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ARGONNE NATIONAL LABORATORY
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**ANL TECHNICAL SUPPORT PROGRAM FOR DOE ENVIRONMENTAL
RESTORATION AND WASTE MANAGEMENT**

**ANNUAL REPORT
OCTOBER 1992 - SEPTEMBER 1993**

by

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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 1993 on the following tasks:

1. A compendium of the characteristics of high-level nuclear waste borosilicate glass has been written and has undergone several review cycles.
2. A critical review of important parameters that affect the reactivity of glass in an unsaturated environment is being prepared. The parameters include radiation, glass surface area-to-liquid volume (SA/V) ratio, and glass weathering. A critical review is also underway on modeling of waste glass performance. Data Reports are also being prepared to cover the experimental work ongoing in the program.
3. A series of tests has been started 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 three years.
4. 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 and high SA/V liquid conditions have been completed, and the data are being compiled.

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5. 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.
6. Analytical electron microscopy (AEM), infrared spectroscopy, and nuclear resonant profiling are being used to assess the glass/water reaction pathway by identifying intermediate phases that appear on the reacting glass. Additionally, colloids from the leach solutions are being studied using AEM.
7. A mechanistically based model is being developed to predict the performance of glass over repository-relevant time periods. This model has been applied to data generated in the testing program.

EXECUTIVE SUMMARY

This report is an overview of the progress during FY 1993 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 1993 on each of the technical tasks is summarized below.

Preparation of the Waste Glass Compendium

The document entitled "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Corrosion Characteristics" was prepared and has undergone four major revisions based on comments received from the Technical Review Group, whose members include Dr. David E. Clark of the University of Florida, Dr. Robert H. Doremus of the Rensselaer Polytechnic Institute, Dr. Bernd E. Grambow of Kerforschungszentrum Karlsruhe in Germany, Dr. J. Angwin C. Marples of the United Kingdom Atomic Energy Authority, and Dr. John M. Matuszek of JMM Consulting. This document is a concise presentation of current scientific information on the alteration of borosilicate glass waste forms under the range of service conditions to which they might be exposed during storage, transportation, and eventual disposal in a geological repository.

The document was prepared by assembling and integrating contributions from authors at Argonne National Laboratory, Westinghouse Savannah River Company, Lawrence Livermore National Laboratory, and Battelle Pacific Northwest Laboratory. The compendium has been submitted to DOE-HQ/EM-343 for publication, which should occur in 1994.

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

Long-Term Testing of Fully Radioactive Glass

The reactivity of simulated (S) and fully radioactive (R) glasses has been compared under repository-relevant conditions as part of a long-term batch testing program. The data indicate little difference in reactivity between radioactive and simulated nuclear waste glasses. Similar leach trends were observed for both simulated and radioactive glasses in static tests at SA/V of 340 and 2000 m⁻¹, for time periods up to 980 days, and on three SRL nuclear waste glass compositions (types 165, 131, and 200). The data also suggest that both simulated and radioactive glasses of the same base composition generally follow the same reaction-controlling processes. The relative glass durability observed for the simulated glasses is 165S > 131S > 200S. The same order of glass durability is preserved for the fully radioactive glasses. The leachate pH's for the fully radioactive glasses are usually lower than the simulated glasses due to the radiolysis-induced formation of nitrogen-related acids and other acids in the leachates. This reduction in the solution pH's of the radioactive glasses, combined with the rate-controlling processes, can be used to explain the observed minor differences in leach behavior between simulated and radioactive glasses at 340 and 2000 m⁻¹, where the radioactive glass reacted slightly less than the corresponding simulated glass for both 131/11-type and 200-type glasses but slightly more for 165-type glasses.

A large difference in reactivity (up to a factor of 1000 in the leach rate of boron) was observed between 200R and 200S when tested at SA/V of 20,000 m⁻¹ within one year. The SRL 200S glass exhibited a reaction rate, 1145 mg/(m²·d), that is close to the initial (forward) glass reaction rate for tests in progress for more than 182 days. The accelerated glass reaction rate with the 200S glass is associated with the formation of crystalline phases, such as a clinoptilolite, and a pH excursion. The radiation field generated by the fully radioactive glass did not have any direct effect on the development of the reacted-glass surface layers, but did reduce the solution pH. This lower solution pH, in turn, may retard the onset of an increased reaction rate. These results suggest that 200R glass may be more durable than the corresponding 200S glass if the leachate pH of 200R can be kept lower than that of 200S. In modeling the performance of glass, all factors, such as the radiation-induced pH reduction in the leachate, that influence glass reaction must be accounted for to make adequate long-term performance predictions. Meaningful comparison of tests between radioactive and simulated nuclear waste glasses should include long-term tests at high SA/V.

Tests using the 200R glass have also been in progress using the drip test procedure for more than two years. In these tests, both as-cast glass and glasses pre-aged by contact with water vapor are contacted by slowly dripping water. The solution collects in the bottom of the test vessel, and periodically the glass samples are moved to a new test vessel, and the solution in the bottom of the old test vessel is analyzed. The purpose of using both as-cast and pre-aged glasses is to simulate two conditions under which glass may contact water in an unsaturated repository. The as-cast glass tests showed little reaction or actinide release. The mechanism by which this glass reacts is controlled mainly by ion exchange and spallation of loosely attached layers from the glass surface. The pre-aged glass showed a different reaction trend. Initially, there was a large concentration of anions (SO₄²⁻, HPO₄⁻, and Cl⁻) in the test solutions, and the truly dissolved actinide fraction in solution was large compared to the as-cast tests. However, with extended reaction, the anionic content of the leachates decreased, and the majority of

actinides were associated with fine particulate phases that were washed from the pre-aged surfaces. These tests are continuing to determine whether or not a steady-state condition is reached.

Effect of Radiation on Glass Reaction at Large SA/V

The objective of this task is to determine if radiation has any significant effect on glass behavior under the high SA/V conditions expected at a geologically unsaturated repository site. These tests examine (1) the effect of radiation on the environment of a moist air system, (2) the extent of glass reaction in a radiolytic field, and (3) the influence of radiation and radiolytic products on the formation and stability of glass alteration phases.

In tests during this period, glass wafers (~1 mm thick) exposed to a gamma irradiation field in a vapor-saturated-air environment at temperatures of 150 to 200°C formed reaction layers 4 to 15 times thicker than their nonirradiated counterparts. The mineral phases that precipitated on the surface were similar to those that formed on the nonirradiated samples, except that the reaction sequence appears to be accelerated in the irradiated tests. The mineral paragenetic trends in these tests are identical to those that occur during the alteration of naturally occurring volcanic glasses in saline-alkaline lakes. This similarity provides a credible link between short-term laboratory tests and analogue materials altered over geologic time scales. It also indicates that the elevated test temperatures did not change the glass reaction mechanism.

Cation release trends (as function of time) from irradiation tests with glass monoliths (types 131, 165, and 202) immersed in EJ-13 water (90°C, SA/V of 340 m⁻¹) generally display parabolic patterns, with decreased release rates occurring after 180 to 360 days of testing. The solution pH trends also correlate with these changes, with leachate pH's leveling out at ~9 after an early increase between 56 and 180 days for actinide-doped 131 and 202 glasses. By contrast, leachate pH values continually increase for the actinide-doped 165 glasses during the entire 720 days of testing. The formation of radiolysis products in the leachate appears to have enhanced release rates of some elements (K and Li) during testing, while Si and U release rates have been reduced due to irradiation exposure.

Relationship between High SA/V Experiments and MCC-1

Static leach tests are being conducted to assess how the SA/V ratio (10-20,000 m⁻¹) affects the rate and mechanism of the glass reaction. Test results available to date (up to 1000 days) show the predominant effect of SA/V to be the extent to which released glass components are diluted. The higher pH and silicic acid concentrations attained at higher SA/V (≥ 2000 m⁻¹) influence the glass corrosion rate. The formation of secondary phases after longer reaction times (>180 days) affects the solution chemistry (particularly the silicic acid concentration) and the glass corrosion rate. A long-term corrosion rate that is higher than that measured in short-term tests was observed under some test conditions. This difference may be due to the formation of critical secondary phases. Analysis of the corroded glass revealed that smectite clay is formed in tests at all SA/V tested and at all reaction times. Other phases have been found in tests showing the higher final 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.

Analytical Electron Microscopy Support

The analytical support staff collaborates with other members of the ANL 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 employ analyses by analytical electron microscopy to provide information necessary to understand the reaction processes on the glasses. This information will contribute to the development of the models needed for prediction of glass behavior.

In addition to the reaction layer analyses, colloidal particles present in the leachate, some of which may carry radionuclides, are being examined. This effort has permitted not only identification of colloidal phases but also the colloidal particle formation in the leachate.

Detection limits of elements and the identification of phases have been improved through use of electron energy loss spectroscopy during detailed analyses of samples.

Modeling Tasks at Lawrence Livermore National Laboratory

The objective of this task is to develop and apply a computer model to the reaction of nuclear waste glasses in a repository environment. In developing the model, we are also performing experiments that are used to quantify parameters in the model. This information is used in the glass dissolution model to simulate site-specific tests (such as the Product Consistency Test), model the corrosion behavior of natural analogs to waste glass, and assess glass durability under repository conditions.

In FY 1993 we performed modeling simulations of (1) experiments with SRL 202 glass carried out at ANL over a range of SA/V ratios, 10 to 20,000 m⁻¹, and (2) unsaturated (drip) tests on SRL 165 glass. We also performed flow-through tests and did nuclear magnetic resonance (NMR) analysis of some simple Na-B-Si glasses, and collected experimental data on glass surface speciation using surface titrations. We continued work on determining the functional form of the affinity term in the rate equation by using data from closed-system tests of CSG glass (a simple analog of SRL 165 glass) and tested the new term with experimental results.

Predictions of long-term glass dissolution rates are highly dependent on the form of the affinity term in the rate expression. Analysis of the quantitative effect of saturation state on glass dissolution rate for CSG glass showed that a simple (1 - Q/K) affinity term does not match experimental results. At 100°C the data are better fit by an affinity term having the form

$\left(1 - \left(\frac{Q}{K}\right)^{\frac{1}{\sigma}}\right)$, where $\sigma = 10$. This revised affinity expression also increases the ability of our model to predict the magnitude of accelerated reaction rates when they occur.

Preliminary results from our surface chemistry investigations show that glass durability depends on reactions occurring at the glass-solution interface. The dissolution and net surface H⁺ and OH⁻ adsorption of the CSG glass (18.2 wt % Na₂O, 5.97 wt % CaO, 11.68 wt % Al₂O₃, 8.43 wt % B₂O₃, and 55.73 wt % SiO₂) are minimal at near neutral pH. In the acid and alkaline pH regions, CSG glass dissolution rates are proportional to [H⁺]/σ(2,adsorbed) and [OH⁻]/σ(0.8,adsorbed), respectively. In contrast, silica gel dissolution and net H⁺ and OH⁻ adsorption are minimal and independent of pH in acid to neutral solutions. In the

alkaline pH region, silica gel dissolution is proportional to $[\text{OH}^-]/\sigma^{(0.9, \text{adsorbed})}$. Although sodium adsorption is significant for CSG glass and silica gel in the alkaline pH regions, it is not clear if this effect enhances dissolution or is an artifact from the depolymerization of the framework bonds.

The atomic-level structures for nine simple sodium-borosilicate glasses were determined by NMR spectroscopic techniques. The ^{11}B NMR data provide the population distribution of the various local boron structural units, including the ratio of three- to four-coordinated boron (B3/B4). Detailed microscopic models for borosilicate glass dissolution were developed by correlating this structural information with dissolution rates of the same samples.

Comparison of the present structural results with the dissolution experiments indicates a qualitative inverse relationship between the population of the B4s (four-coordinate symmetric) component with normalized silica release rates at $\text{pH} = 2$. For the series 20:20:60 - 20:30:50 - 20:35:45 ($\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ratio), an increase of silicon release rates was correlated with a decrease of the fraction of boron atoms in silica-rich environments. However, the silica release rates increased sharply from 20:30:50 to 20:35:45, with small changes in the populations of boron structural units [e.g., $n(\text{B4s})$ from 0.14 to 0.11]. In addition, the silica release rate decreased in going from 20:20:60 to 15:25:60, with $n(\text{B4s})$ decreasing from 0.28 to 0.22 and total B4 from 0.69 to 0.55. These findings indicate that additional structural factors control dissolution behavior in this pH region ($\text{pH} = 2$). Further NMR efforts should include use of those techniques capable of quantifying the concentration of non-bridging oxygens, such as ^{17}O NMR.

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I. INTRODUCTION

The High-Level Nuclear Waste Technical Support Program at Argonne National Laboratory (ANL) is part of a continuing activity performed for DOE's 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). Past progress is given in the annual reports for FY 1990, 1991, and 1992 [1-3]. 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) initiate 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) develop and demonstrate the applicability of models to 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 Review and Data Reports.

To augment the Critical Review reports, "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Corrosion Characteristics" was compiled. This is an overview document, with contributions from Westinghouse Savannah River Company on glass production and Battelle Pacific Northwest Laboratory on international experience. This document will be used to support the decision-making process for DWPF start-up.

During FY 1993, in addition to the Compendium and Critical Reviews, waste glass testing and modeling were conducted. In this report, progress in each active area is reviewed after a general background description applicable to all areas is presented.

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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) Preparation of the Document Entitled "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Corrosion Characteristics,"
- (2) Critical Review of Parameters Affecting Glass Reaction in an Unsaturated Environment,
- (3) Long-Term Testing of Fully Radioactive Glass,
- (4) Effect of Radiation on Glass Reaction at Large SA/V,
- (5) Relationship between High SA/V Experiments and MCC-1,
- (6) Modeling Tasks at Lawrence Livermore National Laboratory.

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

*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.

to most durable based on hydration theory [4]. 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 the blend composition identified in the Waste Compliance Plan (WCP) [5] and, therefore, was expected to be a fair simulation of a production glass.

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 of its expected similarity to production glass, it is used in a more extensive test matrix to assess glass performance under unsaturated conditions. (See Sec. V 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 glasses and are similar to compositions identified in the WCP. 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., and the base 202 frit is based on DWPF start-up frit. Each base frit is modified 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 a "U" glass (e.g., 131U). If a glass contains transuranic elements, it is designated as "A" glasses (e.g., 131A).

At this time, testing has been initiated on all of the fully radioactive and simulated glass, and the glass compositions are shown in Table 1. The starting glasses are still undergoing analysis, so the compositions shown in Table 1 are subject to change. This is especially true for the radionuclide content of the glasses which are now being analyzed by inductively coupled plasma/mass spectrometry (ICP/MS) and alpha counting combined with electroplating. However, 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 composition is listed in Table 2.

Table 1. Composition of Glasses Used in Testing^a

Element	Oxide, wt %								
	131/11R	131/11S	131U/A	200R	200S	202U/A	165/42R	165/42S	165U/A
Al	9.7	9.2	3.27	5.9	5.5	3.84	10.36	8.7	4.08
B	9.4	9.3	9.65	9.7	9.6	7.97	8.02	8.4	6.76
Ba	0.02	0.05	0.16	0.02	0.03	0.22	--	0.4	0.06
Ca	3.9	2.9	0.93	0.9	0.9	1.20	0.33	0.3	1.62
Cr	0.9	0.7	0.13	0.3	0.2	0.08	0.33	0.8	<0.01
Cu	0.02	0.04	0.02	0.1	0.1	0.40	0.03	0.06	--
Fe	4.8	5.1	12.66	9.0	8.8	11.41	5.89	6.1	11.74
K	0.06	0.1	3.86	3.5	3.3	3.71	0.05	0.08	0.19
Li	3.3	3.2	3.00	3.4	3.3	4.23	4.72	4.7	4.18
Ce	--	--	TBA ^b	--	--	TBA	--	--	--
Nd	--	--	TBA	0.1	--	TBA	--	--	--
La	--	--	TBA	0.06	0.01	TBA	--	--	--
Mg	1.4	1.6	1.31	1.6	1.7	1.32	1.02	1.0	0.70
Mn	1.7	1.7	2.43	1.6	1.5	2.21	1.94	1.8	2.79
Mo	--	--	--	0.01	0.02	0.05	--	--	--
Na	16.6	17.5	12.08	15.0	16.0	8.92	11.12	10.8	10.85
Ni	0.5	0.6	1.24	0.9	0.9	0.82	0.61	0.8	0.85
Pb	0.02	0.1	--	0.03	0.05	0.01	0.05	0.01	--
Si	45.5	45.8	43.76	45.5	45.4	48.95	TBA	52.4	52.86
Sr	0.02	0.02	0.01	0.01	0.02	0.03	0.04	0.01	0.11
Ti	1.5	1.7	0.65	0.08	0.1	0.91	--	0.08	0.14
Zn	0.02	0.05	0.02	0.02	0.04	0.02	0.03	0.1	0.04
Zr	0.08	0.1	0.22	0.06	0.09	0.10	0.83	1.4	0.66
Th	--	--	--	--	--	0.26	--	0.01	--
Rh	--	--	--	--	--	<0.05	--	--	--
U	0.25	0.26	TBA	1.8	1.9	1.93	TBA	0.1	0.92
Tc	--	--	0.02	--	--	0.02	--	--	0.02
²³⁷ Np	TBA	--	0.01	--	--	0.01	TBA	--	0.01
²³⁸ Pu	2.7E-4	--	2.1E-4	--	--	--	1.7E-4	--	--
²³⁹ Pu	TBA	--	TBA	--	--	TBA	--	--	0.01
²⁴¹ Am	9.0E-5	--	2.4E-4	--	--	TBA	9.5E-5	--	0.0004
²⁴⁴ Cm	TBA	--	--	--	--	--	--	--	--
¹³⁷ Cs	1.7E-8	--	--	--	--	--	1.1E-4	--	--

^aThe compositions reported are best values at this time. Glass analyses are ongoing, and the compositions are upgraded with new data as they become available.

^bTBA = to be analyzed.

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

III. PREPARATION OF THE WASTE GLASS COMPENDIUM

Current plans call for start-up of facilities, within the next few years, for vitrification of high-level nuclear waste stored in tanks at Savannah River, South Carolina, and West Valley, New York. The products from these facilities will be canistered high-level nuclear waste borosilicate glass. These products will be temporarily stored, transported, and eventually disposed of in a geologic repository. The behavior of the glass, under the range of service conditions that it is likely to experience, is a subject of considerable scientific and public interest. Fortunately, an enormous body of pertinent scientific information has been generated worldwide over the past few decades regarding this subject. A document entitled "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Corrosion Characteristics" has been prepared to consolidate this information. The intent of this ambitious undertaking is to support resolution of issues concerning waste glass degradation that may arise during startup of the vitrification facilities.

The history of the development of borosilicate glass as a waste form reflects a broad international consensus on its suitability as a waste form for immobilization of high-level nuclear waste. After the initial recognition of glass as a promising medium for immobilization of high-level nuclear waste in the mid-1950s [6], the technology for vitrification of high-level nuclear waste has been pursued internationally for four decades. The first production facility to vitrify high-level radioactive waste began operation at Marcoule, in France, in 1978. Borosilicate glass has now been selected as the final waste form in most countries that have high-level nuclear waste from reprocessing of nuclear fuels. In the U.S., borosilicate glass was selected as the reference waste form for tank wastes stored at Savannah River [7], West Valley [8], and Hanford [9] after a review and evaluation of alternatives [10,11].

Subjects discussed in the full compendium include waste glass production, plausible environmental service conditions, experimental effects of glass composition and environmental factors on borosilicate glass corrosion and weathering, observations of alterations in natural glasses, glass dissolution modeling, and uncertainties in long-term simulations. Because waste glass alterations in a geologic repository may include corrosion of the glass network due to groundwater and/or water vapor contact, experimental testing results are described and interpreted in terms of the underlying chemical reactions and physical processes involved. The status of mechanistic modeling, which can be used for long-term predictions, is described, and the remaining uncertainties associated with long-term simulations are summarized.

The compendium contents are summarized in three volumes. Volumes I and II provide information intended for somewhat different audiences. Volume I is a summary-type document intended for managers, decision makers, and modelers. Volume II provides extensive experimental details on factors that influence glass corrosion and is primarily intended for other nuclear waste researchers, and Volume III is a bibliography. The combined set of Volumes I, II, and III is intended for scientists and engineers working in the field of high-level waste.

The entire compendium has undergone an extensive technical review by an international team of experts in the field of waste glass corrosion. The final document is scheduled for publication in calendar year 1994.

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IV. 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 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" [12]. The results from this Task will be used to support start-up of the DWPF and WVDP.

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 [13]. The first detailed report, which reviews the effects of temperature on waste glass performance, has been issued [14]. This report concluded that reaction mechanisms for waste glass dissolution in water are complex and involve multiple simultaneous reaction processes. Understanding the interplay of the reaction processes and their temperature dependences requires a clear understanding of the reaction mechanism, which has not yet been achieved. Until a better understanding of glass reaction mechanisms is available, caution should be exercised in using temperature as an accelerating parameter for glass durability testing.

The parameter reviewed during FY 1993 is the effect of glass composition on waste glass durability. This report is nearly completed but has required extensive review and revision. This report is an expansion of the interim report and includes brief reviews of models of glass dissolution and glass structure and will form a basis for later critically reviewing correlations of glass composition and glass durability.

E. Future Progress

The detailed reviews of radiation, SA/V ratio, glass weathering, and modeling are in progress. Drafts of each report were to be completed during FY 1993; however, work on the Compendium took precedence and the Critical Review reports will now be published during FY 1994.

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.

V. LONG-TERM TESTING OF FULLY RADIOACTIVE GLASS

A. Introduction and Background

Before glass can be stored in a waste repository, it is necessary to predict how the glass may behave in the repository. The behavior prediction will be based on the development of a model. Information that goes into the model includes data describing glass reaction mechanisms, rates of initial and final reaction, the affinity of the glass to react, and dependence of glass reaction on interactions with other components in the waste package. The model must be mechanistically, not empirically based. To demonstrate its predictive capability, the model must be validated. Validation tests include long-term tests that closely simulate the expected conditions for storage, including parameters related to the glass and the repository. This task addresses tests to be performed that will provide information to validate glass reaction models and to demonstrate an understanding of glass reaction processes that will occur in an unsaturated environment. The results will also indicate whether differences exist in the reaction of fully radioactive glass compared to nonradioactive glass of the same nominal composition. This is important to demonstrate because model development has generally been done using results from nonradioactive glass tests. The results of the radioactive and nonradioactive tests can be used to demonstrate glass reaction under potential repository conditions, but they should not be used by themselves to predict glass reaction to repository time frames.

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.

