Only about 1% of the technetium became fixed in the glass, while the rest was volatilized when the glass was melted. The measured contents of the actinides were the same as the amounts added.

The leachant was prepared by reacting tuff groundwater from well J-13 with pulverized tuff rock for about 28 days at 90°C; thus, simulating interaction between groundwater and rock in a repository. The resulting solution was cooled and filtered to remove colloidal tuff particles; it is referred to as EJ-13 water (Table 2). Some tests were conducted using deionized water.

Tests at 10 and 340 m⁻¹ followed the MCC-1 protocol by reacting one or four monolithic samples with about 17 or 2 mL, respectively, of EJ-13 water. Tests at 2000 and 20,000 m⁻¹ followed the Product Consistency Test (PCT) method B [47] by placing 1 or 5 g of crushed glass in 10 or 5 mL, respectively, of EJ-13 water. The SRL 202A and SRL 131A glasses were tested in 304L stainless steel reaction vessels at 90°C, and SRL 202U glass were tested in Teflon reaction vessels at 90°C.

After a predetermined time, the vessels were removed from the oven and opened. The leachate solutions and reacted glasses were removed for analysis. The leachates were removed while still hot to avoid thermal effects, such as precipitation of solids or flocculation of colloids. A portion of some solutions was filtered through a holey carbon grid of the type used for transmission electron microscopy (TEM), to isolate suspended solids for later analysis. An aliquot was also removed for analysis of transuranics. The remaining solution was then filtered through a preheated 450-nm cartridge filter. A portion of this solution was further filtered through an Amicon model CF50A filter, which has an effective filter size of about 6 nm. Solutions were analyzed for pH (by using a combination electrode), anions (by ion chromatography), technetium

and uranium [by inductively coupled plasma-mass spectrometry (ICP-MS)], and transuranics (by alpha spectrometry and ICP-MS). Aliquots of the unfiltered leachates or the 450-nm filtrates were retained for analysis of radionuclides. These solutions were evaporated to dryness, then redissolved in a nitric acid solution and analyzed by using ICP-MS.

The reacted glass was gently rinsed with deionized water, then removed from the vessel and allowed to dry. The vessel was then filled with a nitric acid solution and placed in a 90°C oven overnight to dissolve transuranics that had become fixed to the stainless steel surface. An aliquot of this solution was analyzed using alpha spectroscopy.

Some of the reacted solids were analyzed using optical microscopy, scanning electron microscopy (SEM), and analytical electron microscopy (AEM). Both the scanning electron and transmission electron microscopes are equipped with X-ray spectrometers for compositional analysis, and AEM provides selected area electron diffraction (SAED) for structural analysis. Secondary phases found distributed among the reacted grains were isolated and analyzed separately.

D. Results and Discussion

Results of testing and analyses were published elsewhere [48-56]. This report highlights the observed release and disposition of radionuclides.

The calculated normalized mass losses based on the measured concentrations of technetium, uranium, and neptunium are compiled in Table 8. Either the unfiltered leachates or the 450-nm filtrate solutions were analyzed. The normalized mass losses based on the boron release, which represents the extent of glass corrosion, are included for comparison. Tests were conducted in duplicate for each SA/V and reaction time, and the results of the test having the highest boron release are tabulated. In most cases, the results of duplicate tests were within the expected analytical error ($\pm 10\%$). The normalized mass losses for tests conducted at 2000 or 20,000 m^{-1} with both glasses are plotted against the reaction time in Figs. 11a-d. Lines are drawn to show the trends, but do not represent analytical fits to the data.

The boron data show that SRL 202A glass corrodes at a continuously decreasing rate at 2000 m^{-1} . Technetium was released to solution stoichiometrically with boron, and less uranium and neptunium were released than boron and technetium. The rate of boron release was low through 182 days, after which it increased. Technetium release was also slow (similar rate to boron) through 182 days, and increased thereafter, but the release of technetium after 182 days was less than that of boron. Data from tests of longer duration are needed to determine the long-term behavior of technetium. Analysis of these solutions is in progress. Uranium and neptunium were released at low rates at all times tested, and were not affected by the increased glass corrosion rate after 182 days.

At 2000 m^{-1} , SRL 131A glass corroded at a high rate after about 140 days, as shown by the boron release. Technetium release rate was also constant, but the normalized mass loss of technetium was about half that of boron. Much less uranium and neptunium were released than boron or technetium. Results at 20,000 m^{-1} were similar; boron and technetium were released at nearly constant rates, with boron release a little faster, and uranium and neptunium release was slow at all times tested.

The behavior of technetium, uranium, and neptunium in the presence of glass corrosion products is of key interest due to their known high solubilities in oxidizing groundwaters. In these tests, technetium was released nearly congruently with boron as the glass corroded, indicating that an increase in the glass corrosion rate due to secondary phase formation will probably cause an

Table 8. Normalized Mass Losses for Radionuclides, in g/m²

Time, days	NL(B)	NL(Tc)	NL(U)	NL(Np)
SRL 202A, 10 m ⁻¹				
7	0.69	2.7	0.045	0.67
28	0.75	<1 ^a	0.04	<0.2
94	4.3	<1	0.18	<0.2
238	0.95	<1	0.11	<0.1
600	15	<1	0.29	0.33
SRL 202A, 2000 m ⁻¹				
3	0.096	0.056	0.046	0.049
7	0.19	0.12	0.11	0.099
14	0.27	0.19	0.11	0.14
30	0.41	0.28	0.077	0.14
140	0.57	0.44	0.095	0.20
280	0.67	0.87	0.12	— ^b
560	0.83	0.87	0.17	—
980	0.95	1.1	0.16	—
SRL 202A, 20,000 m ⁻¹				
3	0.13	0.074	0.028	0.025
7	0.17	0.095	0.039	0.037
14	0.20	0.12	0.046	0.041
28	0.24	0.17	0.036	0.031
56	0.31	0.26	0.019	0.021
98	0.36	0.29	0.013	0.014
182	0.57	1.5	0.010	0.072
364	5.2	2.7	0.0038	0.0041
484	12	—	0.0023	—
728	18	—	0.0013	—
SRL 131A, 10 m ⁻¹				
7	1.0	<0.8	0.16	0.59
28	1.8	3.2	0.19	2.6
94	5.2	<0.8	0.45	1.2
238	34	7.3	1.6	3.5
601	53	34	7.7	15
SRL 131A, 2000 m ⁻¹				
3	0.76	0.35	0.12	0.80
7	1.1	0.51	0.20	0.12
14	1.3	0.61	0.19	0.12
30	1.5	0.68	0.12	0.11
70	1.7	0.81	0.081	0.041
140	2.2	0.96	0.083	0.041
280	5.4	0.96	0.082	—
560	9.6	5.4	0.036	—
980	13	7.5	—	—
SRL 131A, 20,000 m ⁻¹				
3	2.6	1.3	0.0033	0.00081
7	4.8	2.5	0.0043	0.00096
14	6.0	3.3	0.0036	0.0011
28	7.5	4.5	0.0052	0.0013
56	9.7	5.4	0.0054	0.0012
98	9.5	9.7	0.0050	0.0017
182	11	8.5	0.0055	0.0041
364	20	12	0.0039	0.0016
552	23	—	0.0036	—
728	36	—	0.0068	—

^aMaximum value based on analyzed radionuclide concentration below detection limit.^bAnalysis not yet performed.

Fig. 11. Normalized Mass Losses vs. Reaction Time for Tests: (a) SRL 202A glass at 2000 m^{-1} , (b) SRL 202A glass at $20,000 \text{ m}^{-1}$, (c) SRL 131A glass at 2000 m^{-1} , (d) SRL 131A glass at $20,000 \text{ m}^{-1}$. ($\square$) NL(B), ($\circ$) NL(Tc), ($\diamond$) NL(U), and (Δ) NL(Np), in g/m^2 .

increase in the release of technetium. More analyses are needed to confirm this behavior in tests with SRL 202A at $20,000\text{ m}^{-1}$, but it was clearly demonstrated in tests with SRL 131A at both 2000 and $20,000\text{ m}^{-1}$.

Other analyses were performed to determine the disposition of the sparingly soluble actinide elements. The amounts of neptunium, plutonium, and americium that were suspended in solution (the fraction that passed through a 450-nm filter but not through a 6-nm filter), dissolved (the fraction that passed through a 6-nm filter), or became fixed to the stainless steel reaction vessel (the fraction in the acid soak solution) were measured by using alpha spectroscopy. The results of these analyses for several, representative tests are presented in Table 9. Actinides not found in any of these fractions were assumed to remain associated with the altered glass.

Although there is scatter in the results, several general trends are apparent in the distributions of actinides between the various fractions in tests conducted at different SA/V and for different times. For both glasses, neptunium was present in the suspended and dissolved fractions, and was fixed to the vessel in tests at 10 and $20,000\text{ m}^{-1}$, but not in tests at 2000 m^{-1} . Significantly more plutonium was present in the suspended fraction than in the dissolved fraction in tests at 2000 m^{-1} , but only small amounts were found in the suspended fractions in tests at $20,000\text{ m}^{-1}$. Some plutonium was fixed to the steel vessel in all tests, and the fraction became greater with test duration. In all tests, only small amounts of americium were dissolved. Similar amounts of americium were suspended in the leachate and fixed to the vessel in tests at 2000 m^{-1} , but, at $20,000\text{ m}^{-1}$, americium was mainly fixed to the vessel.

In all tests, between 75 and 90% of the released uranium was dissolved, and the balance was suspended. The distribution between the dissolved and suspended phases was similar for all times longer than a few days. Uranium was never fixed to the stainless steel.

The amounts of plutonium and americium in the suspended and dissolved fractions generally decreased with reaction time, most noticeably in tests at $20,000\text{ m}^{-1}$, while the amounts found fixed to the vessel generally increased. Temporal changes are probably due to increased glass corrosion, changes in the solution chemistry, and flocculation of colloids.

The highest levels of neptunium, plutonium, and americium measured in the dissolved fractions under any test condition were several orders of magnitude lower than the solubilities of these actinides measured in J-13 groundwater [57]. This may be due to interactions between the actinides, colloidal phases, and the steel vessel surface, or to control of solubilities by different phases in the presence of glass corrosion products. Except for weeksite, which may control the solubility of uranium, solubility-controlling phases remain to be identified.

Actinides that remain associated with the glass during static leach tests can be quantified by comparing the amounts found to be suspended, dissolved, or fixed to the vessel, to the extent of glass corrosion in each test. A "retention factor", defined as the ratio of the normalized boron mass loss (which defines the extent of corrosion) to the normalized actinide mass loss, has been used to describe the ability of corroded glass to mitigate the release of actinides to solution [58]. Retention factors for technetium, uranium, and neptunium were calculated from the ICP-MS results. Normalized mass losses of neptunium, plutonium, and americium were computed from the sum of the amounts in the suspended, dissolved, and fixed fractions. The amounts adsorbed to the steel vessel were included in the total release because the adsorbed material was not retained by the altered glass and was therefore available for transport. The calculated retention factors for each radionuclide, $RF(Rn)$, where Rn is Tc, U, Np, Pu, or Am, are given in Table 10. Values of $RF(Rn)$ near unity indicate that actinide release into solution is similar to that of boron, whereas large values of $RF(Rn)$ indicate that the actinide is retained by the glass as it corrodes. Retention may result from several phenomena, including secondary phase formation, sorption, flocculation of colloidal material, or simply the limited solubilities of the actinides.

Table 9. Mass of Actinides in Various Fractions. Reaction time in days; fractions that are suspended (sus), dissolved (dis), and fixed to the steel vessel (ads) in ng.

Time, d	Np, ng			Pu, ng			Am, ng		
	sus	dis	ads	sus	dis	ads	sus	dis	ads
SRL 202A at 10 m ⁻¹									
7	0 ^a	38	0	0	0.33	0	0	0.005	0.046
28	0	0.65	1.8	0.008	0.015	0.044	0	0	0.0016
94	27	0.28	79	1.3	0	2.4	0.032	0	0.97
238	3.0	3.3	195	0.20	0.033	8.0	0.0041	0.0011	0.15
600	0	0	160	5.9	0	8	0.11	0	0.28
1400	63	0.5	180	6	0.01	10	0.08	0	0.4
SRL 202A at 2000 m ⁻¹									
14	420	96	51	34	0.75	8.6	0.87	0.017	0.24
30	440	100	56	50	1.4	23	1.4	0.029	0.51
70	110	290	15	60	12	30	1.3	0.23	1.2
140	0	670	0	68	38	33	1.6	0.61	1.3
280	540	160	0	140	3.1	170	2.1	0.074	3.6
560	0	550	0	130	34	110	3.2	0.79	2.6
980	87	170	0	74	19	150	1.8	0.39	3.0
SRL 202A at 20,000 m ⁻¹									
14	3000	180	120	180	5.5	17	3.7	0.12	0.59
28	380	150	160	65	11	50	1.4	0.28	1.9
56	180	68	270	10	0.97	38	0.22	0.02	1.6
98	75	89	290	1.3	0.28	52	0.026	0.002	1.8
182	21	76	360	0	1.7	58	0.02	0.003	2.1
364	28	6.8	1100	0.11	0	88	0.01	0	2.6
504	0.43	1.5	860	0	0.01	60	0	0	2.7
728	0	69	660	0	0.37	203	0	0.004	6.9
SRL 131A at 10 m ⁻¹									
7	9.6	6.0	1.2	0	0.06	0.13	0	0.001	0.003
28	5.6	6.4	2.6	0.013	0.004	0.12	0	0	0.0006
94	36	29	3	0.008	0.004	0.13	0.0001	0	0.004
238	39	41	5.7	0.022	0.022	0.32	0.0002	0	0.006
600	190	190	140	0.60	0.037	30	0.0092	0.0007	0.47
1400	24	3.5	320	0.78	0.017	12	0.016	0	0.56
SRL 131A at 2000 m ⁻¹									
14	221	125	580	5.4	0.65	4.5	0.07	0.004	0.097
30	87	130	170	4.2	1.5	41	0.032	0.007	0.35
70	64	230	0	13	4.7	46	0.20	0.036	0.93
140	127	180	0	12	7.0	97	0.14	0.088	2.3
280	41	35	0	2.4	11	92	0.022	0.009	1.0
560	18	17	0	0.25	0.22	109	0.013	0	1.7
980	46	0	0	0	0	122	0	0	1.9
SRL 131A at 20,000 m ⁻¹									
14	2.4	1.9	140	0.78	0.002	15	8.6	0	0.48
28	3.0	1.5	260	0.003	0.001	53	0	0	1.4
56	75	2.2	230	4.6	0.003	32	94	0	1.3
98	1.3	0.95	330	0	0.002	140	0	0	3.9
182	0	7.7	25	0	0.014	33	0	0	1.2
364	0	2.7	383	0	0.012	24	0.05	0	0.78
552	4.6	0	290	0.11	0	81	0.004	0	2.2
728	13	0	330	1.4	0	100	0.006	0	2.8

^a0 indicates negligible or below detection limit.

Table 10. Retention Factors for Radionuclides^a

Time, d	RF(Tc)	RF(U)	RF(Np)	RF(Pu)	RF(Am)
SRL 202A at 2000 m ⁻¹					
14	1.4	2.5	0.91	12	19
30	1.5	5.3	1.3	11	16
70	1.3	12	2.2	9.2	14
140	1.3	6.0	1.8	8.5	13
280	0.77	5.6	2.0	4.5	9.7
560	0.96	4.9	3.0	6.1	9.9
980	0.86	5.9	12	8.3	15
SRL 202A at 20,000 m ⁻¹					
14	1.7	4.3	0.12	1.9	3.6
28	1.4	6.7	0.70	3.8	5.3
56	1.2	16	1.2	13	14
98	1.3	30	1.7	14	17
182	0.38	57	2.3	18	19
364	1.9	1400	9.0	120	160
484		5200	28	400	360
728		14000	54	180	210
SRL 131A at 2000 m ⁻¹					
14	2.1	6.8	6.7	120	570
30	2.2	13	7.7	65	310
70	2.1	21	11	120	120
140	2.3	2.3	14	37	70
280	5.6	66	59	110	380
560	1.8	270	550	180	460
980	1.7		600	220	580
SRL 131A at 20,000 m ⁻¹					
14	1.8	1700	40	800	1000
28	1.7	1400	58	280	430
56	1.8	1800	64	520	600
98	0.98	1900	55	130	190
182	1.3	2000	710	670	730
364	1.7	2800	100	1700	2100
552		6400	160	570	840
728		5300	210	720	1000

^aValues in bold type determined from alpha spectroscopy results. Values in regular type determined from ICP-MS results.

In general, these tests show that (1) actinides are retained by the glass much more strongly than technetium; (2) technetium retention factors are similar for both glasses, at all SA/V ratios, and for all test durations; and (3) the retention factors of the actinides are greater for the less durable SRL 131A glass than for the SRL 202A glass, increase with the SA/V ratio of the test, and increase with test duration. The first finding can be explained by the much greater solubility of technetium compared with any of the actinides. Of the actinides, uranium and neptunium had lower retention factors than the less soluble plutonium and americium. The observation that the technetium retention factor was independent of glass composition, SA/V ratio, and test duration simply reflects the congruence of technetium and boron release, and the similar effects of glass composition, SA/V ratio, and time on the glass corrosion rate and technetium release. Conversely, it is clear that technetium release cannot occur any faster than the glass corrosion (as measured by the release of boron to solution).

The actinide retention varied with glass composition, SA/V ratio, and test duration, indicating that their retention is affected by glass corrosion products, probably as a result of the formation of alteration layers, secondary phases, and colloids. Differences in the dissolved and suspended fractions are shown in Table 9. At short reaction times and low SA/V ratios, most of the plutonium and americium was suspended in solution, but very little at longer times. The change is attributed to the flocculation of colloids at longer reaction times. Analysis of the leachate solution before and after filtration through 6-nm filters indicated that material containing aluminum, iron, and probably silicon becomes suspended in the leachates as the glasses corrode. This material remained suspended in tests conducted at 2000 m³/l, but settled out of solution after 28 days in tests at 20,000 m³/l. Thus, actinides that become associated with suspended material during the initial stages of corrosion are removed from solution as the material flocculates and settles out of solution.

The higher retention of actinides by SRL 131 glass is due to its poorer durability. (The NL(B) values for tests with SRL 131 glass were about an order of magnitude higher than those for tests with SRL 202 glass under the same test conditions.) Colloids containing actinides formed in, and then settled out of, solution faster in tests with SRL 131A than in tests with SRL 202A glass. In addition, thicker alteration layers formed on SRL 131A glass as it corroded, which provided much more surface area for sorption of actinides than the thinner layers formed on SRL 202A glass.

The colloids that have been identified in leachates from these tests include smectite and kaolinite clays, nagelschmidtite, calcite, dolomite, iron oxide, magnesium oxide, titanium oxide, weeksite, uranophane, boltwoodite, and other uranium-titanium-, iron-, and aluminum-rich phases [50]. Smectite clays were the most ubiquitous and abundant phases found in suspension. These clays are known to be an abundant alteration phase of the hydrated surfaces of these glasses [52]. All of the other phases were found either associated with alteration layers formed on individual glass grains or as separate phases mixed with the reacted glass. These phases may nucleate either in the solution or on the reacted glass surface, and may either enter or settle out of the solution, depending on the solution chemistry and the size of the particles.

The suspended phases provide a means of mobilizing actinide elements at levels far above their solubilities, by sorption onto or incorporation into the phases. While several uranium-bearing phases have been identified, the low concentrations of transuranic elements used in testing make it difficult to identify the secondary phases that sequester them and/or affect their solubilities. Previous work showed that plutonium and americium oxides are associated with smectite clay colloids [59], which is consistent with the present results. Work is in progress to identify phases formed during glass corrosion.

These tests and analyses show that radionuclide elements become distributed between dissolved, suspended, and immobile phases as glass waste forms corrode. The disposition of radionuclides measured in laboratory tests may be affected by their interaction with complexants in the leachate, glass corrosion products, and the reaction vessel. Specific solubilities and interactions of the radionuclides are complicated by chemical and physical changes that may occur during the test. These include changes in the solution chemistry as the glass corrodes, especially the ligand concentrations, pH, and the abundance of colloidal material. Similar effects will occur during storage of waste forms in geologic repositories and must be taken into account when assessing the performance of a disposal system. The present tests demonstrate the following:

(1) Technetium is released congruently with boron and is unaffected by the accumulation of glass corrosion products during glass corrosion. (2) The concentrations of complexants and the disposition and solubilities of actinide elements are sensitive to the glass composition, the SA/V ratio of the test, and the reaction time. The amounts of actinides in the solution become insensitive to the glass corrosion rate and are controlled by other phenomena, such as solubility limits, sorption onto alteration products, etc. (3) Association of actinides with suspended corrosion products may significantly increase their abundance in solution. (4) The amount of suspended material depends on the SA/V of the system and the reaction time. (5) The amounts of actinide materials available for transport are affected both by their solubilities and by the stabilities of suspended phases with which they are associated.

E. Future Progress

Several long-term tests remain in progress. These tests will show whether technetium continues to be released congruently with boron or becomes attenuated by the alteration phases. Solutions from other tests remain to be analyzed. Alteration phases from tests with SRL 131A glass will be analyzed to identify solids that may control the solubilities of radionuclides and glass matrix components.

VII. LABORATORY TESTING OF WEST VALLEY REFERENCE 6 AND SRL EA GLASSES

A. Introduction and Background

The West Valley Demonstration Project (WVDP) will produce high-level waste glass from wastes generated during the reprocessing of nuclear fuels. A target glass composition has been identified by the WVDP. Laboratory testing of vitrified high-level waste glasses that are to be disposed in a geologic repository is required to monitor glass production and to project its long-term durability under potential disposal conditions. Argonne National Laboratory (ANL) is assisting WVDP by conducting laboratory tests using a nonradioactive homologue of this target glass. A fully radioactive glass will be tested at ANL when it 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 insights regarding the corrosion behavior of the fully radioactive glass, since a more complete analysis is possible with nonradioactive glass. These tests will demonstrate the acceptability of the waste forms produced by WVDP for disposal in a federal repository.

The Product Consistency Test (PCT) was developed by the Westinghouse Savannah River Company to verify the consistency of glasses produced by the Defense Waste Processing Facility (DWPF). The PCT may also be used by the WVDP to verify product consistency. The PCT is a highly interactive test, which measures the extent of glass corrosion in a solution that becomes highly concentrated in glass components as the test proceeds. An advantage of the PCT is that it can be performed remotely; it also shows acceptable sensitivity to the glass composition, has acceptable precision, and has been accepted by waste form producers.

While the PCT provides information regarding the consistency of the glass produced, no single test can characterize the corrosion behavior of a waste glass over long time periods. The long-term durability of vitrified waste forms emplaced in a repository can only be projected based on a mechanistic understanding of the corrosion processes, which must be deduced from short-term laboratory tests. Previous studies conducted by DOE-EM have shown that glass corrosion occurs in three stages (see Fig. 1) which depend on the solution chemistry: (1) The initial stage occurs under dilute solution conditions where the glass reacts at a characteristic forward rate that is unique to the glass composition, temperature, and solution pH. (2) An intermediate stage occurs as the silicic acid concentration in the contacting fluid increases. As the solution becomes more concentrated in glass components, the glass corrosion slows to a rate that may become immeasurably low in highly concentrated fluids. (3) A third stage occurs as secondary mineral phases precipitate from the fluid and lower the solution concentrations of species which affect the glass corrosion rate. Depending on the secondary phases formed, glass corrosion may proceed at a rate similar to the low rate attained in the late intermediate stage, or may be accelerated to a rate higher than that observed during the initial stage. The rate of glass corrosion will depend primarily on changes in the solution chemistry in response to the assemblage of secondary phases that form. Silicic acid is the most important solution species affecting the corrosion rate. Since the assemblage of secondary phases that are formed depends in large part on the composition of the glass (i.e., corrosion of the glass supplies material to the fluid from which the secondary phases precipitate), and since the nucleation of specific phases cannot be predicted *a priori*, laboratory tests are needed to determine which phases form and how the formation of these phases affects the continued glass corrosion rate. To completely describe the glass stability, it is important that the corrosion behavior of a glass be characterized by tests that access the three different corrosion stages, probably most importantly the third stage, which provides insight into the long-term stability. Once the corrosion behavior of the glass is known, it can be related to anticipated storage conditions through performance assessment models.

B. Objectives

The purpose of these Tasks is to characterize the corrosion behavior of the WV6 and SRL EA glasses in all stages of the corrosion process, i.e., when the corrosion is controlled by the intrinsic durability of the glass, by the glass corrosion products in solution, and by the formation of secondary phases. Tests are performed that measure the glass corrosion rate as corrosion progresses, assess the long-term stability of the glasses, and identify stable secondary phases that are formed as the glasses corrode. These are required input parameters for computer simulation models, currently being developed to project glass corrosion behavior over long time periods for application to repository performance assessment.

C. Technical Approach

Tests designed to access the initial, intermediate, or long-term stages of the corrosion process are being used to characterize the corrosion behavior of WV6 glass. A modified MCC-1 procedure, in which a monolithic sample is immersed in solution to achieve a low glass surface area-to-leachant solution volume ratio (SA/V), is used in short-term tests to provide a measure of the forward reaction rate and to determine the initial corrosion behavior in highly dilute solutions. These tests are conducted in a reference tuff groundwater solution of the Yucca Mountain site. Other tests compare the durabilities of WV6 and SRL EA glass to those of other high-level waste glasses under standard test conditions. The PCT B protocol is used to measure the durabilities of WV6 and SRL EA glasses in a tuff groundwater solution at high SA/V for long reaction times, to measure the intermediate and long-term corrosion rates.

In ANL vapor hydration tests, the conditions are those known to accelerate the glass corrosion rate and to promote secondary phase formation. In these tests, monolithic samples are exposed to saturated steam at 200°C for corrosion times up to 55 days. Glass corrosion is accelerated by the high temperature and the high SA/V achieved in these tests, and secondary phases commonly form within a few days. These secondary phases can be removed from the corroded glass for detailed analysis and identification.

1. Glass

The WV6 glass used in testing was supplied by The Catholic University of America (CUA); the glass composition provided by CUA is given in Table 11. The glass was not analyzed at ANL, although glass was archived for later analysis, if required. Cylindrical cores about 1 cm in diameter were cut from the chunks of glass, then disk-shaped samples about 1 mm thick were cut from the cores for use in the MCC-1 and vapor hydration tests. The faces of the disks were polished to 600 grit using carborundum paper. The disks were ultrasonically cleaned, and selected samples were surveyed by using an optical microscope and a scanning electron microscope to verify that fines had been removed and that a uniform surface finish was achieved on all samples. The remaining glass was crushed and sieved to isolate the -100+200 and -200+325 (U.S. Standard) mesh fractions. The crushed glass was ultrasonically cleaned in deionized water and then surveyed by using a scanning electron microscope to verify that fines had been removed and that the glass particles were of the proper size.

The SRL EA glass used in testing was supplied by WSRC in pulverized form in two bottles containing about 1 kg each, and identified as "WSRC-NB-92-129 pp 15-23". The sample was not analyzed at ANL, although glass was archived for later analysis, if required. The composition determined by WSRC is presented in Table 11. The glass was crushed and sieved to isolate the -100+200 and -200+325 (U.S. Standard) mesh fractions. The crushed glass was ultrasonically cleaned in deionized water and then surveyed by using a scanning electron microscope to verify that fines had been removed and that the glass particles were of the proper size.

Table 11. Composition of WV6 Glass^a and SRL EA Glass^b

Oxide	wt %		Oxide	wt %	
	WV6	SRL EA		WV6	SRL EA
AgO	0.00		NiO	0.25	0.53
Al ₂ O ₃	6.00	3.60	NpO ₂	0.00	
AmO ₂	0.00		P ₂ O ₅	1.20	
B ₂ O ₃	12.89	11.16	PdO	0.03	
BaO	0.16		Pm ₂ O ₃	0.00	
CaO	0.48	1.23	Pr ₆ O ₁₁	0.04	
CdO	0.00		PuO ₂	0.00	
CeO ₂	0.16		Rb ₂ O	0.00	
CmO ₂	0.00		RhO ₂	0.02	
CoO	0.02		RuO ₂	0.08	
Cr ₂ O ₃	0.14		SO ₃	0.23	
Cs ₂ O	0.08		Sb ₂ O ₃	0.00	
CuO	0.03		SeO ₂	0.00	
Eu ₂ O ₃	0.00		SiO ₂	40.98	48.76
Fe ₂ O ₃	12.02	7.58	Sm ₂ O ₃	0.03	
FeO		1.59	SnO ₂	0.00	
Gd ₂ O ₃	0.00		SrO	0.02	
HgO	0.00		TeO ₂	0.00	
In ₂ O ₃	0.00		Tc ₂ O ₇	0.00	
K ₂ O	5.00	0.04	ThO ₂	3.56	
La ₂ O ₃	0.04	0.28	TiO ₂	0.80	0.65
Li ₂ O	3.71	4.21	UO ₂	0.59	
MgO	0.89	1.79	Y ₂ O ₃	0.02	
MnO ₂	1.01	1.36	ZnO	0.02	0.25
MoO ₃	0.04		ZrO ₂	1.32	0.48
Na ₂ O	8.00	16.88			
Nd ₂ O ₃	0.14		Total	100.00	100.41

^aGlass composition as provided by The Catholic University of America.