In the DWPF process, glass will be produced by combining sludge and supernatant waste components with nonradioactive frit. The glass produced in the DWPF will be radioactive and must be processed and handled in remotely operated facilities. However, most testing to evaluate the performance of glass has been done using simulated nonradioactive analogs of the radioactive glass. It must be demonstrated that the simulated experiments are adequate representations of reactions that will occur with the actual glass to be produced by the DWPF. The following issues are of concern: (1) Does the simulated glass react via the same controlling mechanism? (2) Does the analogue glass produce the same secondary phases and in the same sequences? (3) Are there effects due to radioactivity that are not adequately simulated using nonradioactive glass? (4) Are there effects of using glasses without all the nonradioactive components that will be present in the sludge, supernatant, and frit feeds to the DWPF? Nonradioactive glasses are generally produced from pure starting materials; thus, minor components that will be present in the DWPF glass may not be present in the simulated glass. The effect of minor components may be accentuated when glass is reacted under the high SA/V conditions expected in an unsaturated environment. Testing of radioactive glass has been performed by WSRC [15-20]. The present tests will extend the duration of testing to longer time periods and will generate results that permit comparison between radioactive and nonradioactive glasses for three different compositions. A comparison between

the leaching of radioactive and nonradioactive glasses was also done as part of the joint Japanese, Swiss, and Swedish Program (JSS). Results from that program indicated that after one year there may be differences by a factor of two in reaction [21]. The present tests extend the time period to assess glass performance under conditions which should approach the final rate-controlling processes.

C. Technical Approach

To determine the long-term performance of glass under disposal conditions, tests must be conducted such that the "final" reaction conditions (steady state) are achieved. An unsaturated environment presents a challenge in performing long-term testing because the conditions are expected to change, perhaps significantly, over the duration of storage, with respect to the amount of water available to react with the glass and to transport radionuclides.

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 [22] 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 [23].

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, 148 of the planned 212 long-term tests have been terminated. The longest tests have been in progress for more than 43 months. For a complete test matrix refer to Table 3 in Ref. 3. The solution analyses of all the terminated tests are about 95% completed. The surface analyses on the terminated samples are about 50% completed.

We reported previously a factor of 40 difference in normalized leachate concentrations between fully radioactive and simulated SRL 200 glasses [24] at an SA/V of $20,000 \text{ m}^{-1}$. The most updated leach results on these two types of glasses still indicate such a large difference. Our results are the first report of such a finding. Previous studies had always indicated similar leach behavior between simulated and radioactive nuclear waste glasses. The

major difference of our work from previous studies is that we used a longer testing duration at higher SA/V. On the other hand, when the tests were carried out at SA/V of 2000 and 340 m^{-1} , even up to test duration of 980 days, we continued to observe the similar leach behavior between radioactive and simulated nonradioactive glasses of SRL 165/42, SRL 131/11, and SRL 200. This finding should have a large impact on the modeling of the long-term performance of radioactive glasses and the risk assessment of waste glasses. It also suggests that meaningful comparison tests between radioactive and simulated waste glasses should include long-term tests at high SA/V.

a. Results for SRL 165/42 at SA/V = 340 and 2000 m^{-1}

The data in Figs. 1a and 1b indicate that the normalized leachate concentrations [1] at 2000 m^{-1} between SRL 165/42R and SRL 165/42S glasses show only minor differences up to 980 days. Figures 1c and 1d also indicate that the corrosion rates of both types of glasses steadily decrease as the test duration increases. This similarity in leach trends also suggests that the controlling processes of glass reaction for both radioactive and simulated glasses of SRL 165/42 are the same. For example, Figs. 1a and 1b show that the normalized release of Li^+ is several times higher than the release of other elements, indicating a selective release. Boron has long been considered as a good indicator of glass corrosion [25], but Li^+ was observed to leach much faster than boron with SRL 165/42 glasses in the present tests. The observation that the corrosion rate of SRL 165/42R is slightly higher than that of SRL 165/42S is evident only from comparison of normalized release of B and Na, as shown in Fig. 1b, while the Li and Si releases for both types of glass are exactly the same, as shown in Fig. 1a. The leachate pH's (taken at room temperature) in both types of glasses are very similar, as shown in Fig. 1e. The corrosion trends for both SRL 165/42R and SRL 165/42S at SA/V of 340 m^{-1} are similar to those at 2000 m^{-1} .

b. Results for SRL 131/11 at SA/V = 340 and 2000 m^{-1}

Figure 2 compares the leach behavior between SRL 131/11R and SRL 131/11S at SA/V of 2000 m^{-1} up to 980 days. These data show that the normalized leachate concentrations (Figs. 2a and 2b) and the leach rate trends (Figs. 2c and 2d) are similar for both types of glasses. The normalized concentration levels of B, Li, and Na within each type of glass are more similar than those observed for SRL 165/42 glasses. This may indicate that matrix dissolution is the dominant reaction process during corrosion. The slightly higher corrosion rate for SRL 131/11S vs. SRL 131/11R is evident by comparing B and Na normalized release in Fig. 2b, while the Li and Si releases are very similar. The leachate pH's shown in Fig. 2e indicate slightly lower pH in the radioactive glass. Again, the corrosion trends at 340 m^{-1} are similar to those at 2000 m^{-1} .

c. Results for SRL 200 at SA/V = 340 and 2000 m^{-1}

The solution data for SRL 200 tests at SA/V of 2000 m^{-1} and 340 m^{-1} (data not shown) indicate that the SRL 200R glass reacts consistently slower than SRL 200S, but the difference is less than a factor of two (Figs. 3a and 3b). The corrosion trends of both types of glasses are similar. The glass corrosion rates of both types of glasses decrease as the test duration increases (Figs. 3c and 3d). The leachate pH of SRL 200R is consistently lower than that of SRL 200S by 0.6 pH unit. In general, the corrosion behavior of SRL 200 compositions is more similar to that of SRL 131/11 compositions than SRL 165/42. For instance, both SRL 200 and SRL 131/11 glasses had the highest releases of Na and B ions, while SRL 165/42 had the highest release of Li ion. In general, the releases of B, Na, and Li are more similar for SRL 200 and SRL 131/11 than SRL 165/42.

Fig. 1. Corrosion Behavior of SRL 165/42R and SRL 165/42S Glasses at SA/V of 2000 m⁻¹: (a) Normalized Concentrations of Li and Si; (b) Normalized Concentrations of B and Na; (c) Normalized Instantaneous Corrosion Rates of Li and Si; (d) Normalized Instantaneous Corrosion Rates of Li and Si; and (e) leachate pH

Fig. 2. Corrosion Behavior of SRL 131/11R and SRL 131/11S Glasses at SA/V of 2000 m⁻¹: (a) Normalized Concentrations of Li and Si; (b) Normalized Concentrations of B and Na; (c) Normalized Instantaneous Corrosion Rates of Li and Si; (d) Normalized Instantaneous Corrosion Rates of Li and Si; and (e) leachate pH

Fig. 3. Corrosion Behavior of SRL 200R and SRL 200S Glasses at SA/V of 2000 m⁻¹: (a) Normalized Concentrations of Li and Si; (b) Normalized Concentrations of B and Na; (c) Normalized Instantaneous Corrosion Rates of Li and Si; (d) Normalized Instantaneous Corrosion Rates of B and Na; and (e) leachate pH

d. Durability for Both Radioactive and Simulated Glasses

As the data indicated above, the rate-controlling processes may differ for different glass compositions, that is, selective release for SRL 165/42 and matrix dissolution for SRL 131/11 and SRL 200. Also of interest is a comparison between the different compositions for both the radioactive glasses and the simulated analogs to determine whether the order of durability differs between the two glass types. The order of glass durability at SA/V of 2000 m^{-1} for the simulated glasses arranged according to the normalized release of the elements of B, Si, Na, and Li is $165/42\text{S} > 131/11\text{S} > 200\text{R}$. The pH's in Figs. 1 to 3 present the same order as the glass durability at 2000 m^{-1} for simulated glasses, i.e., the most durable glass, 165/42S, has the lowest solution pH values, while the least durable, 200S, has the highest solution pH's. The durability order for the radioactive glasses is the same as that of the simulated glasses in terms of the B, Si, and Na normalized releases. The pH's of the radioactive glasses also show the same order as the corresponding simulated glasses. Moreover, the durability order of glasses at 340 m^{-1} is similar to that of glasses at 2000 m^{-1} . Therefore, the durability order measured by the major element release into solution for both simulated and fully radioactive glasses is the same: $165/42 > 131/11 > 200$.

The minor differences in reactivity for radioactive and simulated glasses at each composition can then be explained by their different leachate pH, as shown in Figs. 1 to 3. This difference results from the effect of the radiation of the radioactive glasses [26]. In general, the solution pH in the leachate of a radioactive glass will be lower than that of a simulated glass. This occurs because nitric acid and other acids are formed in the leachate of a radioactive glass when the test is done with an air atmosphere above the leachate. This is the case for 200 and 131/11 compositions. However, if the dominant glass reaction process is an ion-exchange reaction, such as:

the progress of glass reaction will counter the radiation effect. In some cases, the pH increase due to ion exchange will overcome the pH decrease caused by radiation, as is the case for 165/42 compositions at $\text{SA/V} = 2000\text{ m}^{-1}$.

The slightly lower leach rates of 200R, compared with 200S, at SA/V values of 340 and 2000 m^{-1} can be attributed to the lower solution pH caused by the radiation effect. For example, the dominant glass-dissolution process for both 131/11 and 200 compositions is network hydrolysis. This process is favored by higher solution pH, and thus when the radiation effect lowers the leachate pH, the radioactive glasses react more slowly than the simulated glasses, as shown in Figs. 2 and 3. On the other hand, the dominant reaction process for the 165/42 compositions during the time periods examined is ion exchange. The initial lower pH for 165/42R compared to 165/42S (Fig. 1e) favors the ion-exchange reaction more in 165/42R than in 165/42S. This explains why 165/42R is slightly more reactive than 165/42S in terms of B and Na release, as shown in Fig. 1b. As the ion-exchange reaction continues, the solution pH increases, which in turn begins to promote the network hydrolysis reaction.

e. Results for SRL 200 at $\text{SA/V} = 20,000\text{ m}^{-1}$

The corrosion behavior of 200-based glasses at $20,000\text{ m}^{-1}$ is illustrated in Fig. 4, which shows a distinct difference between radioactive and simulated glasses in both release trend and rate. For the first 182 days, both radioactive and simulated glasses behave similarly, i.e., the glass reaction rates are within a factor of four, as shown in Table 3.

Fig. 4. Corrosion Behavior of SRL 200R and SRL 200S Glasses at SA/V of 20,000 m⁻¹: (a) Normalized Concentrations of Li and Si; (b) Normalized Concentrations of B and Na; (c) Normalized Instantaneous Corrosion Rates of Li and Si; (d) Normalized Instantaneous Corrosion Rates of Li and Si; and (e) Leachate pH

Table 3. Instantaneous Corrosion Rates for SRL 200 Glasses at SA/V = 20,000 m⁻¹

Glass	Instantaneous Corrosion Rates, ^a mg/(m ² •d)						
	15 d	56 d	98 d	182 d	364 d	546 d	728 d
SRL 200S	32.8	6.0	2.7	2.9	1145	-7.4 ^b	14.1
SRL 200R	9.2	10.6	2.7	1.3	1.1	0.3	5.5
Rate 200S/Rate 200R	3.6	0.6	1.0	2.3	1041		2.6

^aBased on the difference between normalized release values for successive time periods divided by the time between periods.

^bA negative rate indicates the normalized release decrease between time periods in the separate batch tests. This decrease in normalized release is likely due to an offset in the time period the secondary phase nucleation occurs in the two tests and does not suggest the rate of reaction actually decreased during these time periods.

However, the rate difference is over 1000 times between 182 and 364 days. As indicated in Figs. 4a and 4b, five separate tests for 200S were terminated after the 182-day tests, and all the leachates in these five tests showed high concentrations of glass reaction products, while the leachate concentrations of all the 200R tests remained low. The corrosion rate for 200S between 182 and 364 days is 1045 mg/(m²•d), which is the highest rate ever measured on this glass and is expected to be close to the forward rate. That the glass reaction rate can approach the forward rate after relatively long-term testing is a surprising result.

During reaction, acceleration, the glass powder of 200S was fused into a cake-like material that stuck to the walls of the test vessel, and a large quantity of white precipitate material formed on top of the glass powders. Examination of the reacted surface layers on the glass samples by both scanning electron microscopy (SEM) and analytical electron microscopy (AEM) revealed rapid thickening of the surface layers, with abundant crystalline phase formation (see Sec. V.D.1.g). The anion concentrations of phosphate, sulfate, chloride, and fluoride also increased up to 70 times after the acceleration. The uranium concentration in the leachate of 200S increased by a factor of 13 after the acceleration. This is somewhat surprising due to the basic pH of the leachates. The increased uranium in solution may be the result of the higher concentration of anions in the glass leachate. During reaction acceleration, the anion concentration increases are 22 times for F⁻ (7 to 147 mg/L), 21 times for Cl⁻ (9 to 187 mg/L), 13 times for HPO₄²⁻ (77 to 950 mg/L), and 70 times for SO₄²⁻ (165 to 11,550 mg/L). The retention of actinides or rare earth elements by waste glass has been found to decrease dramatically when the glasses are tested in brine solutions and other solutions where anion concentrations are high [27,28].

The acceleration of glass reaction for 200S can be correlated with solution pH, as the pH of the solution increased from 11.82 to 12.29 during acceleration (Fig. 4e). The corrosion rates of both 200S (before acceleration) and 200R (up to 720 days) decrease with time, while the corrosion rate of 200S greatly increases with time when the leachate reaches a pH value higher than 12.0. Solution pH is known to be a dominant factor affecting nuclear waste glass reaction [29]. The corrosion rate for 200R at 20,000 m⁻¹ is always lower than the corresponding 200S rate, and the leachate pH for 200R is also always lower than the corresponding values for 200S. The 200S glass leachates have pH values of 11.82 ± 0.05 at 15, 56, 98, and 182 days, while the 200R leachates have pH values of

11.65 ± 0.13 between 15 and 560 days. The pH of 200R leachate at 720 days is still similar to its pH at the beginning of the test (Fig. 4e) and shows no sign of pH excursion. This lower pH of 200R may retard the onset of the increased glass reaction rate. It is possible that no reaction acceleration will occur for 200R glass if its radiation effect maintains the leachate pH below 11.8. The consequences of a pH effect are important because there is likely to be minimal water contacting the glass in a repository setting, and thus the effective radiation field may be able to lower the pH, thereby significantly reducing the glass reaction rate.

If pH is considered to be the only important parameter for affecting glass reaction of 200-based glasses at SA/V of $20,000 \text{ m}^{-1}$, it is difficult to understand why the 200 glass composition is "stable" at a pH value around 11.82 for 200S up to 182 days and around 11.65 for 200R up to 560 days. A pH value of 11.82 is higher than the pK_2 value of 11.77 of silicic acid (25°C) and the pK of 11.20 of H_3AlO_3 (25°C). Another contributing factor for the observed rate acceleration is the formation of a suite of crystalline phases, which is discussed in the Sec. V.D.1.g.

f. Radionuclide Release from SRL 200R at SA/V = 2000 and $20,000 \text{ m}^{-1}$

The radionuclide release data are being compiled for this task. Figures 5 and 6 show some of the results. These data show the total release of ^{238}Pu and ^{244}Cm from glass into solutions and onto test vessels. These release trends are consistent with the release trend of the major glass components, as shown in Figs. 3 and 4. The release of ^{238}Pu and ^{244}Cm is less in tests at SA/V of 2000 m^{-1} than $20,000 \text{ m}^{-1}$. The data on the release of other radionuclides are being compiled, and these data will also be compared with the release of major glass components.

g. Surface Layers of SRL 200S and 200R at $20,000 \text{ m}^{-1}$

The surface layer examinations are in progress for all the reacted glasses. This section gives the results from examining SRL 200S and SRL 200R samples reacted at $20,000 \text{ m}^{-1}$; this comparison is the most dramatic because SRL 200S experienced a large reaction acceleration, while SRL 200R is still reacting at a low rate.

(1) Glass 200S

In shorter term tests of the simulated glass a single-oriented smectite layer was observed (Fig. 7). At later times, the layer bifurcated, and a backbone structure with clay crystallites oriented normal to a backbone grew out into the solution on one side and down toward the glass on the other side of the backbone (Fig. 8). After 182 days, the clay layers changed dramatically in character. An outer preferentially oriented layer remained and at times bifurcated, but beneath this layer, a very thick layer of randomly oriented crystallites was observed (Fig. 9). Diffraction from these longer-term test samples was much stronger than from the earlier tests. In addition, large crystallites of a zeolite (clinoptilolite) were observed, and in the 546-day tests, a potassium silicate, uranium silicate, and a Ca-Si-P phase were observed.

Layer thicknesses also showed a dramatic change after 182 days. Thicknesses were variable but thin, on the order of 80 nm, for the 15- and 56-day tests. The thickness increased slowly and at 182 days was about 200 to 250 nm. A sudden increase occurred between 182 days and 330 days. At 330 days and longer, the outer oriented clay layer was 1-2 μm thick, and the randomly oriented thick layer beneath it was at least 10 μm thick (typically only the outer 10 μm survived embedding and sectioning).

Fig. 5. Total Release of (a) ^{238}Pu and (b) ^{244}Cm from SRL 200R Glass Tested at 2000 m^{-1}

Fig. 6. Total Release of (a) ^{238}Pu and (b) ^{244}Cm from SRL 200R Glass Tested at $20,000 \text{ m}^{-1}$

Fig. 7. Micrograph of 200S Tested at $20,000 \text{ m}^{-1}$ for 56 Days. A single-oriented smectite layer was observed.

Fig. 8.

Micrograph of 200S Tested at $20,000 \text{ m}^{-1}$ for 182 Days. At later times, the layer bifurcates, and a backbone structure with clay crystallites oriented normal to a backbone growing out into the solution on one side and down toward the glass on the other side of the backbone is commonly observed.

Fig. 9.

Micrograph of 200S Tested at $20,000 \text{ m}^{-1}$ for 364 Days. The clay layers have changed dramatically in character. An outer preferentially oriented layer (o) remains and at times bifurcates (b), but beneath this a very thick layer of randomly oriented (r) crystallites.

Compositions of the clay in the morphologically distinct regions were examined using energy dispersive X-ray spectroscopy (EDS). The backbone structure in other glass tests has shown accumulations of iron, while the inner and outer layers remain similar in composition. In this case, the composition of inner, outer, and backbone regions was observed to be essentially the same. Furthermore, the oriented layer and the thick randomly oriented layer of clay on the tests at 330 days and longer also had essentially the same composition, with the exception of sodium content.

Small regions of anomalously high silicon content were also observed (Fig. 10). These amorphous regions are present in some places on the 390-day sample. There is also evidence, in the form of occasional spectra with anomalously high silicon concentration (and correspondingly low iron concentration), that smaller such regions appear as early as 56 days.

(2) Glass 200R

At 364 days, only a single oriented smectite layer had developed on the fully radioactive glass, as shown in Fig. 11. At 546 days some regions of the clay layer began to form the backbone structure, but the most common morphology was still the single oriented layer. By 728 days the backbone structure was fairly common. This single layer structure is very similar to that observed on the 200S glass up to 182 days (compare Figs. 8 and 12). Other evidence has suggested that the glass dissolution process is similar for 200R up to 720 days and 200S up to 182 days [24]. Layer thicknesses ranged from approximately 150 nm to around 350 nm at 728 days. Sodium (again highly variable) was found in the layers at all three durations (182, 364, and 728 days), which is also similar to surface layers of the 200S glass at or before 182 days. There is no evidence yet of regions with anomalously high silicon concentrations and no zeolites on any of the radioactive glass samples.

Fig. 10. Small Regions of Anomalously High Silicon Content Observed on the 200S Glass. These amorphous regions are present in some places on the 364-day sample.

Fig. 11. Micrograph of 200R Tested at $20,000 \text{ m}^{-1}$ for 364 Days. Only a single oriented smectite layer developed on the fully radioactive glass. The glass has been fractured during the sample preparation process.

Fig. 12. Micrograph of 200R Tested at $20,000 \text{ m}^{-1}$ for 728 Days. The backbone structure is fairly common and well developed on the 728-day sample of radioactive glass.

The development of secondary phases on the radioactive glass is significantly retarded in comparison to the nonradioactive analog. That observation continues to hold true through 728 days. Only the smectite has been observed to develop on the 200R glass to date. The backbone structure, a morphology first observed on the 200S glass at only 98 days, developed on the radioactive glass by 546 days and was common at around 728 days (Fig. 12). In addition to these morphological similarities, layer thicknesses of the 200R glass through 728 days are similar to those observed on the 200S glass through 182 days.

h. Conclusions

A comparison of the reactivity between simulated and fully radioactive glasses has been made as part of a long-term testing program. The data discussed above indicate little difference in reactivity between radioactive and simulated nuclear waste glasses. Similar leach trends were observed for both radioactive and simulated glasses in static tests at SA/V of 340 and 2000 m⁻¹, for time periods up to 980 days, and on three SRL nuclear waste glass compositions. The data also suggest that both radioactive and simulated glasses of the same base composition generally follow the same reaction-controlling processes. The relative glass durability observed for the simulated glasses is 165S > 131S > 200S. The same order of glass durability is preserved for the fully radioactive glasses. The pH's for the fully radioactive glasses are usually lower than the simulated glasses due to the radiolysis-induced formation of nitrogen-related acids and other acids in the leachates. This reduction in the solution pH's of the radioactive glasses, combined with the rate-controlling processes revealed above, can be used to explain the observed minor differences in leach behavior between radioactive and simulated glasses at 340 and 2000 m⁻¹, where the radioactive glass reacted slightly less than the corresponding simulated glass for both 131/11-type and 200-type glasses but slightly more for 165-type glasses.

A large difference in reactivity (up to a factor of 1000 in the leach rate of boron) was observed between 200R and 200S when tested at SA/V of 20,000 m⁻¹ within one year. The SRL 200S glass exhibited a glass reaction rate, 1145 mg/(m²•d), that is close to the forward glass reaction rate after tests for more than 182 days. The accelerated glass reaction rate with the 200S glass is associated with the formation of crystalline phases, such as a clinoptilolite, and a pH excursion. The radiation field generated by the fully radioactive glass did not have any direct effect on the development of the surface layers on reacted glasses but did reduce the solution pH. This lower solution pH, in turn, may retard the onset of the increased reaction rate. These results suggest that 200R glass may be more durable than the corresponding 200S glass if the leachate pH of 200R can be kept lower than that of 200S. In modeling the performance of glass, all factors, such as the radiation-induced pH reduction in the leachate, that influence glass reaction must be accounted for to make adequate long-term predictions. Meaningful comparison of tests between radioactive and simulated nuclear waste glasses should include long-term tests at high SA/V.

i. Future Progress

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 trends that are observed.

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 [23,30]. 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.

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 [30]. 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

Table 4. Test Matrix for Long-Term Intermittent Flow Tests at High Salt V-Rates										
Test No.	Test Type ^a	Components ^{b,c}	Test Duration, weeks							
			0	18	55	85	114	145	175	205
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.