^bSRTC analysis from C.M. Jantzen et al., *Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material (U)*, Westinghouse Savannah River Company Report WSRC-TR-346, Rev. 1 (1993).

2. Leachant

Deionized water was used as the leachant in the PCT A and vapor hydration tests. The water was compositionally analyzed prior to use to ensure that it met the requirements of American Society for Testing and Materials (ASTM) Type 1 water, i.e., that it had a measured impedance of 18 MWcm or greater, and contained less than 0.1 g/m³ dissolved material.

The MCC-1 and PCT B tests used an EJ-13 solution as the leachant, generated by reacting pulverized Topopah Springs tuff (that passed through a 100 mesh sieve) with water from well J-13 of the Nevada Test Site at 90°C for 28 days. The composition and pH was measured as part of the preparation procedure, to ensure that the solution met the criteria for acceptance before being used in a test. The measured composition, given in Table 12, was used in elemental background concentration corrections for leachate analyses of test solutions. Water from the same batch of EJ-13 was used for testing the SRL EA and WV6 glasses in the PCT B tests. (Note: The composition of the EJ-13 water used in these tests varies from that shown in Table 2 because this was a separate batch of EJ-13 water.)

The test matrices were designed to provide information regarding the corrosion behavior of WV6 and SRL EA glass at all stages of the corrosion process. A modified MCC-1 procedure at 90°C and SA/V of about 10 m⁻¹ measured the intrinsic corrosion rate. The PCT tests at 90°C and SA/V of 2000 and 20,000 m⁻¹ were performed in deionized water (DIW) or in a tuff groundwater solution (EJ-13 solution) to measure the effects of glass corrosion products, and in saturated steam at 200°C to identify secondary phases and characterize the effects of their formation on the glass corrosion rate. Tests of various durations were conducted under all conditions to assess the corrosion rates. Tests performed in this Task are summarized below.

a. Tests at 10 m⁻¹

Monolithic samples of WV6 in EJ-13 solution were tested at an SA/V of 10 m⁻¹ for periods of 3, 7, and 14 days (in duplicate) to measure the initial corrosion rate, and for 56, 91, and 182 days to study the development of the alteration layer. One sample disk was placed on a 304L type stainless steel support stand inside a steel reaction vessel with a mass of EJ-13 water equal to 10 times the surface area (cm²) of the disk. The vessel was sealed and placed in a 90°C oven for the scheduled time. At the end of the test, the leachate solution and the reacted sample were removed and analyzed. Long-term tests are underway to provide information regarding alteration of the glass surface under dilute solution conditions, for comparison with corroded surfaces generated under other conditions.

Table 12. Analyzed Composition of EJ-13 Water

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

b. Tests at 2000 m⁻¹

Powdered WV6 and SRL EA glass was tested in deionized water at an SA/V of 2000 m⁻¹ for 7 days, to compare to the corrosion to that of other glasses tested under PCT-A conditions in other laboratories. Crushed glass (-100+200 mesh sieved fraction) was placed in a steel reaction vessel with a mass of deionized water or EJ-13 solution equal to 10 times the mass of glass. The vessel was sealed and placed in a 90°C oven for the scheduled time. At the end of the test, the leachate solution and the reacted glass were removed and analyzed. Long-term PCT-B tests in EJ-13 solution will measure the long-term corrosion rate for comparison with similar tests on other high-level waste glasses.

c. Tests at 20,000 m⁻¹

These tests characterize the long-term stability of the glass and generate secondary phases. At this high SA/V ratio, the solution concentrations of glass components approach saturation very quickly and so the corrosion rate of the glass under saturation conditions can be measured. For poorly durable glasses, secondary phases may form in these tests, and the effects of these phases on the corrosion rate and leachate chemistry can be measured. Test durations vary, to provide data over a wide range of reaction times and ensure that testing covers the entire period of secondary phase formation and long-term glass corrosion. Secondary phases that form as the glass corrodes can be characterized and identified. Tests followed the PCT-B procedure, using powdered glass to attain an SA/V of 20,000 m⁻¹. Crushed glass (-100+200 mesh sieved fraction) was placed in a steel reaction vessel with a mass of EJ-13 solution equal to the mass of glass.

Glass within the size fraction -200+350 mesh was also tested at an SA/V ratio of 20,000 m⁻¹. The crushed glass was placed in a 304L type stainless steel reaction vessel with a mass of EJ-13 solution equal to twice the mass of the glass. These tests assess the effects of particle size on the corrosion behavior measured in a PCT test. This information will support other tests to be performed with radioactive glass, so that smaller particles can be utilized in that testing program (Task "Testing Fully Radioactive West Valley Glass: WVGs-II"). Only a small amount of radioactive glass will be available for testing so it may be advantageous to utilize the smaller grains if no differences in corrosive response is observed. Previous tests in the EM Task "Relationship Between Tests at High SA/V and MCC-1" indicated that the glass corrosion rate remains constant in spite of decreasing particle size. However, the particle size may affect the saturation concentration and the nucleation of secondary phases. Therefore, it must be demonstrated that glass corrosion can progress to the long-term stage, and secondary phases be precipitated, in tests utilizing particles smaller than 200 mesh. For all PCT-B tests, the test vessels were placed in a 90°C oven for the prescribed time and, at the end of the test, the leachate solution and the reacted glass were removed and analyzed.

d. Vapor Hydration Tests

These tests reveal the effect of secondary phase formation on the glass corrosion rate. Monolithic samples of WV6 glass were corroded in a steam environment for periods up to 55 days to generate secondary phases, which were characterized and identified. Monolithic samples were suspended from a steel bar within the test vessel by using Teflon thread. A small volume of deionized water was added to the vessel, and the vessel was sealed. The vessel was placed in a 200°C oven for the scheduled test duration. At the end of the test, the reacted glass was removed and analyzed, to characterize and identify alteration phases which formed as the glass corroded.

D. Results and Discussion

Analysis of the polished disk samples of WV6 glass revealed the presence of included primary phases containing ruthenium and iron, or iron, chromium, manganese, and nickel. Ruthenium oxide and iron spinels have been observed in the WV-205 glass [60]. Optical survey of the crushed glasses revealed that about 5% of the glass particles were brick red and the rest were amber. Analysis by SEM showed that the red particles had a much higher density of included spinel phases. Red and amber particles were present in similar proportions in both size fractions. Compositional analysis of the glass phase by using SEM/EDS showed no difference between the red and amber particles. The corrosion of both types of particles was monitored to ascertain whether or not they corroded to similar extents.

Analysis of the crushed SRL EA glass using SEM showed there to be three distinct particle shapes: about 70% of the particles had the common "chunk" appearance of crushed glass, about 15% had a "sheet" or "plate" appearance, and about 10% were "rods." Similar distributions of chunks, sheets, and rods were present in both size fractions. Compositional analysis of the particles showed no difference between the chunks, plates, and rods. The extent of corrosion of the three types of particles was compared.

Tests with scheduled reaction times of 182 days or less have been completed. All tests with longer or unscheduled (i.e., "to be determined" test times) reaction times are in progress. The results of MCC-1, PCT, and vapor hydration tests completed to date are discussed separately below.

1. MCC-1 Tests with WV6

MCC-1 tests were conducted with WV6 glass in EJ-13 water for 3, 7, and 14 days, to determine the initial corrosion rate based on the solution concentrations of key glass components. At the end of the tests, the concentrations of all glass components in the leachate were only slightly above their average background concentrations in EJ-13 water. The calculated NL(B) after 3, 7, and 10 days was about 0.07 g/m^2 (corrosion rate of about $0.01 \text{ g/m}^2/\text{d}$). By comparison, the WV-205 glass had a corrosion rate of about 0.6 g/m^2 over 28 days [61] and the DWPF reference glass SRL 202, tested for 7 days, had an NL(B) value of 0.7 g/m^2 . This indicates that WV6 is a highly durable glass. The MCC-1 test run for 91 days gave NL(B) values of 0.28 g/m^2 (corrosion rate of about $0.003 \text{ g/m}^2/\text{d}$).

2. PCT A Tests with WV6 and with SRL EA

Replicate PCT tests conducted in deionized water for 7 days gave an average NL(B) value of about 0.3 g/m^2 for WV6 and about 9 g/m^2 for SRL EA. By comparison, tests with SRL 202 gave an average NL(B) of 0.4 g/m^2 .

3. PCT B Tests with WV6 and with SRL EA

The solution concentrations of key components of both size fractions of crushed WV6 glass, tested at 2000 or $20,000 \text{ m}^{-1}$, are presented in Figs. 12a-c, which show the normalized mass losses as a function of reaction time. Curves were drawn through the data to show the temporal trend, but do not represent analytical fits to the data. Tests with WV6 glass at 2000 m^{-1} showed that the glass dissolved nonstoichiometrically, with alkali metals and boron being released preferentially to silicon. The release of all components increased with reaction time, which indicates that the solutions were not saturated. Tests with WV6 at $20,000 \text{ m}^{-1}$ gave identical results for the two size fractions of crushed glass, indicating that particle size has no effect in these tests. These tests showed the typical trend in which the corrosion rate decreased with the reaction time as glass components built up in solution.

Fig. 12. Normalized Mass Loss from Tests with WV6 Glass: (a) at 2000 m^{-1} , (b) at $20,000 \text{ m}^{-1}$ with $-100+200$ Mesh Glass, and (c) at $20,000 \text{ m}^{-1}$ with $-200+325$ Mesh Glass. (●) B, (■) Li, (Δ) Na, (◆) K, and (○) Si. The results of duplicate tests are plotted.

The solution concentrations of key glass components in tests with SRL EA glass are presented in Figs. 13a-c as the normalized mass losses as a function of the reaction time. The SRL EA glass dissolved nonstoichiometrically, with alkali metals and boron being released preferentially to silicon at all SA/V ratios. However, the temporal behavior differed for tests at 2000 and 20,000 m^{-1} . The release of all components was similar at all reaction times in tests at 2000 m^{-1} but increased with time in tests at 20,000 m^{-1} , which implies that the solutions in tests at 2000 m^{-1} became saturated, while those in tests at 20,000 m^{-1} did not. Instead, secondary phases formed at 20,000 m^{-1} , which maintained the unsaturated solution conditions. (The solution was saturated with respect to the secondary phases but unsaturated with respect to the glass.) The normalized release of lithium was much lower than that of boron or sodium. This is probably due to incorporation of lithium into secondary phases.

Tests with SRL EA at 20,000 m^{-1} with both size fractions of crushed glass indicated a measurable effect of particle size. The normalized release of each component was significantly lower in tests with -200+325 mesh glass than in tests with -100+200 mesh glass at all times tested. The difference was greatest and most obvious for boron and sodium.

The amount of SRL EA glass that dissolved can be calculated from the measured boron concentrations. In tests run for 182 days, the boron concentrations were about 18,000 ppm and 12,000 ppm for -100+200 and -200+325 mesh crushed glass, respectively. The SRL EA glass contains about 3.5 wt % elemental boron; thus, about half of the -100+200 mesh glass and about 70% of the -200+325 mesh glass dissolved. The lower normalized mass loss calculated for -200+325 mesh glass belies the greater percentage of glass that actually dissolved. This is because the initial surface area is utilized in the calculation of all normalized mass losses (in effect treating the glass as a semi-infinite solid). The more rapid loss of surface area for smaller particles than for larger particles is reflected in the lower solution concentrations for tests with smaller particles, as cited above for boron. Thus, while the SA/V is initially the same for both crushed glasses, it decreases more rapidly as the glass dissolves in tests with -200+325 mesh crushed glass than in tests with -100+200 mesh glass. This difference in SA/V was not taken into account in calculating the normalized release values. Tests with WV6 glass did not show this effect since very little glass dissolved over the test periods and the change in SA/V was negligible.

The maximum value of NL that can be attained in a test is simply the inverse of the surface area per gram of the crushed glass. If the grains are assumed to be spheres with diameter 107 μm for the -100+200 mesh glass and 59 μm for the -200+325 mesh glass, the maximum NL values that can be attained are about 48 and 27 g/m^2 , respectively. Thus, the -100+200 mesh glass was about 50% reacted and the -200+325 mesh glass was about 60% reacted, based on the boron concentrations. This indicates that the normalized mass loss functions should not be directly compared for tests conducted with different grain sizes.

4. Solids Analysis

The corrosion of WV6 glass in PCT tests at 20,000 m^{-1} for 98 days resulted in a slight alteration of the glass surface. The SEM analysis of reacted glass particles showed that the surface developed a chain-mail appearance, similar to that seen on other glasses during the formation of smectite clays. A photomicrograph of the surface of red and amber particles from sample WV6-73 is shown in Figs. 14a and 14b (Photos 0354, 0356). The surface of the amber particles has a more well developed appearance, and the surface of the red particles appears to contain a second alteration phase. The other phase is nearly spherical. Analysis of a polished cross-section of this sample indicated that the layer was too thin to detect using the SEM (i.e., less than about 0.1 μm). However, AEM analysis of the cross-sectioned surface of a sample reacted at 2000 m^{-1} for 70 days revealed the presence of thin strands of clay-like material that formed a narrow layer. It is anticipated that samples corroded for longer times will generate thicker layers amenable to analysis by SEM.

Fig. 13. Normalized Mass Loss from Tests with SRL EA Glass: (a) at 2000 m^{-1} , (b) at $20,000\text{ m}^{-1}$ with $-100+200$ Mesh Glass, and (c) at $20,000\text{ m}^{-1}$ with $-200+325$ Mesh Glass. (●) B, (■) Li, (Δ) Na, and (○) Si. The results of duplicate tests are plotted.

(a)

(b)

Fig. 14. Photomicrographs of WV6 Glass from Test WV6-43 (20,000 m^{-1} with -100+200 Mesh Glass, 98 days): (a) Red Particle (Photo 0354), and (b) Amber Particle (Photo 0356).