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.

b. Results and Discussion

At each sampling period, the solutions were analyzed for cations, anions, total and organic carbon, pH, and radioelements. Additionally, the test solutions were wicked through perforated carbon grids so that the particulate material suspended in solution could be collected for transmission electron microscopy (TEM) analysis, which is used to identify the composition and crystallinity of the particles. Aliquots of solution were also passed through filters of varying pore size to determine the size distribution of the potentially radionuclide-bearing colloids. It is hoped that the particles on these filters can be segregated for additional analyses using autoradiography and AEM.

The results of the solution analyses are shown in Table 5. There is 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 are consistently in the 11.0 to 11.5 range, while the as-cast glass solutions have pH's of about 8. Differences in the anion, cation, carbon, and radioelement release to solutions are also significant.

Major glass cations (such as Li, B, Na, and Si) are detected initially 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 amount of the major elements in solution after the second sampling period is usually less than the first, even though the sampling period was twice as long. While normalized release values could be calculated by employing the rationale used in analyzing the long-term test results of drip tests on SRL 165 [30], the cation results are being checked using ICP/MS against ICP/AES, but the results are not yet available.

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 [31] 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 are 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 continue, the concentration of anions in solution decreases, 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 in last year's report [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, they were augmented by separation methods for the second sampling period. Over the past year, the

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

Test No.	Sampling Period	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	1	7.97	15	15	4.6	<0.5	7.5	5.2	3.3	<1	104	2.8
	2	8.26	8	25	7.6	a	14	15	2.5	<1	38	11
	3	6.73	13	5	2.0	14	1	3	2.1	<1	6	11
	4	7.40	9	4	4.0	13	29	1	3.5	<1	23	6
9	1	8.12	10	20	9.3	<0.5	9.4	9.0	4.0	<1	10	<0.7
	2	7.94	13	13	8.5	a	20	23	4.3	<1	60	11
	3	5.61	10	3	1.2	a	1.5	2	2.8	1.0	13	11
	4	7.94	27	149	61	188	73	11	184	<1	294	332
10	1	8.60	20	25	5.3	a	5.2	6.7	2.4	<1	18	10
	2	8.55	13	35	1.5	12	1.4	2.1	2.5	<1	11	9.2
	3	6.42	12	3	20	30	20	5.3	6.2	<1	31	2
	4	8.72	25	32	5.7	a	10	13	1.9	<1	81	7.8
6	terminated	8.45	11	36	5.7	a	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
2	1	11.28	145	20			167	<15	<25	193	5660	<50
	2	11.27	108	6	11	a	71	<15	42	169	781	56
	3	11.26	140	77	6	<1	7	30	8	135	171	61
	4	11.68	28	141	12	79	25	5.5	31	274	151	<30
4	1	11.37	21	4			211	<15	<25	397	9870	<50
	2	11.13	113	210	11	a	47	<15	40	168	815	60
	3	11.62	52	77	11	22	11	22	7	147	162	69
	4	11.48	29	90	16	74	31	3.4	20	150	175	<30
5	1	11.33	35	0	13	a	256	<15	<25	334	8840	66
	2	11.43	96	6	8	24	36	<15	44	197	886	<50
	3	11.27	44	90	12	86	14	23	7	140	209	80
	4	11.38	33	79	12	a	31	3.7	20	78	137	<30
1	terminated	11.09	125	15	29	a	58	<15	74	286	2376	59
3	terminated	11.11	212	11	12	117	38	5.4	9.3	138	87	<30

^aThe 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.

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 (Table 6).

Table 6. Colloids Identified in the N4 Tests

TEM Grid No.	Test No.	Comments ^a
C:156	N4-7	Clay colloids (Fe-Al-silicates) with iron-rich regions. A double-ring structure in the electron diffraction patterns is indicative of a complex (incommensurate) layering of mineral phases. These phases have been observed in previous tests and were due to the complex arrangement of manganese oxide minerals. In this sample, it is the iron oxide minerals which have produced this pattern.
C:157	N4-8	Some small silicate particles observed.
C:158	N4-9	Calcium phosphate agglomerates observed.
C:159	N4-10	Only contaminant phases observed.
C:160	N4-3	Sodium silicate particles observed; classic examples of Ostwald ripening occurring. These phases are typical of high salt content leachates (either found in high SA/V experiments or long duration tests).
C:161	N4-4	Clay colloids were visible; the electron diffraction ring patterns possessed preferential ordering, which has been observed before in the N4 series. Fe-Cr silicate clay observed. A Ti phase was found within a clay. The clays were mainly agglomerated.

^aNumerous spiny particles, derived from the paper material used during sample preparation, were found on the grids.

There is a degree of controversy whether suspended particles and colloids, present in the leachates from "drip" test conditions, are the result of spallation or nucleation. We can only prove the presence of spallation by indirect means, as we cannot observe the leachate surface while the reaction is in progress. When we compare the morphology of clay smectite colloids produced in immersion tests with those produced during drip tests, there are some interesting differences. Clay colloids which nucleate in solution are well dispersed, and when wicked onto a "holey" carbon grid, they tend to settle with the face of the crystallites to the plane of the carbon film. In drip tests we tend to observe large agglomerates of material, which have undergone face-edge and edge-edge interactions. In solution, smectite clay colloids undergo predominantly face-face interactions, which lead to the observed oblique textured electron diffraction patterns in the TEM. This has also been proved by Vali and Bachmann [32] using a TEM freeze fracture technique on Wyoming smectite clay. As many believe that the TEM causes major changes to the particles, this type of evidence will not be generally accepted; however, the large agglomerated particles observed are not consistent with a nucleation mechanism.

The complex layers containing iron-nickel oxides (observed in these samples, see Figs. 13 and 14) and manganese oxides (observed in previous samples) are unlikely to have formed in solution by nucleation. The arrangement of layers was ordered and can be likened to crystal growth. Further investigation is required on how these phases form but they may be good supporting evidence for the spallation mechanism.

In drip tests the TEM evidence for spallation is based on the large amount of colloidal TEM data collected under different experimental conditions. The particles observed in the drip tests are not the same as those collected in the shorter duration immersion tests. The random arrangement of clay particles is similar to that observed in cross-sectional TEM images of the leached glass and suggests that these particles are the source of suspended material in the drip tests.

The terminated test samples were placed in storage and will be examined as to the alteration of the glass and sensitized stainless steel components in the test.

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. After all of the scheduled tests have been terminated and the samples analyzed, the results from these tests will be compiled in an ANL topical report.

3. Long-Term Repository Environment Tests

The "laboratory analog" test [33] has been 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 is shown in Fig. 15. 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.

Fig. 13. Agglomerated Particles from Test N4-7: (a) Transmission Electron Micrograph, (b) Electron Diffraction Pattern, and (c) Energy Dispersive X-ray Spectrum.

Fig. 14. Transmission Electron Micrographs of (a) Agglomerated Colloids in N4-4, with Transition Metal-Rich Regions (dark contrast) and (b) Iron-Nickel Rich Region in Smectite Silicate Colloids in N4-4.

Fig. 15. Representation of the Laboratory Analogue Test Apparatus (a) with and (b) without the Glass Waste Form. Note that the waste form does not rest on the bottom of the test cavity but on a shelf situated above the cavity, as shown in (b).

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 104 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. After two years of testing, the solutions were condensed by evaporation and are undergoing analysis with alpha spectroscopy, gamma spectroscopy, and ICP/MS.

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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VI. 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.

Ionizing radiation excites electrons and ionizes water molecules and dissolved gases to form reactive radicals and new molecules. The predominant water radiolysis species formed include the following: hydrated electrons (e^-_{aq}); hydrogen (H^+) and molecular oxygen (O_2^-), hydrogen ($H^\bullet$), hydroxyl ($^\bullet OH$), and hydroperoxyl ($HO_2^\bullet$) radicals; molecular oxygen anions (O_2^-); and molecular hydrogen (H_2) and hydrogen peroxide (H_2O_2). The efficiency of radiation in producing radicals or molecules is expressed as a *G value*, which is the average number of radiolytic species created (positive *G*) or destroyed (negative *G*) per 100 eV of radiation energy absorbed. A comparison of the *G* values for radiolysis of water indicates that gamma radiation produces relatively greater concentrations of e^-_{aq} , H^+ , $^\bullet OH$, and $H^\bullet$, whereas alpha yields are greatest for $HO_2^\bullet$, H_2 , and H_2O_2 [34].

Molecular nitrogen and carbon dioxide dissolved in the water may also undergo radiolytic decomposition, followed by a several-step recombination of the dissociation products with oxygen, water, and other associated radiolytic products to form nitrogen and carboxylic acids [35-37]. Because the solubility of nitrogen in water is low, *G* values for nitric acid production in air-saturated water are also small. Values of $G(NO_3^-)$ reported for irradiated oxidized water systems range from zero to less than 0.2 [38,39]. And *G* values for radiolytic production of nitric acid from moist air or two-phase (air/liquid water) systems are ~2.0 for gamma, alpha, electron, and mixed neutron-gamma irradiation studies [38-42]. The $G(NO_3^-)$ values have also been shown to vary inversely as a function of temperature [3,42] and vary as a function of atmospheric composition [38].

A notable decrease in the pH of deionized water exposed to gamma and alpha radiation occurs due to the formation of nitric acid in the irradiated air above the test solution and its subsequent dissolution in water [35,38,39,41,42]. Burns et al. [35,36] formulated an equation using values determined for $G(NO_3^-)$ to predict the molar concentration of nitric acid accumulating in water, the concentration of N_2 in the atmosphere, gas/liquid ratio, dose rate, and exposure time. Then, the pH values calculated using Burns' method can be used to predict the reaction behavior of glass samples in irradiated systems.

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 [43], 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 [37,44,45]. 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 [36,46]. 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 [15,47,48]. In a few tests, glass dissolution rates were actually reduced, relative to nonirradiated tests, when the samples were exposed to irradiated solutions [49]. Van Iseghem et al. [50-52] 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. Hench et al. [53] also indicate that the effects of radiation are negligible in the presence of granite, bentonite, and silicate waters.

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 [41]. 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 increase in concentration of glass dissolution products will cause the leachate to become saturated with secondary alteration minerals, accelerating the eventual precipitation of secondary 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 [54]

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. Tests have been performed to address three outstanding issues. The first set of tests examines the effect of radiation on moist air systems in the absence of glass (blank experiments) and the distributions and concentrations of radiolytic products. Variables to be tested include radiation type (alpha vs. gamma), temperature, dose rate, and gas/liquid volume ratio (G/L). Results from this first set of tests, which have been reported previously [3,42], indicate that both alpha and gamma radiation can produce nitrogen and carboxylic acids in a moist-air environment, G values for nitrogen acid formation are inversely proportional to the reaction

temperature, and the dose rates do not affect G values for nitrogen acid production. The second set of tests examines 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 will be used to characterize the influence of irradiation on alteration rates. The final set of tests examines 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 will provide a comparison between alteration assemblages developed on glass in irradiated vs. nonirradiated conditions.

C. Technical Approach

The experimental matrix for radiation tests with glass is displayed in Table 7. Duplicate tests were carried out for each configuration to allow for the precision of the testing method to be evaluated.

Experiments were performed in 304L stainless steel Parr vessels with 22-mL capacity. The glass samples for these tests were cut into ~1 x 10 mm wafers. Several different glass compositions were tested, including uranium-doped SRL 131 and 202 glasses and actinide-plus-⁹⁹Tc-doped SRL 131, 165, and 202 glasses (Table 1). The 202 glass is the reference composition for the Defense Waste Processing Facility, while the 131 and 165 compositions represent glasses that are less and more durable, respectively, relative to the 202 glass.

Table 7. Sampling Matrix for Testing Effects of Radiation

Expt. Number	Test Type ^a	Glass Type ^b	Temp., °C	Water Type	Test Length, days
IV9202A	SBL	202A	90	EJ-13 ^c	14, 28, 56, 91, 180, 360, 540, 720
IV9165A	SBL	165A	90	EJ-13	91, 180, 360, 720
IV9131A	SBL	131A	90	EJ-13	14, 28, 56, 180, 360, 720
IVE202A	VH	202A	200	DIW ^d	7, 14, 21, 35, 56
IVE202U	VH	202U	200	DIW	7, 14, 21, 35, 56
IVE165A	VH	165A	200	DIW	7, 14, 21, 35, 56
IVE131A	VH	131A	150	DIW	7, 14, 21, 35, 56
IVE131U	VH	131U	150	DIW	3, 5, 7, 14, 35, 56, 91, 182, 362, 728

^aSBL = saturated batch leach test (SA/V = 340 m⁻¹); VH = vapor hydration test.

^bGlass compositions given in Table 1.

^cReference groundwater for the Yucca Mountain Site Characterization Project (Table 2).

^dDeionized water.

Two types of tests were conducted on glass monoliths at variable SA/V ratios. The first test type involves immersing four monoliths in 2 mL of EJ-13 water (Table 2) at an SA/V ratio of 340 m^{-1} and a temperature of 90°C (Table 7). This batch monolith test allows for the highest SA/V ratio attainable, yet still allows the glass monoliths to be completely immersed in water and enough solution to be present so that aliquots can be collected for all desired analyses. These experiments were exposed to an external gamma source of $\sim 3000 \text{ rad/h}$ (30 Gy/h) and internally generated alpha and beta radiation from the actinide and ^{99}Tc dopants. Solution aliquots were taken from these tests for determining pH, carbon, cation, anion, and filtered size distributions of actinides. Results from these irradiated tests will be directly comparable to the nonirradiated tests at 340 m^{-1} in the SA/V task (Sec. VII) and to gamma-irradiated tests conducted under identical conditions, but without the presence of glass [42].

The second type of test involves exposing glass disks to an irradiated vapor-saturated air environment while they are suspended inside the test chamber via Teflon (in unirradiated tests) or Pt-Rh (in irradiated tests) support wires. These tests were conducted at relatively high SA/V ratios ($\geq 4000 \text{ m}^{-1}$), although the exact SA/V ratio is difficult to control because the absorption of fluids on the glass surface may vary as the composition of the solution evolves over time. Enough DIW was added to each vessel to saturate the air inside the heated vessel but not cause solution runoff from the suspended samples. The experimental temperatures were 150 and 200°C (Table 7). These elevated temperatures are used to accelerate the glass reactions to reasonably short experimental time frames.

The actinide-and- ^{99}Tc -doped samples from the saturated vapor-air test were exposed to an external gamma dose rate of $\sim 3500 \text{ rad/h}$ (35 Gy/h) and their internally doped alpha-beta radiation sources. The gamma dose rate was chosen as an upper bounding condition for repository waste and is used to determine whether there is a potential for radiation to affect the glass reaction within a short period. Cumulative gamma exposures for the 56-day tests were $\sim 5 \times 10^6 \text{ rad}$ ($5 \times 10^4 \text{ Gy}$). Because of the small amounts of solution present in these tests, it was not possible to take aliquots directly for analysis. Instead, altered surface and cross-sectioned material were characterized by optical microscopy SEM/EDS, XRD, and AEM techniques.

D. Results and Discussion

1. Vapor Hydration Tests

Water vapor contact with the glass may result in hydration aging and alteration, which may ultimately affect the release of radionuclides when the hydrated glass is contacted by liquid water. The reaction occurs in a thin film of water sorbed onto the glass surface. The result of hydration is the formation of an *in situ* hydrated layer penetrating into the glass and the precipitation of secondary mineral phases on the reacted surface. The goal of the vapor hydration tests is to determine if ionizing radiation will influence the hydration aging of glass. Both the nonirradiated and irradiated samples rapidly developed an *in situ* alteration layer and a ubiquitous cover of precipitates, which formed as the solution contacting the glass became saturated with corrosion products. Further description of the alteration layers and surface precipitates is given below.

a. Layer Formation

Detailed AEM examinations of the alteration layers from the nonirradiated ^{131}U glass revealed the presence of a thin ($0.2 \mu\text{m}$) outer clay layer. This layer was relatively coarse-grained and contained individual platy particles oriented perpendicular to

the original glass surface (Fig. 16a). After five days of testing, this layer had doubled in some regions into two parallel layers with an aggregate thickness of 0.4 μm , while in other regions a single layer still remained.

Lying between the coarse outer layer and the unaltered glass is an inner layer of fine-grained, randomly oriented clay (Fig. 16a). This inner layer progressively thickens during the course of the tests by advancing along an alteration front into the glass. By contrast, the outer layer remains at a relatively constant thickness throughout the tests.

The inner random layer appears to crystallize in a nonuniform manner. For example, the reaction layer from the 56-day sample displayed a crystallization sequence, where amorphous material crystallized into fine-grained clays, which themselves reformed into intermediate-sized clay particles. Numerous crystal nucleation sites lying between regions of amorphous material, along with cavities or microvoids rimmed by intermediate-sized clay grains, support this interpretation (Fig. 16b). These latter features arise due to the higher density of the clay relative to its precursor glass and/or amorphous source material. Tests run for 91 and 180 days display a more uniform layer, which is composed almost entirely of fine-to-intermediate clay particles. This homogenization signifies the near complete crystallization of this altered layer.

The composite clay sequence (outer oriented and inner random layers) for the irradiated 131A glass monoliths developed at a relatively constant rate of $\sim 0.63 \mu\text{m}/\text{day}$ throughout the entire 56 days of testing (Fig. 17a). By contrast, reaction layer growth rates progressively decreased during alteration of the nonirradiated 131U glasses. With these tests, cumulative rates were $0.52 \mu\text{m}/\text{day}$ after 7 days, $0.16 \mu\text{m}/\text{day}$ after 56 days, and a relatively constant $0.1 \mu\text{m}/\text{day}$ between 180 and 720 days of reaction. A comparison of composite clay layer thicknesses after 56 days indicates that layer development was accelerated four-fold due to radiation exposure at high SA/V conditions. This increase was less than the 10- to 15-fold increase previously seen for SRL 202 glass reacted at 200°C (Fig. 17b) [55].

Selected area diffraction (SAD) analyses obtained during AEM study indicate that the clay layers are composed of smectite-group clay minerals (Table 8). The multiple qualitative SEM/EDS (not shown) and quantitative AEM/EDS data suggest the presence of nontronite and/or ferroan saponite.

The inner random layer of the 131U glasses displays a residual enrichment of relatively insoluble elements, such as Ni and Ti, relative to the outer layer. This feature, combined with the previously discussed random crystal orientation, suggests that the inner layer formed *in situ* as a residual material that remained after the more soluble components had been leached from the glass. The perpendicular orientation of the outer layer relative to the original glass surface suggests that the clays were precipitated in open space, where a preferential growth orientation developed. The relatively lower concentrations of insoluble elements also suggests that components incorporated in these clays were derived from material transported through the film of water covering the sample surface.

The AEM/EDS compositional analyses indicate that both clay layers are highly depleted in Na and K, but enriched in Al, Mn, Ti, and Fe relative to the unaltered glass. Nickel is depleted in the outer layer for the first 14 days and then enriched after 56 days, while it is enriched in the inner layer during all periods tested. Magnesium is enriched in the outer layer and depleted in the inner layer, relative to the unaltered glass, for the first 14 days of testing. Thereafter, magnesium concentrations in the inner layer progressively increase until they approach the composition of both the glass and the outer layer. Calcium is generally depleted in both layers, relative to the unaltered glass, but does show some enrichment in the outer layer after 56 days of reaction.

Fig. 16. Transmission Electron Images of ^{131}U Glasses: (a) Low Magnification Image Showing Outer Oriented and Inner Random Clay Layers Overlying Unreacted Glass after Three Days and (b) High Magnification Image of Inner Random Smectite Layer Formed by 56 Days

Fig. 17. Clay Alteration Layer Thicknesses for Gamma Irradiated (~ 3500 rad/h) vs. Nonirradiated Samples Reacted in a Vapor Saturated-Air Environment: (a) Irradiated SRL 131A Glass vs. Nonirradiated SRL 131U Glass Layer Thicknesses after Reaction at 150°C [54] and (b) Irradiated SRL 202A Glass vs. Nonirradiated SRL 202U Glass Layer Thicknesses after Reaction at 200°C [55].

Table 8. Electron Diffraction Data Obtained from Inner Clay Layer of Three-Day ^{131}U Samples and JCPDS Data for Montmorillonite

3-day ^{131}U d-spacings, $\text{\AA}$	JCPDS 29-1499, $\text{\AA}$
4.53 ± 0.12	4.45
	3.15
2.58 ± 0.05	2.56
1.7 ± 0.03	1.69
1.52 ± 0.02	1.495
1.31 ± 0.02	1.325

b. Surface Precipitates

A variety of zeolite, smectite, calcium and sodium silicates, phosphate, evaporitic salts, and uranyl silicate phases were deposited on the sample surfaces of both the irradiated and nonirradiated SRL 131 glasses. The phases identified in this study agree well with the findings of Biwer et al. [56], who identified smectite, calcite, and analcime with SRL 131 composition glass reacted in both saturated and unsaturated air-steam tests at 75°C . With few exceptions, the types of phases present on the reacted glass surface are similar for both the ^{131}U and ^{131}A glasses (Figs. 18). The main differences are the greater abundance of secondary precipitates and the accelerated paragenetic sequence observed on the irradiated ^{131}A glasses. An example of this accelerated sequence is evident in the development of analcime and tobermorite. These phases appear in the ^{131}U reaction sequence as early as 7 days, while they appear in the ^{131}A sequence only after 56 days of reaction or longer. Accelerated glass corrosion rates and the rapid saturation of the leachate with respect to secondary phases appear to be responsible for the more rapid advancement of the paragenetic sequence observed in the irradiated tests. In addition, some differences were observed in element pathways between the two sets of tests (Fig. 19). For example, uranium is contained in sodium-weeksite, haiweeite, and soddyite in the ^{131}U tests, while it occurs chiefly in potassium-weeksite and, to a lesser extent, haiweeite in the ^{131}A tests.

Samples were also scanned at electron accelerating voltages of 30 kV during SEM/EDS analysis to excite the more diagnostic inner electron shells of Tc and the transuranic elements Am, Pu, and Np. None of these elements was detected in the clay layer or any surface precipitates, despite the examination of an extensive suite of sample regions. This absence of discrete ^{99}Tc and transuranic-bearing phases suggests that these elements were being retained within the inner alteration layer at concentrations below SEM/EDS detectability and did not dissolve and reprecipitate on the sample surface; however, discrete K-Tc phases were identified in previous examinations of 202A glasses [55]. More sensitive techniques, such as autoradiography, may be employed in the future to identify the locations of these elements.