Corrosion of SRL EA glass at both 2000 and 20,000 m^{-1} resulted in the formation of a visible coating of a white material on the reacted surface. A photomicrograph of the reacted surface of sample EA-73 after 98 days at 20,000 m^{-1} is shown in Fig. 15. The visible white material is seen as a beady outer layer that rests on a sheet-like underlayer. Analysis of cross-sectioned glass particles revealed an alteration layer, approximately 8 μm thick, surrounding the glass. This is the sheet-like layer seen in Fig. 15. The beady outer layer is too thin to be seen in the cross-sections. Analysis of the glass and layer by EDS showed that the sodium/silicon ratio was much lower in the layer, the aluminum/silicon ratio was slightly lower, and the magnesium/silicon ratio was slightly higher in the layer than in the glass.

In all PCT tests at 20,000 m^{-1} , three morphologically distinct secondary mineral phases were formed as the SRL EA glass corroded. The EDS analyses of these three phases gave essentially identical sodium, aluminum, and silicon peaks. One phase contained a small amount of potassium. Selected area electron diffraction (SAED) was performed on a thin section of that phase by using AEM. The measured d-spacings are presented in Table 13. These match well with those of phillipsite, and dachiardite. Further analyses are required to further identify this and the other phases.

Fig. 15. Photomicrograph of Reacted SRL EA Glass from Test EA-73 (20,000 m^{-1} with -200+325 Mesh Glass, 98 Days, Photo 0373).

Table 13. Measured d-Spacings for Secondary Phase Formed in Tests with SRL EA Glass

Sample	d-Spacings, Å	
	Phillipsite ^a	Dachiardite ^b
6.95		6.91
6.86		
4.98	4.98	4.97
4.91		4.88
4.77		
		4.61
3.43	3.48	3.45
3.41		
3.23	3.21	3.20
3.10	3.09	3.11
2.67	2.66	2.67
2.46	2.47	2.47
2.385	2.34	2.387
1.94		1.96
1.92	1.91	1.92
1.69	1.68	1.66
1.62		1.62

^aPhillipsite $[K_2(Na_4Al_6Si_{10}O_{32}) \cdot 12H_2O]$.^bDachiardite $[(Na,K)_4(Al_4Si_{20}O_{48}) \cdot 18H_2O]$.

5. Vapor Hydration Tests with WV6 Glass

Corrosion of WV6 glass in a saturated vapor environment at 200°C resulted in the generation of an alkali-depleted surface layer and the formation of a variety of secondary mineral phases. A photomicrograph of the thick layer formed on the surface of one of the samples from test WV6-97 after 28 days is shown in Fig. 16. 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 layer in the photo is approximately 53 μm 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 indicates that the layer was formed by chemical alteration of the glass matrix and did not precipitate from the fluid that condensed on the glass during the test. The observation that secondary minerals formed on the outer surface of the altered layer indicates that they precipitated from the leachate fluid, while the layer formed *in situ*. Note the distinct interface between layer and glass, and the uniform thickness of the layer.

Vapor hydration tests identify secondary phases that form as the glass corrodes, key information for modeling long-term corrosion behavior. Tests with SRL EA glass showed that corrosion under PCT conditions for long reaction times leads to the formation of secondary mineral phases that affect the glass corrosion rate. While these phases have yet to be identified by diffraction, most have morphology and composition identical to those previously identified on

Fig. 16. Photomicrograph of Cross-Section of Sample from Test WV6-97 (Vapor Hydration at 200°C for 28 Days) Showing Alteration of Glass and Secondary Phases (Photo 0327).

other West Valley reference glasses [62]. These include analcime, orthoclase (K-feldspar), lithium phosphate, and wecksite. Similar phases are expected to form in PCT tests with WV6 glass after long reaction times, although the assemblage of secondary phases may be affected by the test temperature. Since the ability of the phases to sequester radionuclides will depend on their identities, identification of the secondary phases is important for projecting the disposition of released waste components. Phases formed in the vapor hydration tests are presently being identified.

E. Future Progress

The PCT tests with reaction times between 182 days and one year will be completed during FY 1995. Some tests with WV6 glass having "To Be Determined" reaction times may be conducted for longer than one year. Because of its high corrosion rate, all tests with SRL EA glass are likely to be completed during FY 1995.

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VIII. COMPONENTS FROM DRIP TESTS WITH ATM-10 GLASS

A. Introduction and Background

Samples of reacted ATM-10 glass and 304L type stainless steel, generated as part of the N3 series drip tests sponsored by YMP, have been maintained in storage since 1987 and 1988, respectively. These samples, together with the solution test results, provide a valuable indication of the reaction of ATM-10 glass in the unsaturated environment that may exist at the proposed high-level waste repository site at Yucca Mountain, Nevada.

Tests using the Unsaturated Test Method (drip test) were initiated with the actinide-doped West Valley reference glass ATM-10 [63] on July 6, 1987. Testing is supported by the Yucca Mountain Project. The tests followed the original matrix shown in the Task Plan and in the first 52 weeks, eight tests were terminated. Samples of the glass and 304L type stainless steel were generated, and leachate solutions were collected and analyzed. However, the test samples were never analyzed nor were any results interpreted as part of the YMP program. Solution results from these tests [64] were recently reported.

B. Objectives

The objective of the N3 Components Task is to analyze the solid components of the test by using a combination of techniques to evaluate (1) the process by which the glass reacts, (2) the interaction between the glass and the 304L type stainless steel that makes up part of the test assembly, and (3) the distribution of radionuclides between the glass and the steel. These results can then be combined with the published solution results to provide an indication of the long-term performance of this glass under potential repository conditions.

C. Technical Approach

The Unsaturated Test (drip test) of the N3 batch samples was completed according to standard procedure [27]. In this test, a glass monolith is held in place in the center of a closed test vessel with a perforated 304L type stainless steel metal retainer. The metal retainer consists of a top and bottom section, with two posts to hold the retainer sections together and to position the glass. The 304L type stainless steel was heat treated to provide some degree of metal sensitization such as may occur during glass processing.

Continuous tests from this series are still in progress under YMP guidance. The test matrix of terminated tests completed to date is shown in Table 14. The analyses will assist in understanding reaction mechanisms, rates, and trends, and interactions between the glass waste packages and the containment vessels used in the N3 Tests.

D. Results and Discussion

1. Qualitative Examination of Surfaces

Qualitative optical examinations, including photographs taken in the optical microscope, were completed for all relevant surfaces, both glass and 304L type stainless steel. Scanning electron microscopy (SEM) was completed for selected surfaces, and others will be completed soon. Table 15 lists the status of the components to be analyzed.

Table 14. Terminated N3 Test Sample Identification^a

Description	Test #	Sample ID	Date Started	Date Terminated	Test Period (weeks)
Batch	N3-1	20 ₂	7/6/87	10/1/87	12.5
Batch	N3-2	20 ₃	7/6/87	10/1/87	12.5
Batch	N3-3	20 ₄	7/6/87	1/4/88	26
Batch	N3-4	20 ₅	7/6/87	1/4/88	26
Batch	N3-5	20 ₆	7/6/87	4/4/88	39
Batch	N3-6	21 ₁	7/6/87	4/4/88	39
Batch	N3-7	21 ₂	7/6/87	7/4/88	52
Batch	N3-8	21 ₃	7/6/87	7/4/88	52

^aFour tests, N3 #s 9-12, are still ongoing [64] and the components from these tests are not addressed in this report.

Table 15. Status of N3 Component Analysis

Sample	Test Period (weeks)	Glass Monolith		Stainless Steel Vessel	
		Top	Bottom	Top	Bottom
N3 #1	12.5	O, S, A	O, S, A	O, S	O, S
N3 #2 ^a	12.5	O	O	O	O
N3 #3	26	O, A	O, A	O	O
N3 #4 ^a	26	O	O	O	O
N3 #5	39	O, A ^b	O, A ^b	O	O
N3 #6 ^a	39	O	O	O	O
N3 #7 ^a	52	O	O		
N3 #8	52	O, S ^b , A	O, S, A	O	O

O = qualitative optical examination (with photographs)

S = SEM examination

A = AEM examination

^aNot scheduled for AEM or SEM analysis. Each test was run in duplicate; N3 #1 and N3 #2 were run under the same conditions for the same time period, as were N3 #3 and N3#4, etc. As AEM and SEM irreversibly alter the samples, only one from each pair are scheduled to undergo these analyses.

^bIn progress or submitted for analysis.

Clay and other secondary phases were visible on both the glass and stainless steel components and increased in number and size with test duration. It was noted that the bottoms of the glass displayed more evidence of interaction with the stainless steel retainer than did the tops; likewise, the bottom stainless steel retainers were more corroded than the tops. Figure 17 shows optical micrographs of the N3 #1 (12.5-week test) and the N3 #8 (52-week test) glass surfaces. Note the increased appearance of reaction from N3 #1 to N3 #8 and from top surface to bottom surfaces. Note also the large marks on the bottom of N3 #8, which appeared rust-colored. In the shorter tests (i.e., N3 #1 and N3 #2), the contact areas between the glass and stainless steel often had a light, metallic blue appearance due to pretest sensitization of the steel. This bluish coloration persisted in the longer tests and surrounded the rust-colored markings.

Optical examination of the stainless steel retainers revealed little material attached to the top components, and generally little rust. In sharp contrast, the bottom components were covered with increasing amounts (with test duration) of clay and secondary phases. In addition, heavy rust was seen in the area of the support posts that had been welded to the bottom retainer (Fig. 18). This concentration of rust near the welds is consistent with increased sensitization of the 304L type stainless steel in this area. These areas of heavier rust also explain the diametrically opposed rust (or blue) markings on the bottom surfaces of the glass monoliths (see Fig. 17). These results indicate how sensitization of the stainless steel affects interaction with the waste glass, as different regions of the same glass surface were exposed to differently sensitized stainless steel. Rust appearance, both near the post welds and elsewhere on the bottom stainless steel components, also increased with test duration.

It is instructive to compare the optical and SEM backscattered electron images of the sample surfaces (Figs. 19 and 20). Contrast observed in backscatter SEM images is due to variation in electron density and thus indicates atomic variation; heavier elements appear bright while lighter elements appear dark. In Fig. 19, the same area of the bottom of the N3 #1 monolith is depicted in both optical and SEM backscattered images. Note how the light patches in the optical image appear as dark patches in the SEM image. This low atomic number material was later identified by AEM as an amorphous fluorocarbon (or hydro-fluorocarbon) substance. Its origin is unknown, although it appears well attached to the glass surfaces, with attached clay layer formed upon it, suggesting that it formed *in situ*. Figure 20 shows the same area, including a rust mark, of the bottom of N3 #8 in backscatter SEM and optical modes.

2. Analytical Electron Microscopy Findings

Selected materials were removed from the surfaces of N3 #1, N3 #3, and N3 #8 for examination by analytical transmission electron microscopy (AEM). Materials taken included chips of glass with attached clay layer, and secondary phases from the surface. These samples were imbedded in an epoxy resin and sectioned by ultramicrotomy. The N3 #3 samples have not been fully analyzed at this time, but preliminary findings will be discussed. The N3 #5 monolith is ready to be sampled for AEM analysis.

The N3 #1 samples formed only a thin clay layer (~40-50 nm) upon their surfaces. This clay was generally not highly ordered, lacking the characteristic "backbone" structure often observed in other test series (see, for example, Ref. 65). Samples taken from the "blue" area on the bottom of the monolith had a very iron-rich layer composition, as expected from interaction with the sensitized stainless steel. Figure 21 shows an iron-rich clay layer on the bottom surface of N3 #1. Note the chattering in the glass that occurs during the sample preparation process. Although some fracturing of the glass occurred, regions of the glass and reacted layer have remained intact.

Fig. 17. Optical Images from Two of the Glass Monoliths from the Batch N3 Tests. (a) N3 #1 (12.5-week test) top; (b) N3 #1 bottom; (c) N3 #8 (52-week test) top; (d) N3#8 bottom. The magnification is approximately 4.8X.

Fig. 18. Optical Image (Detail) of the Bottom 304L Stainless Steel Sample Retainer Near the Welded Post. The post is partially visible as a blur in the upper left-hand corner. The magnification is approximately 25X.

Fig. 19. (a) Optical and (b) SEM Backscatter Images of the Same Area of N3 #1 Bottom. The magnification is approximately 15X.

Fig. 20. (a) Optical and (b) SEM Backscatter Images of the Same Area of N3 #8 Bottom. The magnification of (a) is approximately 12X, that of (b) is approximately 24X.

Fig. 21. AEM Micrograph and EDS Spectrum from N3 #1 Bottom Surface. (Above) AEM micrograph from an area of the bottom surface of N3 #1 that had reacted with the stainless steel near a weld. There is very little smectite clay, but there is an iron-rich layer visible on the glass surface, plus some detached colloid-sized iron-silicate particles visible above the surface. (Below) EDS spectrum, normalized to Si-K α intensity, of surface layer and interior glass. The copper (Cu) peaks in the EDS spectra are artifacts of the AEM sample mount.

On both the top and bottom glass surfaces of the N3 #1 samples there was an abundance of particles having a thorium-calcium-phosphorus composition; similar, larger particles from the N3 #8 samples were found to be structurally similar to the mineral brockite. These particles were generally quite small on the N3 #1 samples, the largest being about 50 nm (Fig. 22).

A major finding on the bottom surface of the N3 #8 glass monolith was a substantial iron-rich layer, ~150 nm thick, that had formed on the glass under the clay layer where the glass had contacted the stainless steel holder (Fig. 23). The presence of this layer suggests that sensitized stainless steel may increase acceleration of the glass degradation. In general, the smectite-type clay layers on the bottom surface of the N3 #8 glass were 200-400 nm thick (Fig. 24). As is often observed, the clay layers did not contain substantial thorium or uranium and were severely depleted in sodium and potassium.

Particles having a composition consistent with brockite (Th-Ca-P) were ubiquitous, sometimes longer than 200 nm, and were generally imbedded in the surface clay layer (Fig. 25). Much larger particles with this composition were observed by SEM, the largest being over 2 μ m across (Fig. 26). There appears to be an excellent correlation between the largest brockite particle observed on a surface and the duration of the test from which it came. Small brockite particles, often 50 nm or less, were found on all test surfaces examined to date, suggesting that there is continuous nucleation and growth of this phase. This contrasts with the observation of the smectite-type clay, which grows continuously with time, having nucleated on the original glass surface. Electron diffraction confirmed the brockite structure in at least one sample (Table 16 and Fig. 27).