—— Nonirradiated 131U Glass Samples
 Irradiated 131A Glass Samples

Fig. 18. Interpretive Paragenetic Sequence for Major Alteration Phases Observed on Reacted SRL 131 Glasses. Solid lines represent nonirradiated 131U samples, and dotted lines represent tests with 131A glass reacted while being exposed to an external gamma radiation source. Tests with 131A glass were for a maximum of 56 days, while tests with 131U glass were continued up to a maximum of 720 days [54]

(a)

(b)

Fig. 19. Scanning Electron Photomicrographs of SRL 131 Glasses Reacted for 35 Days in a Saturated Vapor Environment at 150°C. (a) Relatively sparse crystal growth on SRL 131U glass reacted without external radiation exposure, 100X. Scattered precipitate mounds are mostly of smectite clay. (b) Dense crystal growth on SRL 131A reacted under gamma radiation dose of ~3500 rad/h, 100X. Note advanced stage of alteration relative to the 131U glass sample and the dehydration and cracking of the clay layer. Scattered acicular phase is potassium-wecksite with salt covering; button-shaped phase to lower center is analcime; blocky "x" shaped crystals are phillipsite; and fine-grained crystals across entire clay surface are an unidentified Ca-Si phase. See Fig. (a) for scale bar.

c. Comparisons with Natural Analogues

Predictions of long-term alteration trends for nuclear waste materials made with geochemical models are often limited by insufficient thermodynamic and kinetic data bases. Accurate predictions of secondary mineral formation are important because these phases may affect waste form dissolution, solubility-limited release rates of radionuclides, and colloid formation. Studies of geologic analogues can provide information on long-term alteration trends; however, correlations between analogue and short-term laboratory results are hindered by a limited knowledge of the reaction conditions of the former and the relatively short test durations of the latter. The use of elevated temperatures and high SA/V ratios accelerates the corrosion of simulated waste, thus allowing for a comparison between the accelerated vapor tests and natural analogue deposits.

As shown in Table 7, simulated nuclear waste glasses were exposed to condensed steam, at temperatures of 150 and 200°C, for periods of up to two years. As the film of water contacting nonirradiated 202U glass became progressively enriched in corrosion products, the following paragenetic sequence occurred: unaltered glass → smectite → sodium chabazite → analcime + phillipsite → potassium feldspar → illite → albite + tobermorite [57]. This trend is similar to both the horizontal mineral zonation formed during volcanic glass alteration in saline-alkaline lakes and vertical stratifications resulting from downward percolation of water through volcanic materials (Fig. 20). This similarity arises because the release of corrosion products from the test glasses quickly transforms the thin film of water contacting the glass into a saline-alkaline fluid.

The correlation observed between the alteration paragenesis of simulated waste glass and that of naturally occurring volcanic glasses provides a credible link between short-term laboratory tests and geologic analogues altered over tens to hundreds of thousands of years. This similarity also suggests that long-term alteration trends can be replicated using accelerated laboratory tests without changing the underlying reaction mechanism affecting the glass waste. Thus, alteration patterns of volcanic glass in saline-alkaline lake systems may provide an analogue for the study of waste glass alteration in an unsaturated repository setting.

Fig. 20. Mineral Zonation Patterns and Paragenesis Developed during Volcanic Glass Alteration in Saline-Alkaline Lakes as a Function of Increasing Water Salinity and Alkalinity from Basic Margin to Basic Center [58-60]. Both illite and albite have also been detected in advanced alteration stages of saline-alkaline lake sediments from the southwestern U.S. [61].

2. Batch Leach Tests

As shown in Table 7, the 340 m⁻¹ batch tests were run with ⁹⁹Tc- and actinide-doped 202A, 165A, and 131A glasses exposed to an external gamma-irradiated field while immersed in EJ-13 leachant at temperatures of 90°C. Testing periods ranged from 14 to 720 days. Solution analyses showed invariant temporal paths for the anions F⁻, Cl⁻, SO₄²⁻, C⁻OOH⁻, and C₂O₄²⁻. These trends suggest that the presence of reacting glass in the tests does not have a major influence on the anion chemistry of the leachate. An exception to this generalization is the concentration of nitrogenous species. Nitrate is depleted relative to EJ-13, whereas nitrite is significantly enriched. The decrease in the NO₃⁻/NO₂⁻ ratio results in a value that is lower than both the starting EJ-13 solution composition and the ratio derived from results of the alpha and gamma blank tests [2]. The decreased NO₃⁻/NO₂⁻ ratio of irradiated solutions in the presence of glass may be attributed to the increased stability of the NO₂⁻ radical in the presence of an alkali solution buffered by the reacting glass [38]. The lower H⁺ activity in these buffered solutions results in decreased rates for the following two NO₂⁻ consumption/NO₃⁻ production reactions:

The NO produced in Eq. 2 should be rapidly oxidized to NO₂ under oxygenated test conditions. This NO₂ will then react with water to form equivalent amounts of NO₃⁻ and NO₂⁻, with the NO₂⁻ reforming to nitrous acid and repeating the cycle. Equation 3 also demonstrates that increased NO₂⁻ stability can be influenced by catalytic decomposition of radiogenic H₂O₂ by iron and manganese oxides present on the altered glass surface [53].

Irradiated 202A and 131A leachate samples display level pH values of ~9 after earlier increases were observed between 56 and 180 days (Fig. 21a). These pH trends reflect a temporal change in the rate of glass reaction relative to a steady rate of radiolytically produced nitric acid. During the initial alteration process, alkali, alkaline earths, and/or hydroxide are released from the glass in concentrations greater than that necessary to reduce the concentration of H⁺ ions dissociated from radiolytic acids, thus increasing in the solution pH. In longer tests, a buildup of radiolytic acids in the leachate results from a decrease in the rate of ion exchange with the glass. A comparison of pH values from the irradiated 202A tests versus those of the nonirradiated 202U tests indicates that the irradiated solutions are ~0.5 pH units lower than the nonirradiated solutions.

The 165A glass samples continued to display increasing pH values throughout the duration of the tests (Fig. 21a). The 165A glass appears to continuously release alkali, alkaline earths, and/or hydroxide in quantities that are sufficient to inhibit the buildup of radiolytic acids, thereby allowing for continued increases in pH of the test solution.

Normalized release trends for cation elements display variable trends. Comparisons of release patterns for Ca, Mg, Li, Na, K, and Mn show little variation between the irradiated 202A and the nonirradiated 202U glasses. Release of boron is also similar between the two test conditions for the first 180 days, while the release of boron is accelerated slightly in the irradiated tests thereafter (Fig. 21b). With Si and U, the presence of an irradiated solution actually reduced their normalized release relative to the nonirradiated test solutions (Figs. 21c and 21d). The reduced concentration of silicon is attributed to the effect of solution pH in

Fig. 21. Elemental Release for Irradiated Tests with 131A, 165A, and 202A Glasses and Nonirradiated Tests with 202U Glasses: (a) Solution pH, (b) Normalized B Release, (c) Normalized Si Release, and (d) Normalized U Release. Irradiation dose ~ 3500 rad/h, temperature = 90°C , and $\text{SA/V} = 340 \text{ m}^{-1}$.

controlling the solubility of silicic acid, as discussed in Sec. VI.A. The decrease in uranium release as a function of pH was not expected. Although the exact mechanism for this decrease cannot be ascertained in these tests, this pattern may reflect the destabilization of a uranium-containing ligand with decreasing pH.

Comparative release patterns for the three different types of glass indicate that release rates are greatest for all elements, from most time periods, for the 131A glasses. This trend reflects the relatively poor durability associated with the low Si and Al content of this glass (Table 1). Elemental release trends from the 165A and 202A glasses showed some variability. For example, boron release is generally lowest for the 165A glasses until 720 days, when the boron release from the 202A glasses is lowest (Fig. 21b). Uranium release shows the opposite trend, i.e., greater uranium release from the 165A glasses during early tests, and reduced release in the 720-day tests relative to the 202A glasses (Fig. 21d).

E. Future Progress

All experimental work and SEM examinations of altered samples have been completed. Remaining efforts will focus on AEM analysis of altered surface layers and publication of the findings in an ANL Topical Report and peer-reviewed journals.

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

A. Introduction and Background

Static leach tests are being used to develop borosilicate glasses for stabilization of high-level waste and will be used to assure product consistency during operation of the DWPF. Static leach tests are also being used to investigate the mechanism of glass corrosion, which must be known to project the long-term stability of high-level waste forms under anticipated storage conditions. The values of several test parameters can be varied to highlight particular corrosion processes, to simulate likely environmental conditions, or to accelerate the corrosion process. Along with the reaction temperature and the fluid composition, a key test variable in static leach tests is the SA/V. Variation of the SA/V can be used to simulate conditions of limited water contact or contact with large volumes of water during storage, can highlight the corrosion process in systems dominated by water volume or by the glass surface, and can be used to accelerate the corrosion process. An understanding of the corrosion behavior under a wide range of conditions is important for projecting the durability of high-level waste forms over geologic time periods relevant to repository isolation.

The major effect of SA/V on the glass reaction is through dilution of the reaction products. Since the glass reaction rate is known to depend on the solution chemistry (particularly the silicic acid concentration and the pH), the response of a particular waste glass composition may differ in tests at different SA/V because of the difference in dilution; both the dominant reaction step and the measured rate of glass reaction may change as the SA/V is varied. To project the long-term glass durability, it is important to understand how the results of a specific test relate to the overall glass corrosion process.

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 glass corrosion 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 have been 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 composition. Tests were performed with glasses doped with radionuclides to monitor their disposition as the glass corrodes. In addition, the results of these tests provide insight regarding how tests performed at different SA/V are related, if the SA/V can be used as an accelerating parameter for static leach tests, how the SA/V influences the assemblage of secondary phases which form, and what is the long-term glass corrosion rate.

An additional 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. 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

Static leaching experiments are being performed at SA/V ratios of 10, 340, 2000, and 20,000 m⁻¹ and 90°C. Two simulated high-level nuclear waste glasses representative of the waste forms to be produced by the DWPF are being tested: SRL 131 and SRL 202, both provided by Westinghouse Savannah River Co. (WSRC). The leachate solutions and reacted

solids are analyzed at selected intervals to compare the mechanism and kinetics of the glass reaction at different SA/V. These tests are being performed to provide detailed solution results with accompanying solids analyses for comparison with computer simulations.

The SA/V ratios were selected to include that specified in the MCC-1 static leach test (10 m^{-1}) and that of the Product Consistency Test (PCT) (2000 m^{-1}). Tests at 340 and $20,000 \text{ m}^{-1}$ follow the MCC-1 and PCT protocols, respectively, but at a significantly higher SA/V. Monolithic samples were used in tests at 10 and 340 m^{-1} , while powdered samples within the size fraction (-100 +200) mesh were used in tests at 2000 and $20,000 \text{ m}^{-1}$.

The SRL 131 and SRL 202 glasses provided by WSRC were doped with Tc-99, U-238, Np-237, Pu-239, and Am-241 to produce glasses referred to as SRL 131A and SRL 202A. Another glass, referred to as SRL 202U, was generated by only doping the SRL 202 with U-238. The doped glasses were poured from the melt into ingots and annealed. Cores were cut from the ingots, and then disks were cut from the cores for use in the tests at 10 and 340 m^{-1} . All surfaces were polished to a 600-grit final finish. The remaining glass in the ingots was crushed, and the -100 +200 mesh fraction separated by sieving for use in the tests at 2000 and $20,000 \text{ m}^{-1}$. The crushed glass was washed, and samples were viewed by SEM to assure that fines had been removed. The surface area of the particles based on the average mesh opening corresponds to about $2 \times 10^{-2} \text{ m}^2/\text{g}$ of glass.

Tests with SRL 131A and SRL 202A glass were performed using 304L stainless steel vessels, and tests with SRL 202U glass were performed in Teflon type PFA vessels. Monolithic samples were placed on 304L stainless steel or Teflon support stands while powdered samples were placed directly in the vessel. Tests with SRL 131A, SRL 202A, and SRL 202U glass were performed using J-13 well water that had been pre-equilibrated with pulverized tuff rock at 90°C ; this solution is referred to as EJ-13. The SRL 202U glass was additionally reacted in deionized water (DIW). Nominal SA/V ratios of 10 and 340 m^{-1} were attained by adding one monolithic sample to 17 mL solution and four monolithic samples to 2 mL solution, respectively. The SA/V ratios of 2000 and $20,000 \text{ m}^{-1}$ were achieved by adding one gram of -100 +200 mesh powder to 10 mL solution or 5 g of -100 +200 mesh powder to 5 mL solution, respectively.

The test vessels were sealed and placed in a 90°C oven. Steel vessels were placed directly in a circulating air oven, while Teflon vessels were placed in secondary containers, which were then partially filled with DIW, sealed, and placed in the oven. (Earlier tests in Teflon vessels were performed by placing the vessels in a 90°C water bath. However, as the number of tests decreased, the vessels were transferred to secondary containers for convenience.) At the end of the predetermined test duration, each vessel was removed from the oven, opened immediately, and the leachate removed for analysis. The leachate from tests with powdered glass was filtered using a preheated $0.45 \mu\text{m}$ filter to remove any suspended glass particles. This filtrate and the leachate from tests with monolithic samples were allowed to cool to room temperature then analyzed for pH, carbon, anions, cations, and actinides. The steel vessels were stripped using a nitric acid solution, which was analyzed for actinides to assess the amounts of Np, Pu, and Am that had become fixed to the steel during the test. Solutions from some tests were further filtered using approximately 6 nm filters (Amicon model CF50A) to assess the amount of colloidal material in the solution.

The reacted solids were rinsed with DIW and allowed to dry before analysis. Some samples were then analyzed using optical microscopy, SEM, and AEM. Both the SEM and AEM are equipped with X-ray spectrometers for compositional analysis, and the AEM provides selected area electron diffraction (SAED) for structural analysis. Representative samples of the

reacted glass were fixed in epoxy, and thin sections were prepared for AEM analysis using an ultramicrotome. Grains of powdered glass were fixed in resin directly, while sample chips were removed from reacted monoliths using a diamond knife. Secondary phases found distributed among the reacted grains were isolated and analyzed separately.

D. Results and Discussion

The tests terminated during FY 1993 showed continuation of the corrosion trends seen in shorter tests under the same SA/V conditions. The solution results were discussed in detail in the annual report for FY 1992 [3] and have been published elsewhere [62-67]. The key observation from the solution results was that the SA/V of the test affected the extent of dilution of the glass corrosion products and the solution pH. The effects of the solution pH on the glass corrosion rate were incorporated into the glass dissolution model being developed at Lawrence Livermore National Laboratory based on these test results [68]. Tests at higher SA/V attained higher pH values and higher solution concentrations after short time periods, while tests at lower SA/V maintained more dilute conditions. This effect had a significant influence on the observed corrosion behavior of the glasses. The corrosion rates were lower in tests at high SA/V due to the quenching effects of the silicic acid [69]. The solution concentrations of soluble glass components, particularly boron and the alkali metals, were used to monitor the extent of glass corrosion. Tests at different SA/V highlighted different stages in the glass corrosion process. Tests at low SA/V (10 and 340 m⁻¹) show the initial corrosion process, where the solution concentration has only a minor effect; tests at high SA/V (2000 m⁻¹) show the glass corrosion under silicic acid saturated conditions; and tests at very high SA/V (20,000 m⁻¹) show the long-term glass corrosion in the presence of secondary phases. These tests demonstrate that a complete characterization of the glass corrosion process can be obtained by testing a glass at different SA/V ratios and for different times.

Of special interest is the corrosion rate after long reaction times in tests at SA/V = 2000 and 20,000 m⁻¹. Figures 22a and 22b show the corrosion rates (based on boron release) for tests with SRL 202A glass at 2000 and 20,000 m⁻¹. The results of duplicate tests at each time period are plotted. The tests at 2000 m⁻¹ show the commonly observed trend where the corrosion rate decreases from an initially high value to a low value as the reaction time increases. The tests at 20,000 m⁻¹ show the same trend through about 180 days, but the corrosion rate suddenly increases to a higher value beyond about 180 days. This observed behavior raises several important questions: (1) Is the observed behavior in tests at 20,000 m⁻¹ an experimental artifact? (2) Will glass corrosion in tests at other SA/V ratios show a similar rate increase after sufficient reaction times, which may be inaccessible to laboratory tests? (3) Does the behavior in tests at 20,000 m⁻¹ accurately simulate the long-term behavior of HLW glasses in a repository environment?

To address these questions, effort this year has focused on understanding the cause of the accelerated corrosion rate observed in tests with SRL 202A and SRL 202U glass at 20,000 m⁻¹. Results of the analysis of the alteration layers formed after various reaction times in tests at several SA/V ratios are presented below. These results provide evidence that glasses reacted at different SA/V ratios corrode by the same mechanism and provide insight as to how the crystallization of various secondary phases and the evolution of the glass surface may affect the glass corrosion process.

The AEM images of representative alteration layers that formed on SRL 202 glass in tests at SA/V of 340 and 2000 m⁻¹ are shown in Fig. 23. The unreacted glass is seen to have chattered during sectioning, although the alteration layers remained firmly fixed in the mounting resin and were not disturbed during microtoming. Crystalline layers formed at

Fig. 22. Measured Corrosion Rates of SRL 202A Glass in EJ-13 at 90°C as a Function of the Reaction Time at SA/V of (a) 2000 m⁻¹ and (b) 20,000 m⁻¹. Corrosion rate is based on the boron release.

Fig. 23. High Resolution AEM Images of Alteration Layers Formed during the Reaction of SRL 202 Glass: (a) 28 days/DIW, (b) 360 days/DIW, and (c) 360 days/EJ-13 at 340 m^{-1} ; and (d) 140 days/DIW, (e) 360 days/DIW, and (f) 360 days/EJ-13 at 2000 m^{-1} . Bars represent 100 nm.

the glass surface in tests at all SA/V ratios tested ($10\text{--}20,000\text{ m}^{-1}$) and at all reaction times. Fibrous clay crystals formed oriented perpendicular to the glass surface at the shortest reaction times tested at all SA/V ratios (3 days in the tests at 2000 m^{-1} and 7 days in the tests at 10 m^{-1}). These became consolidated into laths of clay and were generally oriented perpendicular to the glass surface as the reaction continued. Note that all crystals have a small degree of curvature and grow predominantly in one direction. A mostly amorphous inner layer developed beneath the original crystalline layer in tests in DIW, with small, randomly oriented crystallites sometimes being distributed throughout the inner layer. Eventually, the inner layer crystallized into discrete laths oriented perpendicular to the surface and resulted in a twinned layer of crystalline laths. A mostly amorphous phase remained as a thin band between the two crystallized layers in some samples. The crystallites were typically found to have separated from the underlying glass.

Samples reacted in either DIW or EJ-13 at $20,000\text{ m}^{-1}$ for 364 days or longer acquired much thicker layers than samples reacted for shorter times. While the glass reacted for shorter times appeared visually unreacted, the glass reacted for 364 days or more was coated with a chalky white phase, which readily spalled from the glass. The layers formed in DIW at $20,000\text{ m}^{-1}$ after 182 and 364 days are shown in Figs. 24a and 24b. The 182-day layer is similar to that formed after 360 days at 2000 m^{-1} in DIW (Fig. 23e). The layer is comprised of coarse crystallites and has separated from the underlying glass. The 364-day layer has two sublayers: an oriented outer layer and a thick inner layer. The inner layer appears to be contiguous with both the outer layer and the unreacted glass. Figure 25a shows the unreacted glass/inner layer interface at a higher magnification. The glass is corroded unevenly on this scale, and crystalline material persists to the interface, in contrast to observed separation of the layer and the glass in the 182-day sample. Figure 25b shows a relatively even interface between the oriented outer layer and the inner layer. Laths of flocculated clay are seen to have settled from solution onto the surface of the outer layer. This is probably the chalky white material seen visually.

Compositional analysis using EDS and SAED showed that the outer and inner layers were composed of the same polycrystalline material, identified as a smectite clay. Table 9 gives representative compositions of the clay laths in the layers formed in DIW and EJ-13 after 364 days of reaction. The compositions of the inner and outer layers are similar; both are depleted of soluble glass components and enriched in aluminum and chloride. Clays with a similar composition form the layers observed on samples reacted in EJ-13. Table 10 gives the lattice spacings measured using several representative SAED patterns of the inner and outer layers and those of some smectite clays for comparison. The formulae for these smectite clays are:

Nontronite:	$\text{R}_{0.33}^{+}\text{Fe}_{2}^{3+}(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$
Montmorillonite:	$\text{R}_{0.33}^{+}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$
Saponite:	$\text{R}_{0.33}^{+}(\text{Mg}_{2.67}\text{Li}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$

where R is an alkali metal. Solid solutions of the end members, nontronite and montmorillonite, are common in nature. Due to the similarities in the d-spacings of these clays, the smectite formed as these glasses react cannot be more precisely defined.

The structure and composition of isolated secondary phases on the SRL 202 glass were also determined by AEM and SEM. Phases identified include the uranium-bearing phases weeksite and boltwoodite, chabazite and heulandite group zeolites, clinoptilolite, and

(a)

(b)

Fig. 24. High Resolution AEM Images of Alteration Layer Formed on SRL 202 Glass in Tests in DIW at $20,000 \text{ m}^{-1}$ (a) after 182 days (bar = 100 nm) and (b) after 364 days (bar = 400 nm).

(a)

(b)

Fig. 25. High Magnification Image of SRL 202 Glass in Tests in DIW at $20,000 \text{ m}^{-1}$ after 364 Days: (a) Unreacted Glass/Inner Layer Interface (bar = 100 nm) and (b) Oriented Outer Layer/Inner Layer Interface (bar = 200 nm).

Table 9. Composition of Alteration Layers Formed on SRL 202 Glass Reacted in DIW and EJ-13 Solution at 20,000 m⁻¹ for 364 Days^a

Element	DIW		EJ-13		Glass
	Outer Layer	Inner Layer	Outer Layer	Inner Layer	
Al	8.5	10	4.7	13	4.9
Ca	0.1	0.1	1.5	0.6	2.2
Cl	3.2	3.2	b	-	<0.5
Fe	20	16	14	21	21
K	0.6	0.9	4.6	0.3	7.5
Mg	1.1	1.5	1.6	1.6	0.2
Mn	4.4	4.7	2.7	5.0	4.3
Na	0.5	0.1	-	-	8.2
Ni	2.5	2.9	-	-	2.1
Si	57.8	59.5	60	58	48
Ti	1.3	1.1	1.1	1.0	1.6

^aIn elemental weight percent, normalized to 100% total for elements present.^bNot included in quantitative analysis.Table 10. Lattice d-Spacings from Selected Area Electron Diffraction Analysis of SRL 202 Glass Reacted at 20,000 m⁻¹ for 364 Days, in Angstroms

Layer ^a			Nontronite (29-1497) ^b	Montmorillonite (12-219) ^b	Saponite (29-1491) ^b
I	II	III			
			15.2	17.6	15.5
9.0 ^c			7.44	9.00	7.73
				5.99	5.11
4.48	4.48	4.42 ± 0.12 ^d	4.48	4.49	4.57
		3.20 ± 0.07	3.58	3.58	3.834
			3.05	2.99	3.07
2.57	2.53	2.58 ± 0.05	2.564	2.57	2.61
				2.242	
		1.70 ± 0.03		1.699	1.731
1.50	1.50	1.50 ± 0.02	1.51	1.504	1.533
1.29	1.29	1.30 ± 0.02	1.336	1.294	1.321

^aLayer I: outer layer of glass reacted in EJ-13; Layer II: inner layer of glass reacted in DIW; Layer III: outer layer of glass reacted in DIW.^bJCPDS file number of representative smectite clay.^cMeasured from lattice fringes in image.^dEstimated measurement errors common to all experimental values.

nagelschmidite. A noncrystalline feature bearing uranium and titanium was also identified within the clay phase or between the clay layer and the underlying glass. Detailed analyses of secondary phases will be presented elsewhere.