A different thorium phase containing substantial iron and titanium was observed within voids or pits in the glass and, to a lesser extent, on the surface between the glass and clay (Figs. 28 and 29). This material did not yield a crystalline diffraction pattern. It is probably related to the "amorphous" group minerals davidite ($(\text{Fe}, \text{Ce}, \text{U})_2(\text{Ti}, \text{Fe})_5\text{O}_{12}$ (JCPDS 13-505), or thorutite ($(\text{Th}, \text{U}, \text{Ca})\text{Ti}_2\text{O}_6$ (JCPDS 14-327), both described as amorphous and metamict, which crystallize after heating for an hour at temperatures near 1000°C. It would, however, be arbitrary to identify this substance with a specific mineral, because amorphous materials are known to have a more variable composition than crystalline matter.

Like the brockite, the thorutite-like phase was more abundant on samples that were reacted for longer times. It also appeared more often in areas where there was substantial interaction with the sensitized stainless steel retainer. It is interesting that this phase was observed within cracks and voids as well as on the surface because the flow, and thus the interacting volume of water, is restricted in such areas, suggesting that high iron content in solution may be an important factor in forming the thorutite-like phase rather than brockite.

Both the brockite and the amorphous "thorutite" phases incorporated measurable uranium, and probably entrained other actinides. This hypothesis is partly supported by previous work [59] in which a combination of autoradiography and AEM identified a correlation between transuranic activity and the presence of brockite in clay colloids. The notion of transuranics being incorporated into the brockite is also supported by the appearance of the brockite, which was often amorphous or highly disordered, consistent with substantial radiation damage. Brockite minerals in nature are generally crystalline, despite self-irradiation from natural thorium and uranium over geologic time periods.

While analysis of the AEM data from the N3 #3 (a 26-week test) surfaces is still in progress, a few comments are in order. A notable observation from the bottom surface is the presence of a sodium-aluminum-silicate, identified by electron diffraction to be a member of the zeolite mineral group, heulandite subgroup. This is the first clear identification of zeolite formation

Fig. 22. AEM Micrograph and EDS Spectrum of Particles from Top Surface of N3 #1. (Above) AEM micrograph of particle having brockite composition found on the top surface of N3 #1. This particle is detached from the glass, which is visible in the upper right. (Below) The EDS spectrum of the particle. The copper (Cu) peaks in the EDS spectra are artifacts of the AEM sample mount.

Fig. 23. AEM Micrograph and EDS Spectra of N3 #1 Layered Structure. (Above) AEM micrograph of layered structure containing clay, an iron-rich precipitate, and glass on a portion of the N3 #8 bottom surface that had contacted the stainless steel retainer near a welded support post. (Below) EDS spectra of the clay and iron-rich layers along with the glass. Neither the iron-rich layers nor the clay layers retained substantial Th. Compare this figure with Fig. 21, from a similar area on N3 #1. The copper (Cu) peaks in the EDS spectra are artifacts of the AEM sample mount.

Fig. 24. AEM Micrograph and EDS Spectra of Smectite Clay Layer on Glass from the N3 #8 Top Surface. (Above) AEM micrograph of smectite clay layer on glass from the N3 #8 top surface. (Below) EDS spectra, normalized to Si-K α intensity, of the clay and glass. Note the enrichment of Al and Fe and the depletion of Na, K, and Th in the clay layer. The copper (Cu) peaks in the EDS spectra are artifacts of the AEM sample mount.

Fig. 25. AEM Micrograph and EDS Spectrum of Brockite Particles from N3 #8. (Above) AEM micrograph of two brockite particles with a small amount of clay from the bottom surface of N3 #8. The glass has torn away from this area during sample preparation. (Below) EDS spectrum of one of these particles. Note the presence of neodymium.

Fig. 26. SEM Backscatter Image of the Largest Brockite Particle Observed to Date From the N3 Test Series. This particle was found on the bottom of the N3 #8 glass. (Left) Backscatter image; (Right) EDS spectrum obtained.

Table 16. Electron Diffraction from a Sample of the Calcium-Thorium-Phosphate Phase Located on the Top of N3 #8. Although the composition might match more closely with cheralite, the diffraction pattern indicates a brockite structure (the EDS spectrum is essentially the same as the material shown in Fig. 22). Major reflections for mineral references ($I/I_0 \geq 30\%$) listed in **bold**.

Experimental d Spacings, Å	JCPDS	JCPDS
C14453	Brockite ^a	Cheralite ^b
6.19	6.06	5.2
4.59	4.37	4.77, 4.664 4.073, 4.167
3.18	3.47, 3.03	3.074, 3.277, 3.481
2.93	2.83	2.965, 2.862
2.48	2.37	2.435
2.226	2.15	2.237
1.926	1.92	1.925

^aBrockite: Nominally, $(\text{Ca,Th,Ln})(\text{PO}_4) \cdot \text{H}_2\text{O}$, rhabdophane group, hexagonal system, space group $P6_{222}$. The reference [66] gives the sample analysis as $\text{Ca}_{0.43}\text{Sr}_{0.03}\text{Ba}_{0.02}\text{Th}_{0.41}\text{Ln}_{0.11}(\text{PO}_4)_{0.83}(\text{CO}_3)_{0.17} \cdot 0.9\text{H}_2\text{O}$.

^bCheralite: Nominally, $(\text{Ln,Th,Ca,U})(\text{PO}_4,\text{SiO}_4)$, monazite group, monoclinic system, space group $P2_1/n$. The reference [67] gives the sample composition by microprobe analysis (oxide wt %) as CaO 5.99, PbO 1.15, ThO₂ 31.64, U₃O₈ 4.33, P₂O₅ 27.10, SiO₂ 2.08, Ce₂O₃ 12.12, La₂O₃ 5.19, Pr₂O₃ 1.20, Nd₂O₃ 5.91, Sm₂O₃ 1.81, with trace levels of other lanthanides.

Fig. 27. AEM Electron Diffraction Image from a Brockite Particle on the Top Surface of N3 #8. The pattern is matched with brockite in Table 16. Note the diffuse appearance of the diffraction spots despite the large volume of the original particle, which was nearly $0.5\text{ }\mu\text{m}$ across. Such diffuse diffraction spots are consistent with a radiation-damaged crystal, perhaps due to entrained transuranics.

Fig. 28. AEM Micrograph and EDS Spectrum of Amorphous "Thorutite" Phase (indicated by arrows) within a Void in the Glass Just Beneath the Iron-Rich Layer (dark material in the upper right corner) Observed on the Bottom of N3 #8. (Above) AEM micrograph; (Below) EDS spectrum of this material.

Fig. 29. AEM Micrograph and EDS Spectrum of the Amorphous "Thorutite" Phase Mixed with Clay from a Central Portion of the Top of N3 #8. (Above) AEM micrograph; (Below) EDS spectrum of this material.

during these tests. Oddly, a few tiny precipitates (<10 nm diameter) of silver were found within the zeolite in selected areas. Both brockite and the thorutite-like phase discussed above were observed on several samples. Intact clay layers were rare on these samples; however, when present, the clay was about 100-150 nm thick. This is probably because, as the clay layers form, they become detached from the glass and are washed from the surface as the water drips onto the glass [59]. When base glass is then exposed, a new clay layer begins to form.

It is important to identify the secondary phases and to analyze the reacted layer, because these alteration products preferentially sequester radionuclides into their structure, and thereby control radionuclide release from the glass and ultimate transportation from the waste form into the near- and far-field environments.

E. Future Progress

Remaining glass samples will be analyzed to complete the first year's batch testing, and to identify, whenever possible, any previously unreported secondary phases. Stainless steel components will be acid stripped to determine actinide concentration in deposits by alpha spectroscopy. Analysis of the stainless steel components to determine sensitization will also be carried out. After the components have been analyzed, a topical report will be written that combines results from the components and solution analyses to provide a concerted description of the long-term reaction of this glass.

IX. ANALYTICAL ELECTRON MICROSCOPY SUPPORT

A. Introduction And Background

Secondary alteration phases, found on the leached surfaces and present as colloids in the leachates of fully radioactive and simulated nuclear waste glasses, continue to be examined by analytical electron microscopy (AEM). These phases were formed in both static and drip tests, conducted at various surface area-to-leachant volume ratios, and for various reaction times. We define AEM as the combination of transmission electron microscopy (TEM) with the analytical capabilities of X-ray energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Structural identifications are accomplished by using electron diffraction, either selected area electron diffraction (SAED) or convergent beam electron diffraction (CBED), although the latter can only be used with reasonably beam stable phases.

Many phases formed during waste glass reaction have been found to be extremely beam sensitive, which has made structural identification difficult, and also compositional analysis on occasions. In this section, the work completed by AEM during FY 1994 will be reported as well as the application of AEM for the characterization of phases from waste glass reaction, and some of the problems in its use. The application and importance of a complete description of the reacted components of a test has been discussed in previous sections, but in general this information, when combined with solution data, allows for a full description of the reaction progress of the glass.

B. Objectives

The Analytical Support staff collaborates with other members of the Technical Support Program to investigate and identify secondary phases produced during the corrosion of nuclear waste forms in simulations of expected environmental conditions. These structural studies provide information necessary to understand the reaction processes. This information contributes to the development of the models needed for prediction of glass behavior.

C. Technical Approach

Work is concerned with characterizing reaction layers that form on the surfaces of leached waste glasses. These layers are frequently 50 μm or more thick and are extremely fragile. In order to identify secondary phases using AEM it is necessary to have extremely thin self-supporting samples. Transverse cross-sections of these reaction layers are prepared by ultramicrotomy, thin sectioning of small particles mounted in epoxy blocks using a diamond knife [52,68]. The sectioned particles are placed on carbon-coated copper mesh grids and examined by TEM. The micrographs produced are used for interpreting the glass dissolution mechanism. The 'surveys' of the samples have been altered so that most of the analysis can be completed without having to perform a later, detailed analysis. The EDS analysis was quantified by using experimentally determined k-factors obtained from glass and mineral thin film standards. The uranium k-factor for the L-X-ray line was determined from synthetic soddyite and uranophane minerals. Secondary phases are identified by a combination of EDS, selected area electron diffraction (SAED), and convergent beam electron diffraction (CBED). The SAED camera lengths were calibrated by using a polycrystalline aluminum sample, and SAED patterns for estimation of d-spacings were made while maintaining a steadfast eucentric height and objective lens current, as well as with the brightness control defocused.

In addition to the analysis of reacted layers, colloidal particles present in the leachate, some of which may carry radionuclides, continue to be examined. Colloidal samples have been collected by wicking the leachate through with an alcohol, onto a 'holey' carbon grid. Examination of colloids present in the leachate has permitted not only identification of colloidal phases but also a picture of colloidal particle formation in the leachate [19,50,59,69].

New facilities were set up for the preparation of TEM samples by methods other than ultramicrotomy. These techniques were utilized in other related glass testing tasks to provide new information on the microstructure of waste materials.

1. Electron Energy Loss Extended Fine Structure and Near Edge Structure

Electron energy loss extended fine structure (EXEFLS) spectroscopy can provide a description of the local environment around an absorbing element. The region beyond the absorption edge of silicon is converted to k -space (where k is the photoelectron momentum) and Fourier transformed to provide a rough approximation to the radial distribution function (rdf), but uncorrected for the phase shifts of the photoelectron wave. Figure 30 shows a number of rdfs determined for a calcium silicate secondary phase. In contrast to X-ray absorption spectroscopy (XAS), the absorption edges in EELS are relatively close, so that an uninterrupted region beyond the absorption edge can be found for good rdf data. However, the large number of elements present in nuclear waste glasses will create similar peak overlap problems for most XAS studies. The main advantage of EXELFS over XAS is the small probe capability of the TEM which allows selection of individual sub-micron sized phases.

Fig. 30. EELS Extended Fine Structure Radial Distribution Function of Calcium Silicate: Solid, Si rdf from Si-K edge; dotted, O rdf from O-K edge; dashed, Ca rdf from Ca-L_{2,3} edge. Compare with bond lengths Si-O (1.6 Å), Ca-O (2.3-2.8 Å), Ca-Ca (3.9 Å). The broad peak from the O-K edge at ~1.9 Å is probably due to the two distinct environments, Si-O and Ca-O, not being resolved. The second peak in the Si rdf is probably due to the Si second neighbor distance (compare Si-O-Si second neighbor distance of 2.6 Å in silica), or possibly due to the presence of amorphous silicon (Si-Si distance of 2.35 Å).

2. Comparison of SEM and TEM/EDS Analysis Routines

The ability to perform quantitative analysis using SEM and TEM is well established, however there is a need to determine whether analysis of nuclear waste glass by SEM and TEM is both accurate and comparable. Analysis of SEM/EDS will typically probe a large area of a glass sample which will tend to average out any inhomogeneities in the glass. Mazer et al. have demonstrated the application of SEM/EDS for the analysis of waste glass [70]. Full confidence of TEM/EDS data has yet to be shown, since this analysis examines much smaller areas and, hence, may see heterogeneities in the composition of the sample. Also, the large number of elements in nuclear waste glass can make analysis difficult. Abrajano et al. have published data on glass and reacted layer TEM/EDS analyses which have errors based on counting statistics (elements >30 wt % have a 5% error, elements <10 wt % have ~30% error, and elements around 1 wt % have a 100% or larger error) [71]; however, comparison with SEM data or other techniques was not performed. Comparison of SRL 202U glass analysis with wet chemical analysis has given good confidence in TEM data, but comparison between the two electron beam methods (TEM/EDS and SEM/EDS) has not been attempted. A comparison of SEM and TEM/EDS analyses of SRL EA and WV6 glasses is shown in Table 17 (WV6 glass is known to contain inhomogeneities). The SEM data (semi-quantitative analysis) shows fairly good agreement with the wet chemical analysis, except for a few elements such as iron and sodium. The TEM shows good agreement in the case of WV6.

Table 17. Comparison of EDS Analysis from Glass Samples by SEM and TEM (Average of Five Analyses)

Element	wt %					
	Chemical Analysis of WV6 Glass	SEM/EDS	TEM/EDS	Chemical Analysis of EA Glass	SEM/EDS	TEM/EDS
Al ₂ O ₃	6.00	7.51	6.82	3.6	3.45	5.04
B ₂ O ₃	12.89	12.89(F) ^a	12.89(F)	11.16	11.16(F)	11.16(F)
CaO	0.48	NA	NA	1.23	0.97	1.09
Fe ₂ O ₃	12.02	13.98	13.00	9.17	9.53	9.67
K ₂ O	5.00	5.34	5.24	0.04	-	0.00
Li ₂ O	3.71	3.71(F)	3.71(F)	4.21	4.21(F)	4.21(F)
MgO	0.89	0.77	0.54	1.79	0.95	1.45
MnO ₂	1.01	1.46	1.57	1.36	1.36	NA ^b
Na ₂ O	8.00	9.80	9.36	16.88	20.21	16.51
SiO ₂	40.98	41.41	39.87	48.76	47.96	47.57
TiO ₂	0.80	1.04	0.93	0.65	0.19	1.13
ZrO ₂	1.32	1.65	NA	0.48	NA	NA
UO ₂	0.59	NA	NA	-	-	-
ThO ₂	3.56	NA	NA	-	-	-

^a(F) = fixed but not detectable with EDS.