Many studies have shown that the SA/V can be employed to accelerate the attainment of high solution concentrations of released glass components. The present tests show that (1) tests at high SA/V also accelerate the alteration of the glass surface and the precipitation of secondary phases from solution, (2) the layer thickness increases upon the generation of secondary phases, and (3) the same alteration phase forms at the glass surface before and after the corrosion is accelerated (smectite clay), but its morphology changes. During the early stages of corrosion, the clays grow slowly and form relatively large crystallites. When the glass corrosion rate increases, the clays grow more quickly and form smaller crystallites. Because smectite is present prior to acceleration of the glass corrosion, it is probably not responsible for the acceleration.

The formation of secondary phases is a natural consequence of glass corrosion and is limited only by the necessity to attain saturated solution conditions and nucleation of the phases. Potential secondary phases are determined primarily by the glass and solution compositions but may be affected by contact of the fluid by other materials in the system, radiolysis of the system, and other factors. The absence of secondary phase formation (other than clays) in laboratory tests may be due to the limited test duration or to inappropriate solution chemistries (such as pH and oxidation conditions). Thus, tests with SRL 202 glass conducted at 2000 m^{-1} may not show the same acceleration as test at $20,000 \text{ m}^{-1}$ because the solution pH or the concentrations of Si, Al, etc., remain too low, or because the nucleation of critical secondary phases is too slow for precipitation to occur within the time constraints of the laboratory tests. Certainly, the high solution concentration of leached elements attained in the tests at $20,000 \text{ m}^{-1}$ is more conducive to nucleation and precipitation than that attained at 2000 m^{-1} .

Perhaps a more important issue than the effects of SA/V on the formation of secondary phases is the issue of which SA/V is more representative of the repository environment. An engineering goal of most potential repositories is to maintain dry conditions, for it is contact with groundwater that presents the primary mode for the release and distribution of radioelements. The high thermal load of the waste forms will likely prevent contact with groundwater during the first few hundred years after waste emplacement in most potential repositories. Many hundreds of years after waste emplacement, most repositories will have cooled sufficiently that liquid water may exist in contact with the waste forms. It is anticipated that only limited amounts of water may contact high-level waste glasses for very long time periods. This scenario is well modeled by tests at high SA/V.

Previous laboratory tests [12] have shown two characteristic glass corrosion rates: a high rate when glass is contacted by highly dilute solutions conditions, and a low rate when glass is contacted by solutions that are highly concentrated in glass components. These rates typically vary by two or three orders of magnitude for high-level waste glasses and may critically influence the suitability of a repository design. The tests in this Task suggest that the long-term corrosion rate will be controlled by the secondary phases (other than clays) that form as devitrification products. These phases are expected to control the solution chemistry and the long-term glass corrosion rate, and the glass corrosion rate may be very different from that measured in either dilute or highly concentrated solutions. A knowledge of which phases form and how they affect the glass corrosion rate is required to project the long-term durability of high-level waste forms.

E. Future Progress

Several long-term tests remain in progress and several reacted samples remain to be fully characterized. Computer modeling of these test results has been successful to date. Recent developments in how the reaction affinity is expressed (Sec. IX) show promise in reproducing the observed rate increase upon the formation of critical secondary phases, including clinoptilolite. This finding may provide insight regarding what is the appropriate long-term corrosion rate.

VIII. ANALYTICAL ELECTRON MICROSCOPY SUPPORT

A. Introduction and Background

Analytical electron microscopy (AEM) continues to be performed for secondary alteration phases found on the leached surfaces and present as colloids in the leachates of fully radioactive and simulated nuclear waste glasses reacted under static test and drip conditions at various SA/V ratios and test durations. This analytical method combines 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. This has made structural identification difficult, and also compositional analysis on occasion. In this section, the AEM work completed during FY 1993 will be reported, as well as the application of AEM for characterizing phases from waste glass reaction, and some of the challenges in its use.

B. Objectives

The objective is 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.

C. Technical Approach

This work is concerned with characterizing reaction layers which form on the surfaces of leached waste glasses. These layers are frequently 50 μm or more thick and are extremely fragile. 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, i.e., thin sectioning of small particles mounted in epoxy blocks using a diamond knife [1,70]. 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. Secondary phases, usually other than smectite clays, are characterized by EDS and their structures determined by SAED patterns and, on occasion, CBED patterns. The camera lengths for SAED were determined by using a polycrystalline aluminum sample.

In addition to the reaction layer analyses, 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 TEM grid. Examination of colloids present in the leachate has not only identified colloidal phases but also provided a picture of colloidal particle formation in the leachate [71-74].

New sample preparation facilities have been set up for the TEM examination of samples by methods other than ultramicrotomy.

D. Methods Investigations

1. Analysis by Transmission Electron Microscopy/X-Ray Energy Dispersive Spectroscopy

Experimentally derived k-factors for the TEM were obtained by using the Cliff-Lorimer method [75] from glass and mineral standards. These k-factors are used in elemental analysis of the sample. The AEM examines areas of sample which are generally less than a micron. So the question arises, can the AEM analysis be considered representative of the bulk? In other words, can the AEM accurately analyze a sample? To answer these questions, glass analyses were performed by AEM, and the results compared with wet chemistry analysis.

The large number of elements in the sample makes quantification by AEM almost impossible. The calculation of the background (the same method is used for both SEM/EDS and TEM/EDS) becomes inaccurate with too many elements. Some of the elements can only be determined by electron energy loss methods, either because their concentration is too low or they cannot be detected by the X-ray detector.

The Cliff-Lorimer procedure for EDS compositional analysis of thin films is a well-accepted method for quantitative analysis. Use of the thin film assumes that the ratio of the characteristic lines' intensities is proportional to the composition ratio:

$$\frac{C_b}{C_A} = k_{BA} \left(\frac{I_B}{I_A} \right) \quad (4)$$

where C is the concentration of element A or B; I is the intensity of the X-ray line generated by element A or B; and k_{BA} is a calibration factor which can be calculated for K lines (and with difficulty for L and M lines) and is a function of the ionization cross section (Q), X-ray fluorescence yield (w), the radiative partition function, and the detector efficiency (η). We have used experimentally determined k factors from well-defined standards.

To determine k_{BA} , data from a sample of known composition are acquired, and k_{BA} is calculated from Eq. 4. This is repeated several times, and an average value obtained. The standard deviation of these data sets is used as an estimate of error for the determined k_{BA} . It is usually difficult to find samples that are homogeneous on a scale sufficient to perform this analysis, but several of our glasses appear to be adequate when a large probe (greater than 1 μm) is used. There are, however, limitations associated with this approach.

Table 11 displays an analysis of a SRL 202 glass by TEM/EDS and wet chemistry. The results show that TEM/EDS can determine the compositions of solids accurately for many elements, including sodium.

2. Detection Limits

The limit of detection for the TEM/EDS method has been investigated over this year. Detection limits depend mainly on the intensity of the TEM electron beam. Tungsten filaments for the beam have lower detection limits than LaB₆ filaments [76]. But the greatest intensities are generated from field emission sources or Schottky devices (which unfortunately, one cannot upgrade to); these are several orders of magnitude brighter than tungsten or

Table 11. Comparison of TEM/EDS Results and Wet Chemical Analysis^a for SRL 202 Glass

Element	TEM/EDS Composition, wt %						Wet Chemical Analysis, wt %
	TW1A ^b		TY2 ^b		TZ2 ^b		
Si	51.2	52.1	51.2	51.2	52.4	49.4	48
Na	7.9	8.1	7.2	8.0	8.2	7.9	8.2
Mg	0.5	0.8	0	0.2	0.5	0.1	0.2
Al	4.4	4.8	3.1	3.7	3.8	3.6	4.9
K	7.1	6.9	7.3	7.1	7.5	7.9	7.5
Ca	2	2.0	1.8	2.2	2.3	2.1	2.2
Ti	1.5	1.5	1.3	1.2	1.4	1.3	1.6
Mn	3.9	3.9	4.8	4.1	4.4	4.3	4.3
Fe	19.6	18.3	21.3	19.2	20.4	19.9	21
Ni	1.8	1.7	2.0	1.9	2.1	1.7	2.1

^aCounting times >600 s.

^bSRL 202 glass sample numbers.

LaB₆ filaments. The detection limit also depends on the element analyzed. The number of X-rays (N_E) depends on the brightness (i , a constant), the number of atoms in the solid (N), the ionization cross section (Q), and the fluorescence yield (ω). That is,

$$N_E = i N Q \omega \quad (5)$$

One has some control of Q by varying voltages and looking at different X-ray lines. Obviously, the main route to improve detection limits is to increase the analysis time.

Detectability limits for TEM/EDS are at a fraction of a percent, but at the nanometer level of spatial resolution, this translates into a minimum detectable mass approaching a few atoms. For example, if the electron beam diameter is 20 nm, and the sample is 100-nm thick, 1 at.% uranium distributed in muscovite is only 800 atoms. Such a level of uranium may be possible to detect. However, the problem is locating the area which contains these uranium atoms.

We have found that, for certain elements, electron energy loss methods can be used to improve detection limits. The technique of using a "second difference" with parallel detectors has recently been used to determine trace levels of elements [77-80].

Boron is an element within the waste glass at fairly high levels (~10 wt %). This element in the glass cannot be quantified by EDS and is very difficult to detect by other methods (with TEM/EDS, it is impossible). The problem arises from the very low energy of the X-ray (boron undergoes self-absorption) and the low fluorescence yield (Auger electron production) [81], which reduces the number of X-rays produced from light elements. However, EELS is capable of detecting boron, although with some difficulty. Figure 26 shows the boron absorption edge obtained from an EELS spectra of a borosilicate glass. However, quantifying this information is difficult because of peak overlap in this energy region. This absorption edge also provides chemical state information on the silicon ion [82]. The near-edge structure is indicative of silicon in the tetrahedral state.

Fig. 26. Electron Energy Loss Spectroscopy Analysis Showing Presence of Boron in Waste Glass. The silicon edge in pure silicon is at 99 eV; however, in SiO_2 , it shifts to ~ 106 eV. This analysis shows that the silicon in glass is in the IV oxidation state.

3. Beam Damage Effects

Because high energy electrons interact strongly with matter, electron beam techniques are useful at obtaining information from sub-micron sized phases. Unfortunately, this strong interaction can sometimes result in damage to the sample being analyzed. Damage can be caused by either ionization (according to the Bethe relationship, i.e., ionization will decrease with beam energy) or by knock-on effects (i.e., it will increase with beam energy). As shown in Fig. 27, sodium is removed from an area of analysis exponentially with time [83]. However, it is possible to analyze glass for sodium (see Table 12) and obtain compositional gradients if the beam current is kept low enough. Information regarding sodium concentration is important because sodium distribution between the glass, reacted layers, and secondary phases is key to understanding the glass reaction process.

4. Electron Energy Loss Spectroscopy

Electron energy loss techniques have seen limited application in the study of waste glass. As well as compositional data, EELS provides structural information through the extended fine structure, including nearest neighbor distances and oxidation state. The technique is completely analogous to X-ray absorption spectroscopy, except that the EEL spectra are complicated by scattering effects and overlapping absorption edges (due to the low energy range used). However, for many elements EELS can have a greater sensitivity than EDS. In colloidal particle studies, it has been shown to detect low levels (<70 ppm) of rare earth elements [80]

Fig. 27. Sodium Depletion in Waste Glass with Time in Electron Beam

Table 12. Compositional Analysis for Sodium through SRL 131 Glass Reacted at 2000 m⁻¹ for 560 Days

	Sodium wt% ^a
Clay Layer	5.6
Alteration Layer	14.5
Alteration/Glass	19.9
Glass	22.5 ^b

^aCalculation based on major elements detectable by EDS.

^bWith a large probe, sodium analysis was 24.5 wt %.

(it also resolves the peak overlap that occurs with EDS for these elements, as discussed in Sec. VIII.F). One problem with EELS is that the integration times required to collect EELS analysis of uninterrupted K edges (these edges are the most suitable for obtaining fine structure information) mostly result in the studied alteration phase becoming amorphous. However, the bond lengths of covalent metamict minerals are unlikely to change during the amorphization (unless there are redox modifications). Therefore, radial distribution functions, obtained from the extended fine structure, will still provide information on nearest neighbor distances, thereby providing some structural data. Further work on this subject is in progress.

E. Ongoing Tasks

A short description of the work being performed in support of the program tasks along with selected results is given below.

1. Analysis of Long-Term Test Glass

The "Long-Term Testing" Task (Sec. V) seeks to evaluate the long-term performance of fully radioactive glass and compare this performance with that of nonradioactive glasses with the same nominal composition. Samples have been prepared of all nonradioactive tests terminated to date in this matrix. Detailed analyses have been performed, and sodium distributions have been determined for the first micron of glass below the reaction layer. This is particularly important for powdered glass samples, which are used to react glass at very high SA/V ratios, where very advanced reactions may be expected.

This section describes the AEM identification of secondary phases that have formed during the reaction of 200-type glass, both on the leached layers of the glass and as colloidal particles within the leachate. Because of the strong interaction of high energy electrons with matter, electron beam techniques are a powerful means of characterizing phases that are less than a micron in diameter. However, the strong interaction can result in beam damage to the sample and loss of structural information (see Sec. VIII.D). This is particularly a problem with secondary phases produced during glass corrosion.

Details of glass preparation and experimental design are given in Sec. V.C and V.D. Powder samples of the SRL 200-type glass were reacted at 90°C with simulated EJ-13 groundwater. The SA/V ratio was 20,000 m⁻¹, and the reactions were run for periods from 15 to 728 days.

The analysis results from the reacted layers of the "Long-Term Testing" Task are summarized in Table 13. A number of crystalline secondary phases were observed in the outer layers in some of the longer reacted samples. These are described in detail elsewhere in this report (Sec. V.D).

The primary conclusion from these analyses is as follows. Long-term samples of simulated glass, which had undergone reaction acceleration after 182 days, possessed a number of silicate secondary phases, including smectite (iron silicate and potassium iron aluminosilicate), weberite (uranium silicate), zeolite (calcium potassium aluminosilicate), tobermorite (calcium silicate), and a pure silica phase. However, uranium silicates and smectite have also been observed in tests in which the glass samples had not undergone the reaction acceleration, in both the leachate and leached layer. This finding suggests that these phases are not responsible for the reaction acceleration [84].

Table 13. Results of Surveys for Long-Term Testing Glass

Test (Sample ID)	Comments	Blocks Prepared
DP10 131/11S reacted at 340 m ⁻¹ for 728 days	The layer structure of the sample was quite complex and in general was separated from the glass. A backbone structure was present with a precipitated layer which varied in thickness from ~100 to 2000 nm.	769, 770, 771, 772, 772, 773
DP24 131/11S reacted at 2000 m ⁻¹ for 560 days	The layer was ~150 -300 nm thick, occasionally separated from the glass.	727, 728, 729, 730
DP82 165/46S reacted at 2000 m ⁻¹ for 560 days	The clay layer in this set of blocks is poorly developed and approximately 75 nm thick, with no secondary phases noted.	763, 764, 765
DP83 165/46S reacted at 2000 m ⁻¹ for 560 days	The clay layer in this set of blocks was poorly developed and ~50-100 nm thick, with no secondary phases noted.	766, 767, 768
DP111 200S reacted at 340 m ⁻¹ for 364 days	Glass and layer intact.	786, 787, 788
DP112 200S reacted at 340 m ⁻¹ for 728 days	Layer separated from glass.	827, 828
DP113 200S reacted at 340 m ⁻¹ for 728 days	Glass and some layer.	829, 830, 831
DP146 200S reacted at 2000 m ⁻¹ for 560 days	The layer was >600 nm thick in some regions. On average it was 300 nm thick.	735, 736, 737
DP147 200S reacted at 2000 m ⁻¹ for 560 days	The composition of the clay was a magnesium aluminum silicate. The layer was ~150-200 nm thick and possessed a backbone structure. Calcite also found.	731, 732, 733, 734
DP184 200S reacted at 20,000 m ⁻¹ for 546 days	Uranium silicate and zeolite particles were sectioned. In one block a large calcium silicate phase was found, which was identified as tobermorite. The zeolite had a high Al/Si ratio, which may account for some of its beam sensitivity.	738, 739, 740, 741, 742
DP184B 200S reacted at 20,000 m ⁻¹ for 546 days	Calcium silicate was a major component; phase consisted of wispy long crystallites (phase was beam sensitive), identified as tobermorite. Uranium silicate (weeksite) and zeolite phases also found in some blocks.	720, 721, 722, 723, 724, 725, 726
DP185 200S reacted at 20,000 m ⁻¹ for 546 days	Uranium silicate and a potassium aluminum silicate (zeolite) were observed. An amorphous silica phase was also observed in one block to be the major component.	743, 744, 745, 746

A comparison of the behavior of simulated and fully radioactive nuclear waste glasses, reacted under static test conditions, has been published previously [85]. Feng et al. [86] found that 200S glass, reacted at $20,000 \text{ m}^{-1}$, undergoes a reaction acceleration between 182 days and 330 days. This coincides with the formation of a zeolite phase, which has been identified as clinoptilolite, and an amorphous silica phase [86]. Our recent AEM results for SRL 200S and 200R are discussed below.

a. Analysis Results from Simulated SRL Glass (200S)

A number of silicate phases were identified in the SRL 200 glass tests, both in the simulated and radioactive glasses. The dominant phase (determined by XRD and SEM analysis), found in the SRL 200S glasses after reaction acceleration, was a potassium aluminosilicate, which was extremely electron beam sensitive in the TEM and has made structural analysis by SAED difficult. This phase and the others are discussed below.

(1) Potassium Aluminosilicate Phases

The SRL 200S glass reacted for 364 and 728 days contained a potassium aluminosilicate phase. The electron diffraction and XRD data of this phase are shown in Table 14. The XRD spacings (see Table 15) from the 728-day test of the zeolite phase matched with phillipsite of the harmotome group, ideally $[\text{K}_2(\text{Ca}_{0.5}\text{Na})_4(\text{Al}, \text{Si})_{16}\text{O}_{32} \cdot 13\text{H}_2\text{O}]$, a monoclinic zeolite with $a = 9.88 \text{ \AA}$, $b = 14.30 \text{ \AA}$, $c = 8.67 \text{ \AA}$, and $\beta = 124$ (zeolite structural type S4R). The TEM analysis for the 330-day test had indicated that the zeolite phase was clinoptilolite, and XRD data suggested that this phase might also be present. X-ray energy dispersive spectroscopy showed a high Al/Si ratio, as well as the presence of Ca and K (Table 14). In the 728-day test, the potassium concentration appeared to be higher, and this phase was, at times, considerably more beam stable than observed for samples reacted for shorter time periods at the same SA/V ratio. Figure 28 shows the interface between the smectite clay and the zeolite phase. (The zeolite phase became amorphous while the micrograph was taken; that is why it has the appearance of glass.) There was some evidence that the zeolites in the 728-day tests contained uranium. This may account for their increased beam stability. Ion exchange of large uranyl cations (UO_2^{2+}) has been found by Zandbergen [88] to result in significant beam stability.

The mineral paragenesis during borosilicate glass reaction, in vapor conditions, has been shown by Wronkiewicz [89] to be the following:

unaltered glass $\rightarrow$ smectite clays $\rightarrow$ sodium chabazite $\rightarrow$ anacrite + phillipsite $\rightarrow$
potassium feldspar

The alteration of SRL 200S glass appears to be following a similar paragenetic sequence; however, anacrite has not to date been identified in any of the 200-type tests. Chabazite has been tentatively identified in the leached layers of SRL 202U glass reacted at $20,000 \text{ m}^{-1}$ for >300 days [90].

(2) Uranium Silicate Phases

Uranium silicate phases were observed in SRL 200S glass after reaction acceleration, but results from other tests, which will be described later, suggest that this phase is not responsible for the observed acceleration. In Fig. 29, a uranium-bearing phase can be seen attached to the clay phases of the leached layer. The uranium silicates were most often elongated crystallites. Table 16 also demonstrates the precision that can be achieved with SAED data for identifying, in this case, a uranium silicate phase (weeksite).

Table 14. Lattice d-spacings for Potassium Aluminosilicate
Formed from SRL 200S Glass

TEM d-spacings, Å		XRD d-spacings at 728 Days, ^{a,b} Å	d-spacings for Phillipsite, ^{b,c} Å
364 Days	728 Days		
		8.2	8.14
	6.9 - 7.29	7.2	7.18
5.67		5.62	
5.20	5.23	5.37	5.38
	4.82	5.0	5.07
	4.72	4.56	
4.25	4.23	4.30	4.30
3.91	4.18	4.12	4.12
3.79		3.73	3.69
		3.57	3.48
3.35	3.33-3.36	3.5	
3.29		3.26	3.28
	3.23	3.18	3.21
3.03		2.93	2.93
		2.75	2.75
2.56	2.65	2.69	2.69
2.41	2.35	2.40	

^aXRD obtained using the Debye-Scherrer method.

^bFigures in bold are high-intensity reflections.

^cFrom Ref. 87.

Table 15. Composition of Zeolite Phases Found in SRL 200S
Glass Tests Determined by X-Ray Energy
Dispersive Spectroscopy

	Comp., at. %			
	Si	Al	K	Ca
364 Days	56.8	28.4	11.7	3.0
728 Days	61.4	30.4	6.1	2.1

Fig. 28. Micrograph (a) of Clay and Zeolite Phases Found in SRL 200S Glass Reacted for 364 Days. The zeolite has gone amorphous due to the electron beam and diffraction (b) along a major zone axis in the zeolite phase from a 728-day test.

Fig. 29. Analysis of Uranium Silicate Particle of SRL 200S Glass Reacted for 728 Days. (a) Micrograph of phase attached to clay layer, (b) electron diffraction taken along a minor axis, and (c) EDS compositional analysis (Cu- $K_{\alpha,\beta}$ fluorescence due to support grid). The peaks in the 16-17 keV region are due to uranium.

Table 16. Lattice d-spacings for Uranium Silicate Formed from SRL 200S Glass

Measured d-spacings, Å			d-spacings for
364 Days	728 Days	Error, ^a ± Å	Weeksite ^b [88], Å
9.07	9.09	0.25	8.98
7.08	7.09	0.16	7.11
5.63	6.01	0.11	5.57
4.53	4.60	0.08	4.58
	3.69	0.07	----
3.56	3.55	0.06	3.55
3.26	3.32	0.05	3.20-3.30
3.03	3.07	0.05	3.06
2.79		0.04	2.80
2.44	2.51	0.04	2.41
	2.39	0.04	2.37
2.29	2.30	0.03	2.28
	1.98	0.02	1.97

^aErrors based on microscope aberrations and experimental accuracy of measurements.

^bFigures in bold are high-intensity reflections.

(3) Calcium Silicate Phases

A calcium silicate phase, consisting of wispy long needles, similar to smectite clay but much straighter, was found in many regions of the leached surface (Fig. 30). Electron diffraction was obtained from this phase but was weak (Table 17). Quantitative analysis by EDS suggests $\text{Ca}_2\text{Si}_7\text{O}_x$; wollastonite is a possible match, but this is a high-temperature phase. Other possibilities include Ca-B containing feldspar; however, solution data, as well as EELS analysis of this phase, suggest that boron is not incorporated into the secondary phases. The best match with SAED data was found with orthorhombic tobermorite $[\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}]$, but a reasonable match was also made with synthetic triclinic gyrolite $[\text{Ca}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4 \cdot 7\text{H}_2\text{O}]$, which matched, in terms of composition, closer than the tobermorite. The tobermorite identified does not appear to possess enough calcium, suggesting that large amounts of silica are between the crystallites. As shown in Fig. 30d, a radial distribution function was obtained from the spectra showing the nearest neighbor distances. The Si-K edge is a promising region for electron extended energy loss fine structure (EXELFS) analysis, as there are no interfering edges in the ~1800 eV energy range and a good signal-to-noise spectra can be generated. [The EXELFS technique is analogous to extended X-ray absorption fine structure (EXAFS). It results from the interference between the outgoing photoelectron caused by an absorption event and backscattering by the surrounding atoms.]

(4) Iron Silicate Phases

A silica-rich phase has been described previously [84], although the phase was rare. More commonly an iron silicate phase was found in the SRL 200S glass samples, which displayed polycrystalline electron diffraction typical of a smectite clay (Fig. 31). The diffraction pattern shown in Fig. 31b gives the $hk0$ reflections of a smectite. Some work

(a)

(b)

(c)

(d)

Fig. 30. Analysis of a Calcium Silicate Phase Found in SRL 200S Glass. (a) Micrograph of phase attached to clay layer, (b) polycrystalline electron diffraction pattern, (c) EDS analysis, and (d) EXEFLS analysis of the Si-K edge, which has yielded a radial distribution function.

Table 17. Lattice d-spacings for Calcium Silicate (Å)
Formed from SRL 200S Glass

Glass d-spacings	Tobermorite ^{a,b}	Glass d-spacings	Tobermorite ^{a,b}
5.51	5.49	2.15	2.15
4.59		2.03	2.00
3.57	3.55	1.86	1.87
3.15	3.16	1.69	1.84
3.04	3.09	1.54	1.54
2.97	3.005	1.43	1.44
2.81	2.83		

^aFigures in bold are high-intensity reflections.

^bJCPDS card 19-1364.

Fig. 31.

Analysis of Iron Silicate Phase in a 330-Day Test of SRL 200S Glass. (a) Micrograph of phase along with a diffraction pattern (b), which is typical of a smectite clay, and (c) EDS analysis.

has been done to determine whether these diffraction patterns can provide information on the structure of smectite clays; however, variations in the spacings are too small (compared to the variations in the instrument's performance) and useful data could not be obtained. Analysis of smectite and transition metal oxide patterns from colloids has, however, provided detailed structural analysis (see later section). The clay was found within the alteration layer, underneath the backbone structure, which is often found in leached glasses.

b. Analysis Results from Radioactive SRL Glass (200R)

In contrast to the simulated glass, SRL 200R glass had not undergone reaction acceleration in tests for up to 728 days. However, a number of secondary silicate phases in the leachate have been observed in these tests, despite the lack of reaction acceleration. The SRL 200R glasses displayed a smectite clay layer, which was depleted in K and Na. This outer clay layer was found to be around 100-150 nm thick at 364 days and 200 nm thick at 546 days, with no evidence of glass alteration.

c. Discussion

Both the radioactive and simulated SRL 200 glasses were compared in terms of solution analysis and TEM layer analysis in Sec. V.D. The zeolite phase, which is responsible for the observed reaction acceleration, underwent slight changes from 364 to 728 days, which has resulted in a more beam-stable phase. The change of the zeolite phase involved some phases possessing a higher potassium content. We did not observe evidence of the formation of feldspar, although the zeolite phases in the 728-day sample appear to be more stable with increasing potassium content and lower aluminum content.

Uranium silicate (wecksite) phases were observed in SRL 200S glass reacted at 340 m^{-1} , both in the leachate and on the leached layer, and in SRL 200R glass leachates reacted at $20,000 \text{ m}^{-1}$. This finding suggests that wecksite is not responsible for the accelerated reaction.

In spite of the electron beam sensitivity of many of the alteration phases, we have found that good structural analysis by SAED can be obtained. The electron irradiation effects, however, impede detailed characterization of these phases, so that fine structures, such as extended defects and stacking faults, common to mineral phases (and which may provide further insight into how these phases are forming) cannot be observed; and the electron beam technique is unable to obtain much more information than the more conventional methods. Often the data collected, through diffraction and EDS, do not match exactly with the XRD data base. However, as many of the phases exhibit solid solution sequences, small variations in composition can be expected.

2. Analysis of Effects of Radiation on Glass at Large SA/V

A limited number of surveys were performed from the "Effects of Radiation on Glass Reaction at Large SA/V" Task (Sec. VI). These were SRL 131 and 202U glasses reacted for various times in a radiation field (see Table 18). The reacted layers developed rapidly, and we had some problem in obtaining a completely intact section.

The results from the 7-day and 14-day vapor hydration tests cannot be compared because no suitable samples were obtained from the 7-day test. The feature, described as white threads according to observation using optical microscopy, was then subjected to TEM analysis

Table 18. Results of Sample Surveys for Effects of Radiation Glass

Test	Comments	Blocks Prepared
IVE131A-7-1b 131A glass reacted in vapor at 150°C for 7 days	Crystalline phase was identified as a calcium-bearing phase. Photo C11604 is a pattern taken along a major zone axis. The phase was beam stable and possessed a small unit cell. Possibly calcite.	841
IVE131A-14-1b 131A glass reacted in vapor at 150°C for 14 days	Complete sections were found on the grid. The layer consisted of an outer ordered clay layer (~0.5 μm), a large alteration layer (~4 μm), and unreacted glass. Uranium was detected in the unreacted glass. Sodium was only found in the unreacted glass. The outer clay layer was found to be rich in iron and potassium. Closer inspection of the clay layer revealed some particularly straight crystallites. The alteration layer was made up of very fine crystallites, which were randomly oriented.	842, 843, 844
202A-540-2c 202A glass reacted in EJ-13 at 340 m ⁻¹ at 90°C for 540 days	The clay layer was ~600-800 nm thick and possessed a backbone structure that was separated from a well-crystallized outer layer (~400 nm thick) by a poorly crystalline inner clay layer. The inner clay layer contained a number of uranium-bearing precipitates.	777, 778, 779
202A-720-2d 202A glass reacted in EJ-13 at 340 m ⁻¹ at 90°C for 720 days	The sample showed widely varying layer thicknesses, 200-500 nm. Layers contain secondary phases rich in U.	783, 884, 785

and was identified as calcite, based on EDS and SAED data. We found Ca-Si compositions during SEM but not TEM analyses, as this phase was not prepared for analysis. Figure 32 shows a possible mixture of illite and smectite in a reacted 131A glass.

The clay crystallites were often exceptionally straight, as is characteristic of illite. Detailed analysis might be required to look for further evidence of this phase. The outer layer was potassium rich, although the Al/Si ratio was very low. There was some indication of a sodium gradient. The EELS method was used to analyze the calcium silicate phase found in the IVE131-56 test and revealed several rare earth elements (see Fig. 33).

3. Analysis of Effects of SA/V Glass

Various glasses reacted at different SA/V ratios in static leach tests were analyzed by AEM to assess their effect on glass reaction. These surveys were carried out for the "Relationship between High SA/V Experiments and MCC-1" Task (Sec. VII), and the results are summarized in Table 19. These tests were run with SRL 131 and 202 glasses.

Table 19. Results of Sample Surveys for Effects of SA/V Glass

Test	Comments	Blocks Prepared
TW11D 202U glass reacted at 340 m ⁻¹ for 360 days	The outer layer consisted of long crystallites (100-200 nm long). There was some evidence of etching.	747, 748, 749
TY14 202U glass reacted at 2000 m ⁻¹ for 280 days	300-400 nm thick layer.	789, 790, 791, 792
TY15 202U glass reacted at 2000 m ⁻¹ for 560 days	50-200 nm thick layer.	793, 794, 795, 796
TZ16 202U glass reacted at 20,000 m ⁻¹ for 364 days	Calcium silicon phosphate (nagelschmidtite), uranium-bearing phases observed.	797, 798, 799, 800, 801
TZ45 202U glass reacted in EJ-13 at 20,000 m ⁻¹ for 364 days	There were intact regions of glass followed by an alteration layer ~1 μ m thick and a clay layer ~200 nm thick. The outer layer contained a backbone structure. The innermost clay is randomly oriented and poorly developed. Dark regions of the clay were found to be enriched in U and Sr.	802, 803, 804, 805, 806
PY17/PY18 131A glass reacted at 2000 m ⁻¹ for 728 days	The layer consisted of an outer clay layer 300 nm in length, a backbone made of fine crystallites randomly oriented, another ordered clay layer, and a disordered alteration layer. The clay layer and alteration layer contained 50 nm precipitates, which were U-Ti phases. A crystalline iron silicate was also found at the end of the sections. The uranium silicates were identified by SAED as weeksite (see Table 20).	845, 846, 847, 848, 849, 850, 851, 852
BZ18 202A glass reacted at 20,000 m ⁻¹ for 546 days	Layers were several microns thick; uranium silicate and zeolite phases were found.	692, 693, 694, 695, 696
BZ19 202A glass reacted at 20,000 m ⁻¹ for 728 days	Uranium silicate and zeolite phases observed.	697, 698, 699, 700

2 of 2

Table 19. Results of Sample Surveys for Effects of SA/V Glass

Test	Comments	Blocks Prepared
TW11D 202U glass reacted at 340 m ⁻¹ for 360 days	The outer layer consisted of long crystallites (100-200 nm long). There was some evidence of etching.	747, 748, 749
TY14 202U glass reacted at 2000 m ⁻¹ for 280 days	300-400 nm thick layer.	789, 790, 791, 792
TY15 202U glass reacted at 2000 m ⁻¹ for 560 days	50-200 nm thick layer.	793, 794, 795, 796
TZ16 202U glass reacted at 20,000 m ⁻¹ for 364 days	Calcium silicon phosphate (nagelschmidtite), uranium-bearing phases observed.	797, 798, 799, 800, 801
TZ45 202U glass reacted in EJ-13 at 20,000 m ⁻¹ for 364 days	There were intact regions of glass followed by an alteration layer ~1 μ m thick and a clay layer ~200 nm thick. The outer layer contained a backbone structure. The innermost clay is randomly oriented and poorly developed. Dark regions of the clay were found to be enriched in U and Sr.	802, 803, 804, 805, 806
PY17/PY18 131A glass reacted at 2000 m ⁻¹ for 728 days	The layer consisted of an outer clay layer 300 nm in length, a backbone made of fine crystallites randomly oriented, another ordered clay layer, and a disordered alteration layer. The clay layer and alteration layer contained 50 nm precipitates, which were U-Ti phases. A crystalline iron silicate was also found at the end of the sections. The uranium silicates were identified by SAED as weeksite (see Table 20).	845, 846, 847, 848, 849, 850, 851, 852
BZ18 202A glass reacted at 20,000 m ⁻¹ for 546 days	Layers were several microns thick; uranium silicate and zeolite phases were found.	692, 693, 694, 695, 696
BZ19 202A glass reacted at 20,000 m ⁻¹ for 728 days	Uranium silicate and zeolite phases observed.	697, 698, 699, 700

Table 20. Electron Diffraction from Uranium Silicate in Test PY17/18

Experiment d-spacings, Å	JCPDS 12-462 Weeksite
8.75	8.98
6.87	7.11
5.47	5.57
4.72	4.83
4.47	4.48
3.82	3.84
3.49	3.55
3.21	3.20
3.14	3.13
3.10	3.06
2.93	
2.88	

In Fig. 34, the layer from a 131A glass reacted for 728 days (Test PY17/18) displays strands of uranium silicate (identified as weeksite, Table 19), which are partially attached to the layer. The U/Si ratio appeared to vary between particles, suggesting another phase, which was determined to be boltwoodite. Underneath the clay layer is a region of disordered fine crystallites and small dark precipitates, which were identified as uranium-titanium-rich phases.

The EELS analysis for Test TZ16 of a Ca-Si phosphate phase demonstrated some interesting applications of EXEFLS (see Fig. 35). The radial distribution functions obtained from the silicon, oxygen, and phosphorus K-edges allow the determination of Si-O (1.6 Å) and P-O bond lengths. A trace amount of Sr can also be seen in this phase. This information helps to characterize the nature of the phase, even amorphous phases. Obtaining data from the calcium edge is more difficult, because of the L_{2,3} edge (i.e., it is much more complex, having two absorption edges which are very close).

4. Colloid Formation during Nuclear Waste Glass Reaction

During this reporting period, we have continued to use AEM in characterizing colloidal material from the leachates of waste glass tests. "Colloidal systems" may be defined as those in which the component phases are highly dispersed, such that the properties are dominated by the interfacial regions. Colloids range in size from 1 nm to 1 µm. Colloids are by definition surface active, and they will readily adsorb metal ions of high ionic charge such as transition metals and actinides. As discussed below, they can form by precipitation of species leached from waste glass or by the breakup of surface layers.

The release of radionuclides from waste glass may result in both real colloid and pseudocolloid formation. Pseudocolloids are formed when radionuclides are adsorbed onto existing colloids, such as those present in natural groundwaters. Real colloids are formed from the hydrolysis of highly charged ions in solution. Hydrolysis is followed by polymerization of metal ions, which leads to the formation of colloids. The rate of hydrolysis depends on the oxidation state of the ion. Experimental data, notably from Bates et al. [71], have suggested that

Fig. 34. Micrograph of the Layer from 131A Glass Reacted at 2000 m^{-1} for 728 Days Showing the Uranium-Bearing Phases and the Ordered Clay Layer. Top left strands of uranium silicate can be seen (weeksite), which are partially attached to the layer. Underneath the clay layer is a region of disordered fine crystallites and small precipitates, which were identified as uranium-titanium rich phases.

Fig. 35. Electron Energy Loss Spectroscopy Analysis for Test TZ16 Showing (a) the Calcium L_{2,3} and Oxygen-K Absorption Edges, (b) Silicon-K and Phosphorus-K Absorption Edges, and (c) Difference Spectra Showing Trace Strontium.

colloids can form via spallation of the surface layers from waste glass (primary colloids), whereas Buck et al. [72] found evidence for nucleation of smectite clay colloids, which were identified by their characteristic oblique textured electron diffraction patterns. Kawano and Tomita [91] have also observed the formation of smectite clays during the laboratory alteration of volcanic glass. Buck et al. [92] demonstrated by TEM analysis that the amount of colloids decreased with time. This TEM observation has been confirmed by light scattering measurements by Feng et al. [74].

Research on the implications of colloids in the proposed high-level waste repository has concentrated on colloids present in groundwater as the likely vehicle for radionuclide transport [93], or the formation of pseudocolloids by actinides [94].

The processes of primary colloid formation and nucleation of smectite clay colloids in leachates may be described, in terms of colloidal chemistry, as dispersion and condensation processes, respectively [95]. Dispersion occurs primarily during dripping water tests [71], whereas condensation processes mainly occur during immersion tests [92].

The aim of this work has been to try to understand colloid formation during waste glass alteration and the conditions necessary for the formation of stable colloids. Unfiltered leachates were collected from three different experiments: long-term testing (Sec. V.D.1), tests to determine relationship between high SA/V experiments and MCC-1 (Sec. VII), and N4 tests (Sec. V.D.2).

a. Colloids from Long-Term Testing

The initial aim of this study was to identify and characterize colloidal material. Table 21 displays the data collected on colloids from the long-term testing over this year (Sec. V.D.1). Obtaining data on size distributions was not possible with the specimen preparation technique used. However, amounts of colloidal material were qualitatively estimated. Colloids from the leachate of Test DP113 (SRL 200S glass reacted at 340 m⁻¹ for 728 days) were examined, and these displayed some interesting features (see Fig. 36).

Table 21. Colloids Analyzed in Leachate from Long-Term Testing Task

Test	Comments	Grid
DP113 200S glass reacted at 340 m ⁻¹ for 728 days	The particles ranged in size from 50 to 200 nm in diameter and were partially agglomerated. Particles were small, located around the holes in the carbon film. Bundles of uranium silicate were observed (see text).	C:134
DP18 131S glass reacted at 2000 m ⁻¹ for 980 days	Amorphous calcium phases. Salt present.	C:138
DP168 200S glass reacted at 2000 m ⁻¹ for 980 days	Little colloidal material present. No salt contamination.	C:133
DP146 200R glass reacted at 20,000 m ⁻¹ for 728 days	Very little on grid.	C:102
DP185 200S glass reacted at 20,000 m ⁻¹ for 546 days	Much of the section was opaque to the electron beam. Grid is covered with Na, K, Si.	C:99

(a)

(b)

Fig. 36. AEM Analysis of DP113 Colloids: (a) Micrograph of "Hair-Like" Uranium-Bearing Phases and (b) EDS Analysis of Phase. The phase was identified as a sodium uranium silicate (boltwoodite).

Smectite clay displayed preferential ordering in some instances. The composition was an iron silicate (Table 22) with a small amount of potassium. The uranium silicate phase consisted of very fine strands of material, 20-50 nm wide though several microns in length. Other phases found were dolomite, calcium phosphate, and a silica-rich phase. Uranium phases were not found in related tests conducted on SRL 200S glass reacted at 340 m^{-1} for 182 days (DP108) and 364 days (DP110). The uranium silicate morphology suggests that these phases did not arise from spalled layers, as they were very different from the uranium silicates observed in Tests TZ45, PY15, and DP167. In these samples, the uranium phases were much thicker and had clumps of clay attached to them. The uranium phases found in DP113 (Table 21) appear as if they formed in solution, i.e, they may have nucleated as uranium real colloids (by uranium hydrolysis) and subsequently grown into uranium silicates in solution. The electron diffraction also contains clay spacings. The diffraction matches with both uranophane and weeksite group silicates, though based on composition the phase is probably weeksite.

The development of colloids in the SRL 200 glass tests will be treated in more detail in a future paper [92]. Smectite clay, which can be identified by its oblique textured electron diffraction pattern, was found within the leachate of SRL 200S glass reacted at $20,000 \text{ m}^{-1}$ up to 180 days; however, after this period no colloidal material was found by TEM. In contrast, leachates from SRL 200R glass tests still contain potassium-rich clay colloidal material at 364 days, as well as uranium silicate particles (see Fig. 37). In fact, uranium silicate phases have been observed in the leached layers and in the leachate as colloidal particles, in tests done at SA/values lower than $20,000 \text{ m}^{-1}$ with SRL 200S glass that has not undergone acceleration. These observations demonstrate that uranium silicates and smectite clay phases do not cause the acceleration of reaction.

b. Colloids from Effects of SA/V Tests

Colloids from the "Effects of SA/V" Task (Sec. VII) are listed in Table 23. Along with smectite clays, a number of uranium-titanium-bearing colloids were located in the leachates from SRL 202 tests (see Fig. 38a). The SAED patterns (see Fig. 38b) of the uranium-bearing particles exhibited preferential ordering; however, the d-spacings were similar to those expected for a clay-like phase. The EDS analysis also determined that the phase contained silicon (Fig. 38c). This phase has been found in the leached layers of the same tests. We could not determine the composition exactly, as the phase is always mixed with clays in the layer; however, in the leachates we have found the phase segregated from clay. The phase is not brannerite (the U/Ti ratio is incorrect) as we had thought before, but is related to a silicate layer.

Table 22. Electron Diffraction Data
from the Uranium Phase
of DP113 (see Table 21)

d-spacing Websites, Å	DP113 d-spacing, Å
4.83	4.70
3.84	3.62
	2.71
	2.35
4.48	1.81
	1.77
3.55	1.58

Fig. 37. Transmission Electron Micrographs of (a) Smectite Clay Colloids and (b) Uranium Silicate (Weeksite) Particle in SRL 200R Leachate Reacted for 546 Days at $20,000 \text{ m}^{-1}$

Table 23. Colloids in Leachates from Effects of SA/V Tests

Test	Comments	Grid
PY17 131A glass reacted in EJ-13 at 2000 m^{-1} for 980 days	Nothing on grid except contaminant particles.	C:142
PZ19 131A glass reacted in EJ-13 at $20,000 \text{ m}^{-1}$ for 552 days	Spiny crystals (mainly potassium, silicon, and sodium). Grid was covered by a thick layer of salt material.	C:97
PY15 131A glass reacted in EJ-13 at 2000 m^{-1} for 560 days	Continued examination of this test has been performed. Zone axis patterns and EEL spectra were obtained.	C:65
BZ19 202A glass reacted in EJ-13 at $20,000 \text{ m}^{-1}$ for 504 days	No colloids present, just salt material. One agglomerate found containing a Mn-Fe rich silicate.	C:87
BY17 202A glass reacted in EJ-13 at 2000 m^{-1} for 980 days	Iron aluminosilicate clay colloids were located around the holes in the carbon film. These tended to be agglomerated. The clay colloidal regions contained small particles of a uranium-titanium-oxide phase. SAED patterns of the uranium-bearing particles exhibited preferential ordering; the spacings were the same as the U-Ti-O phases observed in other tests.	C:136
TW14 202U glass reacted in DIW at 340 m^{-1} for 540 days	The smectite clays had an unusually high calcium content. Oblique textured electron diffraction patterns were observed.	C:116

Fig. 38. Analyses of Smectite Clay from BY17 Test (202A glass reacted at 2000 m^{-1} for 728 days): (a) Micrograph Used to Highlight the Uranium-Bearing Phases; (b) SAED Pattern of Uranium-Bearing Phase; and (c) EDS Compositional Analysis of Phase.

c. Colloids from N4 Test Series

Manganese-rich oxide minerals were found to form within clay colloids produced during waste glass reaction in the N4 tests (Sec. V.D.2). Electron diffraction analysis has enabled a detailed interpretation of the form of these colloidal manganese phases. The major phase produced during glass reaction was a smectite clay, which also contained large amounts of manganese and iron. Colloids were typically around 100-200 nm in length but were often flocculated into particles in excess of 1 μm in diameter. The suspended material produced in these tests resulted from spallation of reacted layers into solution. The manganese minerals were identified as asbolane-type minerals, showing hexagonal sublattices of Mn and Fe, based on the electron diffraction patterns.

When viewed along the textured [001] axis, some clay colloids produced two incommensurate lattice $hk0$ reflection rings, which were the result of a manganese oxide layer and smectite clay. When these textured pattern were tilted, an oblique textured electron diffraction (OTED) pattern was observed (see Tables 24 and 25).