^bNA = not analyzed.

D. Results And Discussion

1. Analysis of Samples from the Long-Term Testing

The Long-Term Testing Task seeks to determine the long-term performance of fully radioactive glass compared to the performance of nonradioactive glasses. Samples of SRL 200S glass that have undergone accelerated reaction are being examined by both AEM and SEM. The results of sample analyses are described in Table 18.

A number of secondary silicate phases were observed in SRL 200S glass reacted for 330 days or more. Four major phases were located in the cross-sectioned samples of DP 187 (reacted at $20,000 \text{ m}^{-1}$ for 728 days). These were unaltered glass, clay, sodium-rich uranium silicate, potassium aluminosilicate (zeolite), and a silicon phosphorus phase. Surface analysis of the same samples also found spiny calcium silicate phases, possibly tobermorite in addition to the other phases found in the cross-sectioned samples. The phosphorus-rich phase was found during TEM examinations of related tests. The zeolite phase was identified through the SEM images as phillipsite, because of its characteristic elongated morphology (see Fig. 31). Both XRD and electron diffraction data confirmed this analysis in related tests, although electron diffraction indicated that some other zeolite phases were also present [72]. These minerals are characterized by short, prismatic, pseudo-orthorhombic crystals with *a*-elongation. The phillipsite crystals are extensively twinned, in fact untwinned phillipsite and harmotome have not been observed. Phillipsite minerals generally display a wide range of chemical composition.

A thorium titanium phase, similar to uranium titanium precipitates found in SRL 202 glass tests, was observed in a SRL 131R glass reacted at 2000 m^{-1} for 980 days (see Fig. 32). Electron diffraction was not obtained from this phase, but it could be structurally related to the U-Ti phases. It may also be a phase that can concentrate actinides. Further analysis will be required to confirm this speculation.

The development of analytical techniques to profile boron is considered important for understanding glass durability. Sample DP 167 (SRL 200R glass reacted at $20,000 \text{ m}^{-1}$ for 546 days) was examined with EELS to determine whether boron could be profiled through the reacted layer. When the instrument is set up correctly, the B-K edge at around 188 eV can be detected. Figure 33 shows that the concentration of boron is reduced near the surface of the leached glass, as expected. The SEM can routinely detect boron using the wavelength dispersive spectrometer; however, there may be interference from chlorine. Also, with SEM the spatial resolution is limited to about $1 \mu\text{m}$, whereas with TEM the spatial resolution is $<20 \text{ nm}$. There is little overlap problem for most elements with EELS, which has an energy resolution of $\sim 1.6 \text{ eV}$.

Electron diffraction is used to identify secondary mineral phases formed during glass reaction. Tables 18 and 19 show electron diffraction data for zeolite and uranium silicate phases, respectively, for a number of glass tests, including some from the Long-Term Testing Task. Although there are at least 40 known zeolite species, only six types are commonly formed during the alteration of volcanic glasses in alkaline solutions; analcime, chabazite, clinoptilolite, erionite, mordenite, and phillipsite. Like alkaline volcanic glasses, the alkali-rich SRL EA nuclear waste glasses were zeolitized mainly to phillipsite. Geological evidence indicates that acidic glasses alter to clinoptilolite, but at a slower rate than alkaline glass converts to phillipsite. In general, phillipsite prevails over clinoptilolite in geological systems. However, as phillipsite is not observed in sediments older than Jurassic, there is a suggestion that phillipsite might convert to clinoptilolite [73].

Table 18. Results of Sample Surveys for "Long-Term Testing"

Test Identification	Comments	Blocks Prepared
DP18 SRL 131/11R glass reacted at 2000 m ⁻¹ for 980 days	The layer was 150-200 nm thick. In several locations within the layer there were titanium- and thorium-rich layers.	977, 978, 979, 980
DP25 SRL 131/11S glass reacted at 2000 m ⁻¹ at 980 days	The layer was ~100-250 nm thick and possessed a backbone structure. The clay was beginning to grow into the etched region beneath the layer.	916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926
DP131 SRL 200R glass reacted at 2000 m ⁻¹ for 980 days	In some samples there was an extensive amount of reaction. The particles were stuck together and the alteration layers had connected. The layer thickness varied from 200 to 500 nm with a backbone structure.	1008, 1009, 1010
DP49/50 SRL 165/42S glass reacted at 340 m ⁻¹ for 1456 days	The clay layer developed was about 100-300 nm thick. Some zeolite-type phases were found.	1072, 1073, 1074, 1075, 1076
DP66 SRL 165/42R glass reacted at 2000 m ⁻¹ for 980 days	A reacted layer 75-150 nm thick was found.	981, 982, 983
DP147 SRL 200S glass reacted at 2000 m ⁻¹ for 560 days	The layer, which was 300-600 nm thick, possessed a backbone structure.	947, 948, 949, 950
DP83 SRL 165/42S glass reacted at 2000 m ⁻¹ for 980 days	Mostly amorphous silica. A Calcium aluminum silicate phase was observed. The reacted layer was 100 nm thick.	943, 944, 945, 946
DP148 SRL 200S glass reacted at 2000 m ⁻¹ for 980 days	The clay layer was 300-375 nm thick with a backbone structure. A uranium silicate (boltwoodite) was observed in the samples.	962, 963, 964, 965, 966

contd.

Table 18 contd.

Test Identification	Comments	Blocks Prepared
DP149 SRL 200S glass reacted at 2000 m ⁻¹ for 980 days	The clay layer possessed a backbone structure and was 300 nm thick. The clay layer was depleted in alkalis and enriched in Mg, Fe, and Ni.	967, 968
DP169 SRL 200R glass reacted at 20,000 m ⁻¹ for 728 days	The clay layer was 125-300 nm thick with well defined backbone in some areas, and in others, only a partly formed backbone structure.	1006, 1007
DP184 SRL 200S glass reacted at 20,000 m ⁻¹ for 546 days	Block was re-examined for EELS and confirmation of phase identification by electron diffraction. The phase was determined to be tobermorite	
DP186 SRL 200S glass reacted at 20,000 m ⁻¹ for 728 days	Zeolite (phillipsite), calcium silicate (tobermorite) and uranium silicates (weeksite and boltwoodite) secondary phases were found.	895, 896, 897, 902, 903, 904, 905, 906
DP187 SRL 200S glass reacted at 20,000 m ⁻¹ for 1095 days	Zeolite (phillipsite), uranium silicate (weeksite), and calcium silicates (possibly gyrolite) were found in the samples.	1066, 1067, 1068, 1069, 1070

Fig. 31. Analysis of Zeolite Phase from SRL 200S Glass Reacted at $20,000 \text{ m}^{-1}$ for 728 Days. (Above) SEM Image; (Below) EDS Analysis.

Fig. 32. (Above) TEM Image of Reacted Layer from SRL 131R Glass Reacted at 2000 m^{-1} for 980 Days (DP 18) and (Below) EDS Analysis of Thorium Titanium Precipitates Found in the Layer.

Fig. 33. EELS Analysis of Boron through the Leached Layer of DP 167

Table 19. Electron Diffraction Data from Crystalline Alumino-Silicate Phase

Experimental d-Spacings, Å				Paulingite Wenatchee, WA ^a	Phillipsite Casal Runori, Italy ^a
EA 41	EA 71	DP 187	PZ 20		
6.95	7.23	7.22		7.18	
6.86	6.83	6.30	6.63	6.88	7.18
4.98	5.03		5.30		6.42
					5.07
4.91	4.90		4.29	4.96	4.94
4.77		4.73			
			3.91		3.92
3.43, 3.41	3.92, 3.59	3.57	3.44, 3.79	3.875	3.48
3.23		3.23		3.58	3.69
3.10, 3.10	3.03	3.03		3.08	3.09
2.67	2.64	2.58	2.56	2.615	2.66
2.46	2.46			2.48	2.45
2.385		2.21		2.53	2.54
1.94, 1.92	1.89				1.91
1.69, 1.62	1.76				1.68

^aReference [72].

2. Analysis of Samples for the Effects of SA/V

A number of AEM examinations of SRL 131 and SRL 202 glass tests were conducted this year (see Table 20). The SRL 202A glass reacted at 2000 m^{-1} showed a thin reacted layer with extensive formation of uranium titanium precipitates below the backbone structure (see Fig. 34).

Analysis of uranium silicate phases from an SRL 131A glass test (PY17) by EELS indicated that barium and a trace amount of lanthanum is present in these phases (see Fig. 35). This may account for some of the differences between d-spacings determined by electron diffraction and the literature values (see Table 21). The EDS analysis also illustrates the trace amount of barium present in the phase, and the ability of EELS to detect these elements.

Estimations of layer thickness from TEM data revealed a steady increase in layer thickness with reaction time (see Fig. 36). The degree of reaction was greater at higher SA/V. At $20,000 \text{ m}^{-1}$, layer thickness increased sharply after about 180 days. This corresponds to an acceleration in reaction and the formation of a range of secondary silicate phases. Zeolite phases were characterized by electron diffraction and are displayed in Table 19.

3. Analysis of Samples from the Effects of Radiation on Glass at Large SA/V

A limited number of samples from the Effects of Radiation on Glass at Large SA/V Task were analyzed. These samples, which show extensive reaction, are described in Table 22. Figure 37 shows that the reacted layer of a 131A glass test was depleted in sodium compared to the glass. By using overlying EDS plots normalized to silicon the change in composition between regions can often be more easily understood. In Fig. 38, the EDS analysis of clay and glass in a reacted 165A glass is shown.

4. Analysis of Samples from SRL EA and WV6 Glass Testing

The West Valley 6 reference glass and the SRL EA glass are being tested to determine the glass corrosion rate, assess the long term stability of the glass, and identify the secondary phases that form when the glass corrodes.

The WV6 glass contains a number of devitrification phases, which have been identified by electron diffraction as spinel phases, and by EDS, as iron chromium oxides. Figure 39 shows a WV6 glass containing a spinel phase. The glass also contains a number of rare earth elements (REEs) at trace levels. The second difference technique, which uses a parallel electron energy loss spectrometer, is a simple method for detecting low levels ($\sim 10\text{-}50 \text{ ppm}$) of some elements [74]. The techniques of EDS and EELS were applied to detect low levels of REEs and other minor elements within EA and WV6 glass samples. For the REEs, EELS was more sensitive than EDS, due to the high cross section of their $M_{4,5}$ edges. There is also severe overlap in the L X-ray-lines of the REEs; however, the better energy resolution of EELS can resolve this. It will be necessary to use EELS to study the distribution of these elements in the reacted glasses. In Fig. 40, a second difference EEL spectrum shows the distribution of REEs in WV6 glass. The concentrations of REEs and barium in WV6 glass are roughly similar, except for La and Pm; BaO (0.16 wt %), La_2O_3 (0.04 wt %), CeO_2 (0.16 wt %), Pr_6O_{11} (0.04 wt %), Nd_2O_3 (0.14 wt %), Pm_2O_3 ($<0.01 \text{ wt \%}$). The intensity of the absorption edge for the REEs decreases at higher edge energy. The distribution of these elements (and their reaction products) in the glass can indicate how the distribution of actinide elements in the reacted products should be evaluated.

Table 20. Results of Sample Surveys for the "Effects of SA/V Glass"

Test Identification	Comments	Blocks Prepared
TY17 SRL 202U glass reacted at 2000 m ⁻¹ for 980 days	The clay layer was 100-150 nm thick. The clay layer showed enrichment of iron.	1091, 1092, 1093
BY15 SRL 202A glass reacted at 2000 m ⁻¹ for 560 days	The layer was about 150-200 nm thick. Uranium titanium precipitates were visible underneath the clay layer.	1023, 1025
BY17 SRL 202A glass reacted at 2000 m ⁻¹ for 980 days	Clay layer and uranium precipitates were present. The clay layer was 150-300 nm thick and possessed a backbone structure. A devitrification phase identified as augite, a pyroxene mineral, was found in one sample.	1026, 1027, 1028, 1029
BX6 SRL 202A glass reacted at 340 m ⁻¹ for 91 days	The layer was very small in the samples, about 50-100 nm thick.	1042, 1043, 1044
PY17/18 SRL 131A glass reacted at 2000 m ⁻¹ for 980 days	The uranium silicate (uranophane and weeksite) were found in the sections. Small uranium titanium phases were found in the layer. Devitrification phase, an iron nickel oxide spinel (cubic), was also found.	845, 846, 847, 848, 849, 850, 851, 852
PZ20C SRL 131A actinide doped glass reacted at 20,000 m ⁻¹	A zeolite phase was found containing potassium and calcium. Mainly iron silicate. The ring diffraction pattern showed some ordering, suggesting well developed clay phases. Iron silicate with potassium and calcium. The powdered diffraction pattern exhibited a slight oblique pattern, due to preferential ordering.	1052, 1053, 1054, 1055
PZ20A SRL 131A actinide doped glass reacted at 20,000 m ⁻¹	An iron silicate with a high chlorine content was observed.	1045, 1046, 1047, 1048
PZ20B SRL 131A actinide doped glass reacted at 20,000 m ⁻¹	Some uranium precipitates were observed in the layer.	1049, 1050

Fig. 34. (Above) TEM Image of Reacted Layer in SRL 202A Glass Reacted at 2000 m^{-1} for 980 Days (BY 17) and (Below) EDS Analysis of the Uranium Titanium Precipitates. Using a 20 nm S-mode probe the uranium-rich phase was analyzed by EELS, which determined that iron is not a major component of the phase.

Fig. 35. EDS and EELS Analysis of a Uranium Silicate from SRL 131A Glass Reacted at 2000 m^l for 980 Days (PY 17). With EDS, barium is hardly visible in the phase, but using EELS it is possible to detect the presence of both barium and lanthanum. There is significant chemical shift in the absorption edges, which has shifted the Ba-M₅ edge to an energy higher than U-N₄. This may be a consequence of both Ba and U being bonded to the same oxygen atom. The energy scale was calibrated using the iron (708 eV) and uranium (738, 780 eV) edges. The intensity of uranium N-edges is extremely weak.