When clay crystallites settle onto the "holey" carbon grid with c^* perpendicular to the carbon film, the resulting reciprocal lattice is a series of concentric circles lying on top of one another. When the grid is tilted, the circles result in the Ewald sphere passing through an ellipse [96]. As the grid is tilted, the colloids exhibit an OTED pattern with a turbostratic structure typical of smectite clays. The manganese content of the clay colloids was high in all samples. Occasionally, the clay colloids showed a hexagonal pattern, which was due to manganese oxide phases within the smectite clay.

The suspended material produced in these tests has resulted from spallation of reacted layers into solution. Electron diffraction patterns obtained were consistent with Mn-Fe asbolane minerals (see Fig. 39). These hybrid mixed-layer minerals consist of two alternating layer types having different cationic compositions. The asbolane structure can be described as two incommensurable hexagonal sublattices having a common origin, the same orientation, and the same period along the c -axis. The mineral sublattice showed differing intensity distributions. Birnessite, a mineral commonly found in natural clays, consists of alternately stacked sheets of MnO_6 octahedra linked through oxygen ions and water molecules which occupy the interlayers [97].

There is some question whether suspended particles and colloids, present in the leachates during "drip" tests and other types of glass tests, are the result of spallation or nucleation. We can only prove the presence of spallation by indirect means, as we cannot obtain an image of the leached surface while the reaction is in progress. When we compare the morphology of clay smectite colloids produced in immersion tests with those produced during drip tests, there are some interesting differences. Clay colloids which nucleate in solution are well dispersed, and when they are wicked onto a "holey" carbon grid, they tend to settle with the face of the crystallites to the plane of the carbon film. In drip tests, we observed large agglomerates of material, which have undergone face-edge and edge-edge interactions. In solution, smectite clay colloids undergo predominantly face-face interactions, which led to the observed OTED patterns in the TEM. The predominance of face-edge interactions in smectite suspensions has been demonstrated by Vali and Bachmann [98] using a TEM freeze fracture technique on Wyoming smectite clay. Because the TEM causes major changes to the particles, this type of evidence will not generally be accepted; however, the large agglomerated particles observed are not consistent with a nucleation mechanism.

Table 24. Colloids in Leachates from N4 Tests

Test No. ^a	Comments	Grid
N4-7	Clay colloids (Fe-Al-silicates) with iron-rich regions. A double ring structure in the electron diffraction patterns indicative of a complex (incommensurate) layering of mineral phases. These have been observed in previous tests and were due to the complex arrangement of manganese oxide minerals. In this sample, it is the iron oxide minerals which have produced this pattern.	C:156
N4-8	Some small silica particles.	C:157
N4-9	Calcium phosphate agglomerates.	C:158
N4-10	Only contaminant phases.	C:159
N4-3	Sodium silicate particles, classic examples of Ostwald ripening occurring. These phases are typical of high-salt content leachates (either found in high SA/V experiments or long-duration tests).	C:160
N4-4	Clay colloids were visible, the electron diffraction ring patterns possessed preferential ordering, which has been observed before in the N4 series. Fe-Cr silicate clay. A Ti phase was found within a clay. The clays were mainly agglomerated.	C:161

^aSee Table 4.

Table 25. X-Ray Diffraction Analyses of Colloids from N4 Tests

d-spacings, Å			Scattered	
Hex Pattern	Diffuse	Double Ring	d-spacings, Å	± (Å)
4.76	4.65	4.86		
1.59	2.65	2.95	4.70	0.08
2.73	1.78	2.75	2.52	0.04
1.79	1.57	1.71	1.57	0.02
1.32		1.63	1.49	0.02
		1.40

Fig. 39. Analyses of Clay Colloids Produced during Drip Testing of Waste Glass:
(a) Micrographs of Colloids, (b) SAED Pattern of Mn-Bearing Smectite Clay Colloid Showing ($hk0$) Reflections, and (c) EDS Analysis of Phase with Mn-Rich Areas.

The complex layer phases of Fe-Ni oxides (observed in these samples) and manganese oxides (observed in previous samples) are unlikely to have formed in solution by nucleation. The arrangement of layers was ordered and can be likened to crystal growth. Further investigation is required on how these phases form, but it may be good supporting evidence for the spallation mechanism.

In drip tests, the TEM evidence for spallation is based on the large amount of colloidal TEM data collected under different experimental conditions. The particles observed in the drip tests are not the same as those collected in the shorter duration immersion tests. The random arrangement of clay particles is similar to that observed in cross-sectional TEM images of the leached glass and suggests that these particles are the source of suspended material in the drip tests.

F. Future Work

Future work will involve TEM investigation of uranyl silicates and zeolites formed in the glass tests, using a recently installed GATAN slow-scan CCD camera, which is a digital imaging system. Fine structure has not been possible to observe due to the beam sensitivity of these phases. Further work is required on the nature of the zeolites. Questions include: What types of zeolites are forming? Are the zeolites forming in the long-term testing task similar to those found in the SA/V task? Pan and Crosier [99] have demonstrated that high-resolution images can be obtained from zeolites by using a CCD camera, with which it should be possible to overcome the fine-structure problem with the beam-sensitive zeolites. Nevertheless, the very high aluminum content of the waste-glass-derived zeolites makes them more unstable to electron irradiation than those used in industrial applications, which have very low aluminum contents [88].

We will also apply EELS to probe the local structure of elements within phases. This has been most successful with silicon, and Si-O bond lengths have been determined with this technique. The challenge is to determine whether this technique can be applied to other elements, particularly transition metals and actinides, where we want to know the oxidation state.

IX. MODELING TASKS AT LAWRENCE LIVERMORE NATIONAL LABORATORY

A. Model Development

1. Introduction

The objective of this task is to develop and apply a computer model to the reaction of nuclear waste glasses in a repository environment. The model, once validated by successfully simulating laboratory experiments and selected natural systems, will be incorporated into a performance assessment model for the repository and used to estimate glass performance for a given set of repository conditions.

Modeling work in FY 1993 concentrated on: (1) simulations of closed system tests of SRL 202 glass performed at ANL, (2) simulations of unsaturated (drip) tests on SRL 202 glass, and (3) analysis of the mathematical form of the affinity term in the rate equation. The modeling work on SRL 202 glass was presented at the annual American Ceramic Society Meeting. The work related to the affinity term was presented at the annual Materials Research Society meeting and published as part of the proceedings [100].

2. Simulations of Saturated Tests of SRL 202 Glass Dissolution

We have modeled the results of glass dissolution tests using the geochemical modeling simulator called "React" [101]. Static leach tests similar to the Product Consistency Test (PCT) were performed for times up to two years to assess the long-term reaction of high-level waste glasses similar to those to be produced at the DWPF [62]. The tests were performed in equilibrated J-13 water at a temperature of 90°C and SA/V = 10, 2000, and 20,000 m⁻¹ (see Sec. VII).

We used React to simulate the results of these tests. The React model included provisions for kinetically controlled dissolution following the rate law described by Aagaard and Helgeson [102], and for ion exchange using the methodology of Bourcier et al. [68]. The rate-controlling solid phase was assumed to be a simple silica phase [103]. The rate constant was obtained from previously reported flow-through experiments for SRL 202 glass [3]. Precipitation and dissolution of secondary phases were also included in the model. The data base of phases used in the simulation was restricted to about 70 phases known to precipitate in previously performed glass dissolution tests. Only these phases were allowed to precipitate. Some thermodynamically more stable phases were therefore excluded from the simulation. The phases predicted to precipitate were dominated by clay (Ca-rich nontronite, Na-rich saponite) and zeolites (clinoptilolite), with lesser amounts of calcite, bixbyite, muscovite, uranophane, and various calc-silicates.

The predicted amounts of B released from the glass, and the pH, as a function of time, are compared with the experimental data in Fig. 40. The simulations show good agreement with the experimental data. Note, however, that the simulations do not predict any accelerated reaction, as observed experimentally after about 182 days for SA/V = 20,000 m⁻¹ (see Sec. IX.A.4.b).

The use of our model of ion exchange [68] necessitates an estimate of the total mass of glass that undergoes ion exchange. Presently, we use the measured 25°C pH data (corrected for temperature) to estimate that mass. This is done by varying the mass of exchanger until the calculated pH's agree with the measured pH's. Figure 41 shows the

Fig. 40. Predicted (lines) versus Measured (symbols: squares, $20,000 \text{ m}^{-1}$; diamonds, 2000 m^{-1} ; circles, 10 m^{-1}) Elemental Concentrations and pH for Dissolution Tests of SRL 202 Glass in EJ-13 Water [62]. Measured 25°C pH values are corrected to 90°C .

Fig. 41. Calculated Thickness of the Ion-Exchanged Layer (diffusion layer) of SRL 202 Glass as a Function of SA/V

thickness of ion exchanger needed as a function of the SA/V ratio of the test. The observed trend is in good agreement with experimental measurements of the thicknesses of the diffusion layers on reacted glasses [104], which decrease as the SA/V ratio of the test increases. However, the SRL 202 glass is predicted to have much thinner ion exchanged layers than the 76-68 glass used in the tests by Pederson et al. [104], which had measured diffusion layer thicknesses of up to several microns. This observation is consistent with the relatively higher overall durability of the SRL 202 glass relative to the 76-68 glass, and is also consistent with EDS and secondary ion mass spectroscopy (SIMS) profiles of the reacted 202 glass (not shown).

3. Simulations of Unsaturated (Drip) Tests of SRL 202 Glass Dissolution

A likely repository scenario for the Yucca Mountain potential repository site is that of exposure of the waste forms to dripping water. For that reason, an unsaturated test methodology was developed in order to predict glass waste form performance in this type of environment [105]. These tests had previously not been analyzed using the models developed to understand and predict glass behavior in saturated environments.

We used our glass model and the rock-centered reaction mode of the React code to simulate the response of the SRL 202 glass to the unsaturated test conditions. The test consists of dripping a single drop (0.075 mL) every 3.5 days on top of a glass wafer (13.5 cm²) secured in a stainless steel frame. If the water is assumed to contact the entire glass wafer, the test has an effective SA/V ratio of about 18,000 m⁻¹. In the modeling, we assume that each drip

contacts the entire glass surface for 3.5 days, and then is completely replaced with a new drop. In a real experiment, some of the water probably transports over the glass before the 3.5-day interval is over, and collects on the bottom part of the metal retainer. Also, the new drop probably mixes to some extent with the previous drop on the glass surface.

The model predicts that after one year, about 3.5 mg of glass will have reacted to form clays, zeolites, calcite, and uranophane (see Fig. 42). The predicted extent of reaction and types of secondary phases are in good agreement with experimental results [106], although the reported data are for 105-type glass. The model also predicts that the pH of the drop while on the glass surface will initially rise to a value of about 9.25 from the starting pH of EJ-13 water of 7.8, and then fall with time to a value near 9 after one year (Fig. 43). This is caused by the glass surface becoming less reactive with time as the glass reacts with successive drops. Note that the pH curve shown in Fig. 43 is the pH of the drop after it has reacted for 3.5 days prior to being displaced by the next drop. Figure 44 shows the predicted elemental concentrations of species in the drop as a function of time. There is no way to compare these predictions with experimental data because the drop cannot be sampled while in contact with the glass surface. It may be possible to compare the integrated solution composition determined by adding up each predicted drop composition with the composition of the residual solution in the vessel bottom at the completion of the run. This has not yet been attempted.

Fig. 42. Secondary Phases Predicted to Form by Reaction of SRL 202 Glass in EJ-13 Water under Unsaturated (drip) Test Conditions

Fig. 44. Predicted Elemental Composition of Fluid Phase (drop) While in Contact with SRL 202 Glass Surface in Unsaturated Test

Fig. 43. Predicted pH of Liquid Drop While in Contact with SRL 202 Glass Surface during Unsaturated Test (90°C)

4. Analysis of the Affinity Term in the Rate Equation

In closed system tests, the rate of glass dissolution decreases with time due to the approach of the solution composition to glass saturation. Last year, we reported on our attempts to use data from closed-system dissolution tests of CSG (a simple SRL 165 analog) glass to determine the mathematical form of the affinity term in the glass dissolution rate expression. This year we report additional work in this area and revise our previous functional form.

The saturation effect is incorporated in current rate expressions for glass dissolution as the term $(1 - Q/K)$, where Q is the ion activity product for the glass dissolution reaction, and K is the solubility product for glass. As species build up in solution, the value of Q increases, and the term approaches a value of zero at saturation. The affinity term has its origin in the rigorously derived rate law [104]:

$$\left(\frac{dn}{dt}\right) = Sk + \prod_i a_i^{-n} (1 - \exp(-A / \sigma RT)) \quad (6)$$

where S is surface area, k is the rate coefficient, a_i is the aqueous solution species activities, A is the reaction affinity, σ is the average stoichiometric number for the reaction, R is the gas constant, and T is the temperature in kelvin.

Because reaction affinity (A) is defined as $A = RT \ln(Q/K)$, Eq. 6 can be simplified and rearranged to give:

$$\left(\frac{dn}{dt}\right) = Sk(pH) \left(1 - \left(\frac{Q}{K}\right)^{1/\sigma}\right) \quad (7)$$

where now all solution compositional dependencies of the rate coefficient other than pH are ignored.

Kinetic rate theory does not predict the form of the affinity term in the rate equation. In fact, there may be one or more exponential terms on the factor, which can be written in a more general form as:

$$\left(1 - \left(\frac{Q}{K}\right)^{1/\sigma}\right)^v \quad (8)$$

where $1/\sigma$ and v are exponents which must be determined experimentally. Transition state theory predicts a form where $v = 1$ and σ is some real number. In transition state theory, σ is defined as the average stoichiometric number, which gives the rate of the rate-limiting reaction step relative to the overall rate [102,107]. The nonlinear case where $v \neq 1$ is also possible.

To better constrain the affinity term in our rate equation for glass dissolution, we have used the results of closed-system dissolution tests of CSG glass (in wt %: 18.2 Na₂O, 6.0 CaO, 11.7 Al₂O₃, 8.4 B₂O₃, 55.7 SiO₂) at 100°C in a dilute (0.003 molal) sodium bicarbonate solution to calculate values of the affinity term in the rate equation. This carbonate solution has approximately the same pH and pH buffer capacity as J-13 well water at the Yucca

Mountain potential repository site, but because it has only one dissolved salt, it simplifies analysis of the dissolved species data. Analysis of how the affinity term changes with reaction progress should allow us to constrain the functional form of the affinity term.

a. Methods and Analysis

Closed-system tests of CSG glass at 100°C show nearly stoichiometric release of Si, B, Al, and Ca until about 30 days (Fig. 45). After 30 days calcium concentrations decrease, probably due to calcite precipitation. Analysis of the solutions at 30 days shows supersaturation with respect to both calcite and calcium zeolites. However, the glass is probably still dissolving stoichiometrically. Resolution of sodium release rate (not plotted) was poor because it was present in the leachate.

The rate of release of elements from the glass is given by the slope of the elemental release curves in Fig. 45. Therefore, we use data for the fastest released element (silicon in this case) and calculate the derivative at each data point (Fig. 46). The derivative curve gives the glass dissolution rate as a function of time. The form of this curve should, therefore, match the form predicted by the affinity term in the rate equation.

Two corrections must first be made to the silicon release rate data before the analysis. In our closed-system experiments, the total volume of the system decreases as samples are withdrawn. Therefore, the rate of increase of dissolved silicon concentration must be corrected for the progressively smaller solution volume into which it is dissolving (see Table 26). The second correction is for the pH effect on the rate coefficient. Other experiments have shown that the rate coefficient for CSG glass increases with $a_H^{-0.4}$ [108]. As the glass dissolves, the pH rises from 7.9 to 8.6, which increases the value of the rate coefficient by a factor of 1.4. Applying both these corrections results in the silicon release rate curve shown in Fig. 46. We also assume that at these pH and temperature conditions, total silica is approximately equal to the concentration of uncharged and unpolymerized $\text{SiO}_2(\text{aq})$.

Fig. 45. Normalized Elemental Concentrations vs. Time for CSG Glass Dissolving at 100°C in 0.005 M NaHCO_3 Solution

Fig. 46. Cumulative and Derivative Silicon Release from CSG Glass at 100°C

Table 26. Measured and Corrected Normalized CSG Glass Dissolution Rates

Day	Measured Release Rate, $\text{moles}_{\text{Si}}/\text{cm}^2/\text{s}$	pH	Rate $k(\text{pH})$ Factor	Volume of Fluid, mL	Volume of Fluid Factor, mL	Corrected Release Rate, $\text{moles}_{\text{Si}}/\text{cm}^2/\text{s}$
0	1	7.88		213.3	1.00	1.00E+00
1	0.5	7.88	1	199.6	0.94	4.68E-01
2	0.22	8.04	0.95	185.5	0.87	1.82E-01
4	0.16	8.04	0.95	171.5	0.80	1.22E-01
8	0.13	8.15	0.92	158.8	0.74	8.90E-02
16	0.1	8.26	0.88	146.6	0.69	6.05E-02
32	0.06	8.45	0.79	133.9	0.63	2.98E-02
49	0.04	8.48	0.77	120.7	0.57	1.74E-02
64	0.026	8.49	0.77	107.9	0.51	1.01E-02
85	0.015	8.56	0.71	94.7	0.44	4.73E-03

The form of the affinity term is a function of both the value of K used in the expression and the values of the exponents in the affinity term. The value of K , the equilibrium constant for the dissolving solid, depends on two assumptions: (1) the solid assumed to be controlling dissolution rate and (2) the thermodynamic model chosen for that solid. Potential solids that could be rate controlling include the anhydrous glass, the hydrous alkali-depleted surface gel layer of the glass, and a simple silica phase, depending on what specific reaction is rate controlling. Earlier modeling results [109,110] showed that the anhydrous glass is too thermodynamically unstable to be the rate-controlling phase. The value of K for the glass is so large that the ratio Q/K never approaches one. The value of $(1 - Q/K)$, therefore, never gets significantly smaller than one, and the model predicts no decrease in rate as species such as silica build up in solution. This contrasts with the experimental data.

For this analysis, we have assumed that the saturation of a simple silica phase is rate controlling [103]. The experimental data will be used to estimate the thermodynamic stability of the hypothetical silica phase. The use of more complex solids, such as the surface gel layer, did not provide sufficient improvement in the fit of the experimental data to warrant its continued use in this analysis.

Once we have selected a thermodynamic model for the rate-controlling solid, we can investigate the form of the affinity expression. Figure 47 compares our measured rate (solid squares) with calculated values for the affinity term. The curve with solid triangles shows the values for the term $(1 - Q/K)$, where $\log K$ is -3.1 . Comparison of the measured and calculated rates indicates that the saturation effect is appreciable much further from equilibrium than the simple $(1 - Q/K)$ term predicts. Even if the value of K is decreased to force the curve toward the experimental data (curve with open boxes in Fig. 47), the agreement is poor, with the rate equation predicting glass precipitation after only 20 days. Thus, a different functional form is necessary to match the observed rates.

If we fit the experimental data to a function of the form shown in Eq. 8 and set $v = 1$, we get values of -3.1 for K and 10 for σ . The resulting curve, marked with solid diamonds, shows good agreement with the experimental data.

Fig. 47. Computed Normalized Rate of Glass Dissolution Based on Two Thermodynamic Models for Glass Alteration Layer. (See text for explanation of curves.)

b. Application of the Revised Rate Equation

We can use results from SRL 202 glass dissolution tests of Ebert et al. [62] to provide partial validation of the new affinity term for our rate expression. As noted previously, the glass dissolution model is not capable of predicting accelerated reaction conditions. However, modeling can be used to evaluate potential accelerating mechanisms.

A potential accelerating mechanism, proposed by Ebert et al. [62], is that as glass reaction proceeds and dissolved species increase in concentration, eventually secondary phases which were previously supersaturated nucleate and grow quickly. This causes the solution to become suddenly depleted in species such as dissolved silica, thereby reducing the degree of glass saturation and causing the glass dissolution rate to increase.

We can evaluate this potential mechanism by applying our model to the SRL 202 dissolution test results shown in Fig. 48. Up until 182 days, the glass is reacting slowly at what might appear to be its long-term rate. The rate then increases to a value about 13 times faster than the overall rate up to 182 days. The accelerated rate is nearly that of the initial rate measured in the first few hours of glass reaction in highly undersaturated solutions.

We can compare the ratio of predicted glass dissolution rates using measured solution data at day 91 (before acceleration) and day 504 (after acceleration). The rate of glass dissolution is predicted by the model to be a function of pH and dissolved silica concentrations. At day 91, pH = 11.3 and total dissolved silica is 0.019 molal. At day 504, pH = 11.9 and total dissolved silica is 0.054 molal. The increase in pH from 11.3 to 11.9 causes the rate coefficient in the rate expression to increase by a factor of 1.5 (based on flow-through experiments). The affinity term in our rate expression, using our new form, increases by a factor of nine. Note that although more silica dissolved in the 504-day sample than in the 182-day sample, the saturation state (Q/K) actually decreases because silica becomes much more soluble at the higher pH's due to ionization and formation of polymeric species. The two factors (rate coefficient and affinity term) combine to predict a rate about 11.5 times higher than the rate measured at 182 days (Fig. 48). This agrees well with the observed acceleration of 13 times.

c. Discussion

Previous workers have analyzed dissolution rates of solids close to saturation and found deviations from behavior which follows the $(1 - Q/K)$ term. Jørgensen [111] found that amorphous silica precipitation and dissolution follow a trend given by $(1 - Q/K)^3$. Experimental measurements of calcite (CaCO_3) precipitation/dissolution conform to $(1 - Q/K)^n$, where n commonly ranges from 2.7 to 4.3, but was as large as 17 in one study [112]. Nagy and co-workers [113] found that dissolution of kaolinite $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$

followed a rate law given by $\left(1 - \left(\frac{Q}{K}\right)^{0.85}\right)$, whereas Burch and others [114] found that albite

followed a similar expression but with an exponent of 0.73 instead of 0.85. Rimstidt and Barnes [115] fit their experimental data for various silica polymorphs to a simple $(1 - Q/K)$ expression. Experimental dissolution rate data which follow a simple $(1 - Q/K)$ affinity expression appear to be rather uncommon, so our data are not unique in that respect.

Fig. 48. Boron Release Data for SRL 202 Glass at 90°C Dissolving in EJ-13 Water at $SA/V = 20,000 \text{ m}^{-1}$. After 182 days, measured rate is 13 times faster than cumulative rate up to that day. Model predicts rate acceleration by a factor of 11.5, based on solution data at days 91 and 504.

A mechanistic interpretation of our results is not yet possible. More detailed information is needed on the microscopic rate-limiting reaction mechanism. This information will become available as further work is performed on characterizing the solution-glass interface through macroscopic techniques, such as surface titrations, and through spectroscopic examination of both the reacted and unreacted glass.

In future work, we will model additional experimental results for different glasses by using our modified affinity term function. The results will be used to determine the general applicability of this model. The mathematical form of the affinity term is clearly of great importance in extrapolating our test results to long time periods and must be accurately defined to obtain justifiable long-term predictions of glass dissolution rates. Further identification of the reaction products formed during the accelerated phase of the reaction could be used to narrow the choice of phases used in the data base.