Table 21. Electron Diffraction Data from Uranium Silicate Phases

Experimental d-Spacings, Å			Weeksite JCPDS 12-462	Uranophane JCPDS 29-1044
DP 148	DP 187	PZ 20		
	8.85	9.285	8.98	
6.96		6.88	7.11	6.92
6.67	4.37	6.63	5.57	6.71
6.36		6.19		6.37
5.56		5.54		5.39
5.26		4.85	4.83	
4.74		4.64	4.58	4.70
4.52	4.42		4.48	
4.32			3.84	4.24
3.46		3.44	3.55	3.49
3.34		3.31	3.30	
3.09	3.10	3.09		
2.97	2.93			2.92
2.77	2.77	2.77	2.615	
	2.35		2.48	2.34

Fig. 36. Increase in Layer Thickness Estimated from TEM Images for SRL 202U Glass Reacted at Three Different SA/Vs. Results from the 20,000 m⁻¹ show a jump in layer thickness which corresponds to the development of secondary phases. The reacted layer in these samples was difficult to determine.

Table 22. Results of Sample Surveys for "Effects of Radiation at Large SA/V"

Test Identification	Comments	Blocks Prepared
131A-720-2a SRL 131 glass reacted for 720 days	The layer consisted of an outer fringe layer about 200-300 nm thick and an alteration layer, which possessed uranium-titanium precipitates. There were also illite particles within the smectite layer.	1000, 1001, 1002
165A-360-2d SRL 165 glass reacted for 360 days	The clay layer was 200 nm thick. A backbone structure appeared to be developing in some regions.	1003, 1004, 1005
IVE131A-56-1b SRL 131 glass reacted for 56 days	A silica rich calcium phase was observed to contain a number of rare earth elements.	1011, 1012, 1013, 1014, 1015

Fig. 37. (Left) TEM Image of Reacted Layer from 131A-720-2a and (Right) EDS Analysis of Glass and Clay Layer from 131A-720-2a. The layer is depleted in sodium and potassium, but enriched in iron relative to the layer. Note that because the clay region analyzed was small, the Cu X-ray fluorescence is more noticeable. According to the spectra, sodium appears to be present in the layer, however the peak is displaced relative to the glass Na peak, and is, in fact, due to the Cu-L line.

Fig. 38. EDS Analysis of Glass and Layer from 165A-360-2

Fig. 39. TEM Image of WV6 Glass Showing the Presence of a Cubic Iron Oxide Spinel Phase

Because of the short testing times to date, only a limited number of SRL EA and WV6 glasses have been examined. The results of samples surveys are summarized in Tables 23 and 24. In 7-day PCT tests the pH of WV6 glass test leachates reacted in EJ-13 well water was around 9.7, whereas the pH of leachates from SRL EA glass tests was a little higher (10.9). This may reflect the high alkali content in the EA glass compared to the WV6 glass. In EA glass tests conducted at an SA/V of 20,000 m⁻¹, a series of secondary phases started to form by 56 days. Electron diffraction data from these secondary phases are displayed in Table 19. The zeolite phase is similar to phillipsite, which is the same zeolite found in other glass tests. Solution data showed that in 7-day PCT tests, the corrosion rate in deionized water was greater than that in EJ-13 well water; a few samples reacted in DIW have been examined by TEM. The leached layers of WV6 and EA test glasses reacted in DIW for 7 days are shown in Fig. 41, which demonstrates the large difference in appearance and thickness of the reacted layers.

5. Examination of Colloids by Analytical Electron Microscopy

Long term intermittent flow tests are being conducted by using a modified version of the drip test procedure developed by YMP, to assess glass performance in an unsaturated environment [75]. Glass reacts with water to form a range of secondary phases, which were found to spall off the reacted layer into solution and remain suspended as colloidal material during waste glass drip tests [59].

We used AEM to characterize the suspended particles and colloids present in the leachates from these tests. Results from analysis of tests from the N4 series (high SA/V) were reported previously. These studies are ongoing, and recent data analysis is displayed in Table 25. A small quantity of leachate was extracted from the drip test and passed through a 'holey' carbon grid, which acts as a filter, capturing the colloids. In Fig. 42, a group of colloidal particles from a N4 #8 test is shown.

The surfaces of oxides are amphoteric in nature; the surface charge is dependent on the pH and will vary depending on the type of oxide. In most groundwaters the surface charge (i.e., zeta potential) will be negative for clay colloids, whereas the sols of metal hydroxides mostly carry positive charges in groundwaters (e.g., Fe₂O₃·nH₂O and TiO₂·nH₂O) [76]. Hence, there will be an electrostatic attraction between metal hydroxide sols and clay colloids. We observed this effect in other glass tests, where corrosion took place in the test vessel. Particles of iron oxide from the container vessel were attracted to the smectite clay particles; this created larger agglomerates, which may be less able to remain in solution.

The formation of colloids during waste glass reaction was recently discussed by Feng et al. and Buck et al. [69,76]. During the process of glass alteration under drip test conditions, phases formed on the surface of the glass can spall off into solution resulting in the formation of colloids [59]. These were found by TEM analysis to be mainly alkali-rich smectite clay particles. The number of colloids that remain in solution is strongly dependent on experimental test parameters, and, in the N4 test series, depended on whether the glass was as-cast or had been vapor hydrated prior to contact with dripping water.

Fig. 40. EELS Analysis of Rare Earth Elements in West Valley WV6 Glass

Table 23. Results of Sample Surveys for "Effects of WV6 Glass Testing"

Test Identification	Comments	Blocks Prepared
WV6-23 WV6 glass reacted in DIW at 2000 m ⁻¹ for 7 days	Layer was very thin at about 50 nm.	1099, 1100, 1101, 1102
WV6-27 WV6 glass reacted in EJ-13 at 2000 m ⁻¹ for 30 days	Most sample blocks showed little reaction although in some instances a reacted layer 100-150 nm thick was found. Iron chromium spinel phases were also observed in the glass.	1118, 1119, 1120, 1121
WV6-29 WV6 glass reacted in EJ-13 at 2000 m ⁻¹ for 70 days	A few iron chromium oxide devitrification crystals were visible in the glass. Slight evidence of surface etching was seen.	1122, 1123, 1124, 1125

Table 24. Results of Sample Surveys for "EA Glass Testing"

Test Identification	Comments	Blocks Prepared
EA 23 glass reacted in DIW at 2000 m ⁻¹ for 7 days	Extensive reaction was observed. An ordered clay layer about 150 nm covered the alteration layer which was about 1 μ m thick.	1103, 1104, 1105
EA 29 glass reacted in EJ-13 at 2000 m ⁻¹ for 70 days	The degree of reaction varied tremendously between blocks. In some cases a layer about 100 nm thick was present but in other cases the particle appeared to reacted all the way through.	1109, 1110, 1111
EA 41 glass reacted in EJ-13 at 20,000 m ⁻¹ for 56 days	A crystalline phase was observed. The composition was that of an alumino-silicate. The phase was fairly beam stable but did eventually go amorphous after observation.	1126, 1127, 1128
EA 71 glass reacted in EJ-13 at 20,000 m ⁻¹ for 56 days	A major alumino-silicate phase was identified as phillipsite (see also Table 19).	1129, 1130, 1131
EA75 glass reacted in EJ-13 at 20,000 m ⁻¹ for 182 days	A series of secondary silicate phases were found in samples, which were characterized as smectite clay, anaclime, and phillipsite.	1222, 1223, 1224, 1225, 1226, 1227, 1228

Fig. 41. TEM Image of Reacted Layer in (Left) EA-23 and (Right) WV6-23 Glass Reacted in DIW for 7 Days

Table 25. Results of Surveys from N4 Series Colloidal Particle Examinations

Grid No.	Sample	Comments
C:174	N4#8 (3/94)	Large agglomerates were found on grid. Calcium rich regions were found in the agglomerates. Cr-Pb particles and Fe-Cr-Mn particles.
C:175	N4#9 (3/94)	Agglomerates of particles found. CaF_2 particle found. Some clays contained lead and uranium. FeCrO_x particles.
C:176	N4#10 (3/94)	Calcium oxide particles and clay material. The clay was nickel rich.
C:177	N4#2 (3/94)	Barium sulfate particles. Mn-Fe and Zn, Fe, Mn clays were present, as well as Ca Al silicates with trace strontium. A magnesium aluminosilicate was also found.
C:185	N4#8 (9/94)	Calcium aluminosilicate phases and iron rich clay observed.
C:186	N4#10 (9/94)	Very little found on grid
C:187	N4#2 (9/94)	A large amount of clay material was found. Evidence of iron chromium particles, possibly corrosion products.
C:188	N4#4 (9/94)	Calcium silicon phosphorus phase, possibly nagelschmidtite, found. A small amount of strontium was observed in the phase which may have been natural strontium. Nickel-rich clay (smectite).
C:189	N4#5 (9/94)	Silicate agglomerates were found. Clay electron diffraction patterns were observed.

Fig. 42. TEM Image of Particles from N4 #8

The presence of large amounts of smectite clay does suggest that uptake of actinides may occur. The absorption of americium on quartz and montmorillonite (smectite clay) was studied by Olofsson et al. [77]. The smectite clay removed 80-90% of the dissolved americium, whereas the quartz was only able to remove 50%. Uranium and plutonium are both strongly sorbed onto colloidal bentonite clay, but neptunium is only slightly sorbed [78]. This observation is in agreement with leachate filtration studies performed by Ebert on reacted waste glass [51]. Albinsson has also demonstrated that Pu^{4+} and Am^{3+} strongly sorb on bentonite [79]. Smectite clays produced by the action of waste glass corrosion will strongly sorb actinide elements. If spallation of the reacted layer occurs, a higher concentration of radioactive elements will be present in colloidal form. The distribution of actinides in the N4 tests was also evaluated using sequential filtering. The results of these analyses will be combined with the AEM analyses to more fully characterize actinide release and the role colloid formation plays in facilitating transport of actinide elements from the glass.

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REFERENCES

1. J. K. Bates, C. R. Bradley, J. P. Bradley, N. L. Dietz, W. L. Ebert, J. W. Emery, T. J. Gerding, J. C. Hoh, J. J. Mazer, and J. E. Young, *Unsaturated Glass Testing for DOE Program in Environmental Restoration and Waste Management, Annual Report, October 1989-September 1990*, Argonne National Laboratory Report ANL-90/40 (1991).
2. J. K. Bates, C. R. Bradley, W. L. Bourcier, E. C. Buck, J. C. Cunnane, N. L. Dietz, W. L. Ebert, J. W. Emery, R. C. Ewing, X. Feng, T. J. Gerding, M. Gong, W.-T. Han, J. C. Hoh, J. J. Mazer, L. E. Morgan, J. K. Nielsen, S. A. Steward, M. Tomozawa, L. M. Wang, and D. J. Wronkiewicz, *ANL Technical Support Program for DOE Environmental Restoration and Waste Management, Annual Report, October 1990-September 1991*, Argonne National Laboratory Report ANL-92/9 (1992).
3. J. K. Bates, W. L. Bourcier, C. R. Bradley, E. C. Buck, J. C. Cunnane, N. L. Dietz, W. L. Ebert, J. W. Emery, R. C. Ewing, X. Feng, T. J. Gerding, M. Gong, J. C. Hoh, H. Li, J. J. Mazer, L. E. Morgan, L. Newton, J. K. Nielsen, B. L. Phillips, M. Tomozawa, L. Wang, and D. J. Wronkiewicz, *ANL Technical Support Program for DOE Environmental Restoration and Waste Management, Annual Report, October 1991-September 1992*, Argonne National Laboratory Report ANL-93/13 (1993).
4. J. K. Bates, W. L. Bourcier, C. R. Bradley, N. R. Brown, E. C. Buck, S. A. Carroll, J. C. Cunnane, N. L. Dietz, T. DiSanto, W. L. Ebert, J. W. Emery, X. Feng, T. J. Gerding, M. Gong, L. D. Hafenrichter, J. C. Hoh, J. J. Mazer, L. Newton, B. L. Phillips, R. Pletcher, and D. J. Wronkiewicz, *ANL Technical Support Program for DOE Environmental Restoration and Waste Management, Annual Report, October 1992-September 1993*, Argonne National Laboratory Report ANL-94/19 (1994).
5. C. M. Jantzen, *Glass Compositions and Frit Formulations Developed for DWPF*, memo to M. J. Plodinec, Savannah River Laboratory Report DPST-88-952 (1988).
6. *Defense Waste Processing Facility Waste Form Compliance Plan*, Westinghouse Savannah River Company Report WSRC-SW4-6, Rev. 1A (1992).
7. J. C. Cunnane, Ed., *High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics*, U.S. Department of Energy Report DOE-EM-0177 (1994).
8. J. K. Bates, T. A. Abrajano, Jr., B. M. Biwer, C. R. Bradley, W. L. Ebert, J. J. Mazer, D. J. Wronkiewicz, and J. E. Young, *Critical Review of Parameters Affecting Glass Reaction in an Unsaturated Environment*, to be published.
9. J. J. Mazer, *Temperature Effects on Waste Glass Performance*, Argonne National Laboratory Report ANL-91/17 (1991).
10. W. L. Bourcier, *Critical Review of Glass Performance Modeling*, Argonne National Laboratory Report ANL-94/17 (1994).
11. D. J. Wronkiewicz, *Effects of Radionuclides Decay on Waste Glass Behavior - A Critical Review*, Argonne National Laboratory Report ANL-93/45 (1994).
12. A. J. G. Ellison, J. J. Mazer, and W. L. Ebert, *Effect of Glass Composition on Waste Form Durability: A Critical Review*, Argonne National Laboratory Report ANL-94/28 (1994).

13. A. R. Hall, A. Hough, and J. A. C. Marples, *Leach Testing of Fully Active MW Glass*, Harwell Laboratory, United Kingdom Atomic Energy Authority Report AERE-R-13071 (1988).
14. L. Werme, I. K. Bjorner, G. Bart, H. U. Zwicky, B. Grambow, W. Lutze, R. C. Ewing, and C. Magrabi, "Chemical Corrosion of Highly Radioactive Borosilicate Nuclear Waste Glass under Simulated Repository Conditions," *J. Mater. Res.* 5, 1130 (1990).
15. *JSS-Project Phase II: Final Report of Work Performed at Studsvik Energiteknik AB and at Swiss Federal Institute for Reactor Research*, Japanese, Swiss, and Swedish Project Report JSS-85-01 (1985).
16. J. A. C. Marples, N. Godon, F. Lanza, and P. Van Iseghem, "Radionuclide Release from High-Level Waste Form under Repository Conditions in Clay or Granite," in *Radioactive Waste Management and Disposal*, L. Cecille, Ed., Elsevier, Amsterdam, pp. 287-301 (1991).
17. J. K. Bates, "Disposal of Vitrified Waste in an Unsaturated Environment," *High-Level Radioactive Waste Management*, Proc. 2nd Ann. Inter. Conf., 1, 700-707 (1991).
18. X. Feng and J. K. Bates, "Initial Comparison of Leach Behavior between Fully Radioactive and Simulated Waste Glass through Long-Term Testing, Part 1. Solution Analysis," Proc. Third Internat. Conf. on High-Level Radioactive Waste Manage., 925-933 (1992).
19. X. Feng, J. K. Bates, E. C. Buck, C. R. Bradley, and M. Gong, "Long-Term Comparison of Dissolution Behavior between Fully Radioactive and Simulated Waste Glasses," *Nucl. Technol.* 104, 193-206 (1993).
20. N. E. Bibler, "Leaching of Fully Radioactive SRP Nuclear Waste Glass in Tuff Ground Water in Stainless Steel Vessels," *Adv. Ceram.* 20, 619 (1986).
21. N. E. Bibler, G. G. Wicks, and V. M. Oversby, "Leaching Savannah River Plant Nuclear Waste Glass in a Saturated Tuff Environment," *Mater. Res. Soc. Symp. Proc.* 44, 247-256 (1985).
22. N. E. Bibler and J. K. Bates, "Product Consistency Leach Tests of Savannah River Site Radioactive Waste Glasses," *Mater. Res. Soc. Symp. Proc.* 176, 327-338 (1990).
23. N. E. Bibler and G. G. Wicks, *Leaching Savannah River Plant Nuclear Waste Glass in a Saturated Tuff Environment*, Lawrence Livermore National Laboratory Report UCRL-91258 (1984).
24. N. E. Bibler, "Characterization of Borosilicate Glass-Containing Savannah River Plant Radioactive Waste," *Am. Chem. Soc. Symp. Ser.* 246, 359-372 (1983).
25. J. K. Bates and T. J. Gerding, *One-Year Results of the NNWSI Unsaturated Test Procedure: SRL 165 Glass Application*, Argonne National Laboratory Report ANL-85-41 (1986).
26. J. K. Bates, T. A. Abrajano, Jr., D. J. Wronkiewicz, T. J. Gerding, and C. A. Seils, *Strategy for Experimental Validation of Waste Package Performance Assessment*, Argonne National Laboratory Report ANL-90/21 (1990).

27. J. K. Bates and T. J. Gerding, *Application of the NNWSI Unsaturated Test Method to Actinide Doped SRL 165 Type Glass*, Argonne National Laboratory Report ANL-89/24 (1990).
28. J. I. Kim, W. Treiber, Ch. Lierse, and P. Offerman, "Solubility and Colloid Generation of Plutonium from Leaching of a HLW Glass in Salt Solutions," *Mater. Res. Soc. Symp. Proc.* 44, 359-368 (1985).
29. J. K. Bates et al., *Annual Report to the Repository Technology Program*, submitted to the Repository Technology Program (1990).
30. W. J. Weber, "The Effect of Radiation on Nuclear Waste Forms," *J. Min. Metals and Mater. Soc.*, pp. 35-39 (July 1991).
31. A. Barkatt, A. Barkatt, and W. Sousanpour, "Gamma Radiolysis of Aqueous Media and Its Effects on the Leaching Processes of Nuclear Waste Disposal Materials," *Nucl. Technol.* 60, 218-227 (1983).
32. G. L. McVay, W. J. Weber, and L. R. Pederson, "Effects of Radiation on the Leaching Behavior of Nuclear Waste Forms," *Nucl. Chem. Waste Manage.* 2, 103-108 (1981).
33. W. G. Burns, A. E. Hughes, J. A. C. Marples, R. S. Nelson, and A. M. Stoneham, "Radiation Effects and the Leach Rates of Vitrified Radioactive Waste," *Nature* 295, 130-132 (1982).
34. W. J. Weber and F. P. Roberts, "A Review of Radiation Effects in Solid Nuclear Waste Forms," *Nucl. Technol.* 60, 178-198 (1983).
35. N. E. Bibler, "Leaching of Fully Radioactive SRP Nuclear Waste Glass in Tuff Ground Water in Stainless Steel Vessels," *Adv. Ceram.* 20, 619 (1986).
36. R. A. Van Konynenburg, *Radiation Chemical Effects in Experiments to Study the Reaction of Glass in an Environment of Gamma-Irradiated Air, Groundwater, and Tuff*, Lawrence Livermore National Laboratory Report UCRL-53719 (1986).
37. W. L. Ebert, 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 in 1E3 R/h and 0 R/h*, Argonne National Laboratory Report ANL-90-13 (1990).
38. J. K. Bates, D. F. Fischer, and T. J. Gerding, *The Reaction of Glass during Gamma Irradiation in a Saturated Tuff Environment, Part I: SRL 165 Glass*, Argonne National Laboratory Report ANL-86-62 (1986).
39. P. Van Iseghem, K. Berghman, and W. Timmerman, "The Interaction between Nuclear Waste Glasses and Clay-II," *Mater. Res. Soc. Symp. Proc.* 176, 291-298 (1990).
40. D. J. Wronkiewicz, J. E. Young, and J. K. Bates, "Effects of Alpha and Gamma Radiation on Glass Reaction in an Unsaturated Environment," *Mater. Res. Soc. Symp. Proc.* 212, 99-106 (1991).
41. D. J. Wronkiewicz, C. R. Bradley, J. K. Bates, and L. M. Wang, "Effects of Radiation Exposure on SRL 131 Composition Glass in a Steam Environment," *Mater. Res. Soc. Symp. Proc.* 333, 259-267 (1994).

42. D. J. Wronkiewicz, "Radionuclide Decay Effects on Waste Glass Corrosion," Mater. Res. Soc. Symp. Proc. 333, 83-97 (1994).
43. J. C. Cunnane et al., *High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics, Volume 2*, Section 2.5, "Effects of Radionuclide Decay," pp. 87-108 (1994).
44. D. J. Wronkiewicz and J. K. Bates, "Alpha and Gamma Radiation Effects on Air-Water Systems at High Gas/Liquid Ratios," Nuclear Technology (in press).
45. D. J. Wronkiewicz, J. K. Bates, J. C. Hoh, and J. W. Emery, *Radiation Effects on Moist-Air Systems and the Influence of Radiolytic Product Formation on Nuclear Waste Glass Corrosion*, Argonne National Laboratory Report ANL-94/30 (1995).
46. J. R. Fowler and M. J. Plodinec, "Projected Compositions and Radiogenic Properties of DWPF Glasses," Proc. of Third International High-Level Radioactive Waste Management (IHLRWM) Conference, Las Vegas, NV, Apr. 12-16, 1992, pp 904-910 (1992).
47. C. M. Jantzen, N. E. Bibler, D. C. Beam, W. G. Ramsey, and B. J. Waters, *Nuclear Waste Glass Product Consistency Test (PCT) Version 5.0(U)*, Westinghouse Savannah River Company Report WSRC-TR-90-539, Rev. 2 (1992).
48. J. K. Bates, W. L. Ebert, X. Feng, and W. L. Bourcier, "Issues Affecting the Prediction of Glass Reactivity in an Unsaturated Environment," J. Nucl. Mater. 190, 198-227 (1992).
49. W.L. Bourcier, W.L. Ebert, and X. Feng, "Modeling Surface Area to Volume Effects on Borosilicate Glass Dissolution," Mater. Res. Soc. Symp. Proc. 294, 577-582 (1993).
50. E. C. Buck, J. K. Bates, J. C. Cunnane, W. L. Ebert, X. Feng, and D. J. Wronkiewicz, "Analytical Electron Microscopy Study of Colloids from Nuclear Waste Glass Reaction," Mater. Res. Soc. Symp. Proc. 294, 199-206 (1993).
51. W. L. Ebert, J. K. Bates, E. C. Buck, M. Gong, and S. F. Wolf, "Disposition of Actinides Released From High-Level Waste Glass," Ceram. Trans. 45, 231-241 (1994).
52. W. L. Ebert, J. K. Bates, E. C. Buck, and C. R. Bradley, "Accelerated Glass Reaction Under PCT Conditions," Mater. Res. Soc. Symp. Proc. 294, 569-576 (1993).
53. W. L. Ebert, J. K. Bates, and E. C. Buck, "The Reaction of SRL 202 Glass in J-13 and DIW," Mater. Res. Soc. Symp. Proc. 294, 137-144 (1993).
54. W. L. Ebert, "The Effects of the Leachate pH and the Ratio of Glass Surface Area to Leachant Volume on Glass Reactions," Phys. Chem. Glasses 34(2), 58-65 (1993).
55. W. L. Ebert and J. K. Bates, "A Comparison of Glass Reaction at High and Low Surface Area to Volume," Nucl. Technol. 104(3), 372-384 (1993).
56. W. L. Ebert, J. K. Bates, C. R. Bradley, E. C. Buck, N. L. Dietz, and N. R. Brown, "The Long-Term Alteration of Borosilicate Waste Glasses," Ceram. Trans. 39, 333-340 (1993).

57. H. Nitsche and N. M. Edelstein, "Solubilities and Speciation of Selected Transuranium Ions. A Comparison of a Non-Complexing Solution with a Groundwater from the Nevada Tuff Site," *Radiochim. Acta* 39, 23-33 (1985).
58. E. Y. Vernaz and N. Godon, "Leaching of Actinides from Nuclear Waste Glass: French Experience," *Mater. Res. Soc. Symp. Proc.* 257, 37-48 (1992).
59. J. K. Bates, J. P. Bradley, A. Teetsov, C. R. Bradley, and M. Buchholtz ten Brink, "Colloid Formation During Waste Form Reaction: Implications for Nuclear Waste Disposal," *Science* 256, 649-651 (1992).
60. D. McPherson, I. Joseph, A. Mathur, C. Capozzi, S. Armstrong, 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).
61. L. R. Eisenstatt, *Description of the West Valley Demonstration Project Reference High-Level Waste Form and Canister*, U.S. Department of Energy Report DOE/NE/44139-26 (1986).
62. 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 Mgmt.* 11, 205-221 (1991).
63. G. D. Maupin, W. M. Bowen, and J. L. Daniel, *Fabrication and Characterization of MCC Approved Testing Material- ATM-10 Glass*, Pacific Northwest Laboratory Report PNL-5577-10 (1988).
64. J. K. Bates, J. A. Fortner, P. A. Finn, D. J. Wronkiewicz, J. C. Hoh, J. W. Emery, E. C. Buck, and S. F. Wolf, *Yucca Mountain Project - Argonne National Laboratory, Annual Progress Report, FY 1994*, Argonne National Laboratory Report ANL-94/42 (1995).
65. A. B. Woodland, J. K. Bates, and T. J. Gerding, *Parametric Effects on Glass Reaction in the Unsaturated Test Method*, Argonne National Laboratory Report ANL-91/36 (1991).
66. J. Bowles et al., "A Re-Examination of Cheralite," *Mineral. Mag.* 43, 885-888 (1980).
67. F. G. Fisher and R. Meyrowitz, "Brockite, a New Calcium Thorium Phosphate from the Wet Mountains, Colorado," *Am. Mineral.* 47, 1346-1355 (1962).
68. E. C. Buck, N. L. Dietz, and J. K. Bates, "Electron Beam Analysis of Nuclear Waste Glass," *Proc. 52nd Annual Meeting of the Microscopy Society of America Conf.*, New Orleans, LA, July 31-August 5, 1994, pp. 656-657.
69. X. Feng, E. C. Buck, J. K. Bates, C. Mertz, J. C. Cunnane, and D. Chaiko, "Colloid Formation during Nuclear Waste Glass Dissolution," *Radiochim. Acta* 66/67, 197-205 (1994).
70. J. J. Mazer and J. K. Bates, "Analysis of an Altered Simple Silicate Glass Using Different Mineral and Glass Standards," *Scanning* 11, 237 (1989).
71. T. A. Abrajano, J. K. Bates, J. P. Bradley, A. B. Woodland, and W. L. Bourcier, "Secondary Phase Formation during Waste-Glass Dissolution," *Clays and Clay Miner.* 38, 537-548 (1990).

72. E. C. Buck, J. Fortner, J. K. Bates, X. Feng, N. L. Dietz, C. R. Bradley, and B. S. Tani, "Long Term Behavior of Nuclear Waste Glass: Analytical Electron Microscopy Examination," *Mater. Res. Soc. Symp. Proc.* 333, 585-593 (1994).
73. *Mineralogy and Geology of Natural Zeolites*, Review in *Mineralogy*, Vol 4, F. A. Mumpton, Ed., Mineralogical Society of America (1986).
74. R. D. Leapman, "Limits of Detectability for Parallel Electron Energy Loss Spectroscopy," *Inst. Phys. Conf. Ser.* 119(3), Bristol, U.K., September 10-13, 1991.
75. J. K. Bates and E. C. Buck, "Results of Drip Tests on Sludge-Based and Actinide-Doped Glasses," *Inter. High-Level Rad. Waste Mgmt. Conf.*, Las Vegas, NV, May 22-26, 1994, pp. 1088-1101 (1994).
76. K. H. Leiser, A. Ament, R. Hill, R. N. Singh, U. Stingl, and B. Thybusch, "Colloids in Groundwater and Their Influence on Migration of Trace Elements and Radionuclides," *Radiochim. Acta* 49, 83-100 (1990).
77. V. Olofsson, B. Allard, B. Torstenfelt, and K. Anderson, "Formation and Transport of Americium Colloids in Aqueous Systems," *Mater. Res. Soc. Symp. Proc.* 50, 729-736 (1985).
78. J. W. Shade, L. L. Ames, and J. E. McGarrah, "Actinide and Technetium Sorption on Iron Silicate and Dispersed Clay Colloids," in *Geochemical Behavior of Dispersed Radioactive Waste*, ACS Symp. Ser. 246, G. S. Barney, J. D. Navratil, and W. W. Schulz, eds., pp. 67-77 (1984).
79. Y. Albinsson, B. Christiansen-Statmark, I. Engkist, and W. Johansson, "Transport of Actinides and Tc through a Bentonite Containing Small Quantities of Iron or Copper," *Radiochim. Acta* 52/53, 283-286 (1991).

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