B. Experimental Support for Modeling

1. Introduction

The purpose of this task is to perform experiments that can be used to quantify the effects of glass composition and solution composition on glass durability. This information is fed directly into the glass dissolution model and used to (1) simulate a wide range of test types, including MCC and PCT tests and site-specific tests, (2) model the corrosion behavior of natural analogs to waste glass, and (3) do performance assessments of glass durability under repository conditions. Present long-term models for glass dissolution are limited because they rely on fitting parameters obtained through regression analysis of data from short-term

laboratory experiments. Our approach is to perform experiments that supply the necessary modeling parameters based on a mechanistic understanding of glass dissolution (such as temperature and pH dependence of the glass rate constant) and validate the resulting model using site-specific test results and natural analog observations. The validated model can then be used with confidence to assess the glass performance in a repository.

Only a limited amount of experimental work was possible in FY 1993 due to funding limitations. Most of the work concentrated on understanding the surface chemistry of dissolving glasses obtained by performing surface titrations of glasses. One flow-through test on some simple Na-B-Si-O glasses was performed along with NMR analysis of the glass structures.

2. Surface Chemistry of Glasses

Important glass-water interactions are poorly understood for borosilicate glass radioactive waste forms. This is because glass-water interactions are a complex function of solution, bulk glass, and surface glass compositions. Much of the experimental glass kinetic data are from dissolution of multicomponent glasses in batch reactors. These experiments are too complicated to allow mechanisms controlling glass dissolution to be determined. In batch reactors, solution composition and secondary mineral precipitation are not controlled. Therefore, the effects of glass composition and glass-water surface reactions on dissolution cannot be isolated.

This work compares the surface chemistries and dissolution behaviors of CSG glass (nonradioactive analog for SRL 165 glass) and silica gel at 25°C. The objective of this preliminary effort is to determine the surface complexation reactions that control the durability of borosilicate glasses. We chose to compare silica gel with CSG glass, because silica is the dominant component in waste glasses and layers enriched in silica are known to form at glass surfaces during dissolution. The surface chemistries are inferred from potentiometric titrations of glass and gel suspensions according to surface complexation theory. Surface complexation theory has been successfully applied to simple oxide dissolution kinetics [116-119]. The dissolution rates are determined from flow-through and pH-stat (the pH is maintained at a constant value) experiments for CSG glass [108] and silica gel, respectively.

a. Experimental Methods

Potentiometric titrations were performed on suspensions of CSG glass and silica gel by using a Mettler DL21 automatic titrator. The CSG glass, a nonradioactive analog for SRL-165 waste glass (18.2 wt % Na₂O, 5.97 wt % CaO, 11.68 wt % Al₂O₃, 8.43 wt % B₂O₃, and 55.73 wt % SiO₂), and Silicar[®] silica gel were washed repeatedly with distilled and deionized water to remove fines. The CSG glass and silica gel surface areas were determined to be 0.13 and 273 m²/g by BET N₂(g) adsorption. Approximately 2.5 g of CSG glass or 0.5 g of silica gel was added to 50 mL of 10⁻² M NaNO₃, purged with N₂(g) for at least 60 min, and continuously stirred overnight. Acid and alkaline titrations were performed on separate suspensions. The pH electrode was calibrated with the appropriate buffers prior to the background electrolyte blank titration. The net H⁺ or OH⁻ concentrations adsorbed at the solid surface were calculated from the difference between the blank pH and the suspension pH corrected for the hydrolysis of any dissolved species. High purity N₂(g) was slowly bubbled through the reaction vessels during the blank and suspension titrations to ensure a CO₂ free environment. The equilibration time for the adsorption reactions was 10 min. A sample was taken at the end of each experiment, filtered, and analyzed for dissolved Na, Ca, B, Al, and Si by ICP/AES.

Silica gel Na^+ - H^+ ion exchange and dissolution studies were performed with a Mettler DL21 automatic titrator in pH-stat mode at pH = 3, 4, 5, 6, 7, 8, 9, 10, and 11. The duration of each pH-stat experiment was approximately 5 h. For each experiment, 8 to 10 samples were taken, filtered, diluted with distilled and deionized water, and analyzed by ICP/AES for dissolved Na and Si. The suspension pH was recorded every 10 min over the duration of the experiment.

b. Surface Complexation Theory

According to surface complexation theory, dissolution rates of oxides and silicates are controlled by the breaking of metal-oxygen framework bonds, which are accelerated by the adsorption of H^+ and OH^- ions at surface reaction sites [118,120]. Surface adsorption reactions are rapid, such that the rate-limiting step is the detachment of the cation from the mineral-solution interface. For a simple oxide, the important surface reactions are protonation and deprotonation of the surface metal reaction site:

respectively. The $>\text{M}$ symbol represents metal surface species, K_{a1} and K_{a2} are conditional constants for the mass balance expressions for the respective adsorption reactions, and the brackets and braces indicate the respective concentrations and activities of the i^{th} surface or aqueous species. Note that the deprotonation reaction is equivalent to the adsorption of an OH^- ion at the neutral metal site, producing a negatively charged surface species and water. Breaking of the critical metal-oxygen bonds occurs if a significant number of H^+ or OH^- ions are adsorbed to neighboring metal surface sites. The overall dissolution rate, R , may be expressed as:

$$R = k_H [>\text{MOH}_2^+]^n + k_{OH} [>\text{MO}^-]^m \quad (11)$$

where k_i is the dissolution rate constant attributed to the i^{th} adsorbing ion. Exponents n and m are experimentally determined reaction orders, and represent the number of ions adsorbed prior to the detachment of the metal ion into the bulk solution.

c. Results and Discussion

Qualitatively, net adsorption of H^+ at the solid-solution interface shows good correlation with net dissolution. The net dissolution and adsorption of H^+ depend on the bulk solid composition. The dissolution and adsorption behavior of CSG glass differ from that of silica gel. As shown in Fig. 49, the CSG glass dissolution rates [108] are at the minimum near neutral pH, and increase at more acid and alkaline pH's. This correlates well with an increase in H^+ adsorption from near neutral to acid pH and increasing desorption of H^+ from near neutral to alkaline pH. Unlike CSG glass, the dissolution behavior of silica gel is at a minimum and independent of solution pH from acid to near neutral pH, and increases with increasing pH at pH > 8. This finding is consistent with minimal sorption of H^+ in the acid to near neutral pH and increasing H^+ desorption in the alkaline pH region. The dissolution and net

Fig. 49. Log Dissolution Rates (R) vs. pH for CSG Glass (a) and Silica Gel (b) and ΔH^+ vs. pH for CSG Glass (c) and Silica Gel (d)

H^+ adsorption behavior for CSG glass and silica gel is identical to the dissolution behavior of many aluminosilicate minerals [117, 121-129] and quartz [116,129], respectively. Note also that the release of Al and Si from CSG glass differs as a function of pH. The Al and Si dissolution rates were normalized to their respective mole percent in the bulk glass and, if dissolution were congruent, should have been equal at a given pH. The higher rate of aluminum removal (Fig. 49) indicates that an enriched silica layer forms at the glass-water interface. Only at $pH > 10$ is dissolution the same.

Figure 50 shows log-log plots of dissolution rates versus net H^+ adsorption for CSG glass and silica gel. Assuming that the release of silicon into solution reflects the net durability of a glass, we determined that CSG glass dissolution rates are proportional to $[H^+]^2_{adsorbed}$ in the acid pH region and $[OH^-]^{0.8}_{adsorbed}$ in the alkaline pH region. Silica gel dissolution rates are proportional to $[OH^-]^{0.9}_{adsorbed}$. Surface complexation theory interprets microscopic surface reactions from macroscopic changes in the bulk solution composition. Based on the dissolution and adsorption behavior of feldspars and quartz as a function of solution pH, Brady and Walther [116,123,124] interpret $[OH^-]_{adsorbed}$ to be equal to $[>SiO^-]$, and the $[H^+]_{adsorbed}$ to be equal to the $[>AlOH_2^+]$. Similar interpretations could be made for CSG glass.

Fig. 50. Log Dissolution Rate vs. (a) log [H⁺]_{adsorbed} and (b) log [OH⁻]_{adsorbed} for CSG Glass and (c) Log Dissolution Rate vs. log [OH⁻]_{adsorbed} for Silica Gel

Important surface complexation reactions for CSG glass are the protonation and deprotonation of >AlOH, the deprotonation of >SiOH, and the exchange of alkalis and alkaline earths for H⁺ at >SiOH and >AlOH. It is thought that the strong hydration of alkalis and alkaline earths in the bulk solution prevents them from forming inner sphere complexes at the Al and Si sites. However, in the acid pH region, exchange of Na⁺ for H⁺ bonded to tetrahedrally coordinated Al may be an important mechanism controlling the net dissolution of CSG glass. Recent studies [130-132] have shown that Na⁺ adsorption enhances pure silicate dissolution. Note that the deprotonation of >SiOH to a negative >SiO⁻ and the exchange of Na⁺ for H⁺ at >SiOH to >SiO⁻Na⁺ both result in consumption of OH⁻ from the bulk solution. The surface chemistry of boron oxides is unclear.

To determine the rate-catalyzing adsorption reactions, the alkali and alkaline earth exchange reactions must be better understood. For this effort, we investigated exchange of Na⁺ for H⁺ at silanol sites on silica gel from pH = 3 to 11 at 25°C. This is the first study that has measured both the dissolved Na and Si concentrations and the pH to determine the importance of sodium adsorption to silica gel dissolution.

In agreement with previous studies [133], no sodium adsorption occurred at pH less than 7, where the dominant silanol surface species is the neutral $>\text{SiOH}$. At pH's greater than 8, the sodium adsorption was significant and exceeded the net change in $[\text{OH}^-]$ (Fig. 51a), as indicated by the slope of 1.4. If sodium adsorption occurs only at silanol sites as an exchange reaction, then $\Delta[\text{OH}^-]$ must be greater than or equal to $\Delta[\text{Na}]$. Note that the extent of sodium removal from solution approaches the total concentration of silanol sites for silica gel, $8.303 \times 10^{-6} \text{ (mol m}^{-2}\text{)}$ [134].

Figures 51b and 51c show the net sodium adsorption from silica gel and CSG glass potentiometric titrations. Unlike the ion exchange experiments, the amount of sodium adsorbed at the silica gel-solution interface is approximately 50% of the total $[\text{OH}^-]$ removed from solution (indicated by slope of 0.46). This result implies that Na^+ and the background electrolyte counter ion, NO_3^- , diffuse into the silica gel with increased reaction. The net adsorption of sodium at the CSG glass-solution interface reaches a maximum at $\Delta[\text{OH}^-] > 1 \times 10^{-4} \text{ (mol m}^{-2}\text{)}$. Note also that $\Delta[\text{OH}^-]$ is two orders of magnitude greater than $\Delta[\text{OH}^-]$ on the silica gel. This indicates that the number of reactive sites increases with increasing H^+ or OH^- adsorption, or that the BET surface area underestimates the reactive CSG glass surface area.

Fig. 51. Plots of $\Delta[\text{Na}]$ vs. $\Delta[\text{OH}^-]$ Removed from Solution Measured in (a) Ion Exchange Experiments, (b) Silica Gel Titration, and (c) CSG Glass Titration

d. Concluding Remarks

For glasses and gels, the net adsorption H^+ at the surface is well correlated with the net dissolution. However, we do not have enough information on the exchange of Na^+ for H^+ at framework reaction sites ($>SiOH$ and $>AlOH$) to determine the rate-controlling reactions. Our experiments also show that uptake of sodium by silica gel differs from the uptake of sodium by CSG glass, which contains 18.2 wt % Na_2O . Both Na and OH removal from solution in silica gel suspensions increases with increasing solution pH. Sodium adsorption at the CSG glass surface reaches a maximum at $1 \times 10^{-4} OH^-$ ($mol\ m^{-2}$), and net adsorption of H^+ and OH^- exceeds the total number of surface sites estimated from silica gel by two orders of magnitude.

Bunker and co-workers [135-137] have shown with NMR and Raman spectroscopy that glass durability is controlled by polymerization reactions at the glass-solution interface. Very simply, the greater the number of non-bridging silanol bonds, the less durable the glass. Surface complexation theory assumes that the total number of silanol sites is constant, and that the adsorption or desorption of H^+ from the silanol sites accelerates the dissolution of the glass. Future studies should include the combination of potentiometric titrations and NMR experiments to determine the mechanisms controlling the dissolution kinetics of glasses as a function of glass and solution composition.

3. Investigations of Na-B-Si-O Glasses

Kinoshita et al. [138] reported an abrupt decrease in glass durability as the B/Si ratio of simple Na-B-Si-O glasses increases. They note a similarity in this behavior to observations of Feng and co-workers [139] for more complex glasses. To determine whether this behavior is due to glass structural changes or is mainly a function of solution composition-pH effects, we measured the dissolution rates of compositionally identical glasses in flow-through tests and performed NMR analyses of these glasses.

a. Flow-Through Tests of Na-B-Si-O Glasses

The glass compositions listed in Table 27 were tested in flow-through reactors described previously [108]. Glass disks 1 cm in diameter and 4-mm thick (approximately 1 g in weight) were reacted with a 0.005 M HCl-potassium orthophthalate mixture having pH 2. The fluids were pumped through the system at a rate of about 100 mL/day, a flow rate low enough that dissolved species from the glass are above detection limits, but high enough that they do not exceed saturation with respect to alteration phases.

Table 27. Simple Glass Compositions (in mol % oxides) Tested in Flow-Through Reactor

Glass	NaBSi-1	NaBSi-2	NaBSi-3	NaBSi-4	NaBSi-5
SiO ₂	60	50	45	30	60
B ₂ O ₃	20	30	35	54	25
Na ₂ O	20	20	20	16	15
Totals	100	100	100	100	100

The tests, therefore, measure the intrinsic dissolution rate of the glass unaffected by secondary phase precipitation in the bulk solution or at the glass-solution interface. Once steady-state conditions were reached (where measured solution concentrations were constant with time), the flow rate was doubled, and the tests continued until steady state was again achieved. The second steady-state dissolution rates were approximately the same at both flow rates, indicating no kinetic effects related to flow and transport around the dissolving glass inside the reaction vessel. The reactors, therefore, behaved as continuously stirred reaction vessels.

b. Determination of Sodium-Borosilicate Glass Structure

The atomic-level structure of the sodium-borosilicate glasses for which dissolution rates were measured were determined by NMR spectroscopic techniques. The ^{11}B NMR data provide the population distribution of the various local boron structural units, including the ratio of three- to four-coordinated boron (B3/B4). Correlation of this structural information with dissolution rates of the same samples will help us to develop detailed microscopic models for borosilicate glass dissolution.

(1) Sample Preparation

The series NaBSi-93 glasses were prepared by fusing appropriate mixtures of Na_2CO_3 , H_3BO_3 , and SiO_2 (Table 28) at 1200°C for 3 hours. After the temperature was raised to 1400°C , approximately 10 g of liquid was poured into a 25 mL Pt-10% Au crucible that had been pre-heated to 1000°C . The molds were then placed into a muffle furnace at 1000°C and allowed to cool slowly to room temperature by cutting the power to the furnace. The glass monoliths were separated from the crucibles by gently heating the outside of the crucible until the container wall had pulled away from the glass. The samples were stored in a dessicator to prevent hydration by atmospheric water.

Normalized release rates [108] for Na, Si, and B were computed from the measured solution compositions and are plotted as a function of time on Fig. 52. These data show an abrupt decrease in durability as the B/Si ratio increases. The data are consistent

Table 28. Composition and Distribution of Boron Structural Units for Sodium-Borosilicate Glass Samples Investigated

Sample	Nominal Composition, mole fraction			Population of Boron Structural Units (± 0.03)			
	Na_2O	B_2O_3	SiO_2	n(B3s)	n(B3a)	n(B4b)	n(B4s)
NBS93-1	0.20	0.20	0.60	0.20	0.11	0.41	0.28
NBS93-2	0.20	0.30	0.50	0.32	0.12	0.42	0.14
NBS93-3	0.20	0.35	0.45	0.36	0.11	0.42	0.11
NBS93-4	0.16	0.54	0.30	0.57	0.12	0.28	0.03
NBS93-5	0.15	0.25	0.60	0.31	0.13	0.33	0.22
NBS93-6	0.15	0.30	0.55	0.41	0.14	0.32	0.13
NBS93-7	0.15	0.40	0.45	0.53	0.14	0.28	0.05
NBS93-8	0.20	0.40	0.40	0.45	0.12	0.35	0.08
NBS93-9	0.15	0.35	0.50	0.48	0.13	0.32	0.07

Fig. 52.

Normalized Release Rates of Na, B, and Si from Na-B-Si-O Glasses. Titles on top of each figure indicate composition of glasses as mol % oxides of Na₂O-B₂O₃-SiO₂.

with the data of Kinoshita [138]. For the less durable glasses in these tests (20:35:45 and 16:54:30), the glass disk was dissolved away nearly to completion in the first few days of the test so that longer-term release data at relatively low rates are an artifact of the highly reduced surface area.

(2) Analysis Method

The Boron-11 magic-angle-spinning (MAS) NMR data were obtained with a home-built instrument at the University of Illinois. The spectrometer is based on an 11.7 T superconducting magnet, corresponding to a resonance frequency of 160.35 MHz for ^{11}B . The MAS rate was about 12 kHz for all spectra. Additional ^{11}B NMR spectra for some samples were obtained at 96.24 MHz on a Chemagnetics CMX 300 spectrometer at Lawrence Livermore National Laboratory (LLNL). The chemical shifts are referenced to an external sample of boron trifluoroetherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$), and a sample of the mineral datolite was used as a secondary reference standard at LLNL, taken to be +1.2 ppm from $\text{BF}_3 \cdot \text{Et}_2\text{O}$ [140].

The populations of boron structural units were obtained from least-squares fits of the ^{11}B NMR spectra to quadrupolar MAS line shapes using a program which employs the line shape described by Samoson [141]. The initial quadrupolar coupling parameters were those of Yun and Bray [142]. The raw relative intensities were corrected for two effects. The first effect is the extraneous B4 intensity due to the central spinning sideband of the satellite $\pm(3/2, 1/2)$ transitions, which overlaps the B4 central transition due to its small quadrupolar coupling constant. The second effect is the B3 central transition intensity located in spinning side bands, which fall outside the fitted center band. The diagrams presented by Massiot et al. [143] do not give the right correction factor for spin $I = 3/2$ nuclei. Therefore, the intensity values were obtained from calculations of the MAS side-band patterns for all transitions by using the known experimental conditions and best-fit quadrupolar coupling parameters. The latter were obtained from the algorithm described by Massiot et al. [143]. For these ^{11}B spectra at 160.36 MHz, the B3 intensities are too low by 1.01 and the B4 intensities too high by $1.03(\pm 0.03)$. We applied these methods to spectra of the mineral colemanite and obtained nuclear quadrupolar coupling parameters that agree well with those reported previously [3] based on single-crystal NMR measurements and intensities within 1% of those expected based on the 1:2 crystallographic B3/B4 ratio.

(3) Results

The ^{11}B NMR spectra at 160.36 MHz for the NaBSi-93 series contain a sharp peak near 0 ppm due to four-coordinated B and a broader asymmetrical doublet centered at about +12 ppm assigned to three-coordinated B (Fig. 53). These spectra are similar to those reported previously for borosilicate minerals and glasses [137,142]. The present series of glasses comprises two sets having constant sodium content (15 and 20 mol %) and varying Si/B ratio. For each set, the relative intensity of the B3 component increases monotonically with increasing boron content.

The fits to the ^{11}B NMR spectra required four components (Fig. 54), the relative intensities for which are given in Table 27. The B4 spectral region appears to contain two poorly resolved peaks, at about 0 and -2 ppm, which we have labeled B4b and B4s, respectively. The relative intensity of the B4s component increases with increasing silicon content for both sets of samples. Based on the similarity of their chemical shifts with model compounds (Fig. 55), we tentatively assign the peak near 0 ppm to four-coordinated boron with linkages to other boron atoms (B4b), as in the mineral danburite, and the peak at -2 ppm to B4 linked only to silicon atoms, such as found in the B-feldspar

Fig. 53. The ^{11}B MAS NMR Spectra for Sodium-Borosilicate Glasses Studied. Numbers on right side of each spectrum refer to the composition as mole percent Na₂O:B₂O₃:SiO₂. Values on x-axes are ppm.

Fig. 54. Examples of Least-Squares Fits to ^{11}B MAS NMR Spectra Obtained at Different Magnetic Field Strengths. The same quadrupolar coupling parameters for B_{3s} and B_{3a} were used for both spectra.

Fig. 55. Range of NMR Chemical Shifts for Four-Coordinated Boron in Borates and Borosilicates. Dashes in structural diagrams represent cation-oxygen-cation bonds.

reedmergnerite [140]. Danburite-like units had previously been reported for sodium-borosilicate glasses of similar composition based on Raman spectra [137]. Two B4 peaks have been observed previously for phase-separated sodium-borosilicate glasses [140], which were assigned to boron in the borate- and silicate-rich phases, but this is the first report of two B4 NMR peaks for nominally single-phase Na-B-Si oxide glasses.

The B3 portion of the spectra required more than one component to produce a low-frequency singularity (+8 ppm) more intense than the high-frequency peak and the intensity between the B3 doublet and B4b peak (around +4 ppm). We used a bimodal distribution to fit the B3 portion of the spectra, because a sum of two B3 components produces adequate fits to the spectra at both 160.35 and 96.24 MHz. The width of the MAS quadrupolar line shape (in frequency units) scales with the inverse square of the resonance frequency. Although the B3 line shape may have resulted from a quasi-continuous distribution of boron environments, there is not enough spectral information to justify fitting the spectra with more sophisticated statistical models.

The quadrupolar coupling parameters for the two B3 components (B3s and B3a) were chosen such that the same set of parameters gave good fits for the spectra at 160.35 and 96.24 MHz; then, the quadrupolar coupling constant and asymmetry parameter for B3a were held constant for all spectra. At this time, the two B3 components cannot be assigned without further investigation. Two B3 components have been reported previously from low-field ¹¹B NMR studies and assigned to symmetrical (B3s) and asymmetrical (B3a) boron

environments, based on the symmetry of the electric field gradient at the nucleus [142,144]. The B3a resonance was assigned to boron having one or two non-bridging oxygens. However, the chemical shift of the B3a component in the present glasses is probably too low for such an assignment.

For both sets of constant-sodium samples, the principal change in the spectra arises from an increase of $n(\text{B4s})$ and corresponding decrease of $n(\text{B3s})$ with increasing silicon content. For all samples, the population of B3a varies very little, from 0.11 to 0.12 for the $\text{Na}_2\text{O} = 20$ series and 0.13 to 0.14 for the $\text{Na}_2\text{O} = 15$ series. Also, for constant sodium content, the population of B4b shows little variation: from 0.28 for 15:54:30 to 0.33 for 15:25:60, and from 0.35 for 20:40:40 to 0.41 for 20:30:60. In contrast, the population of B4s is near the detection limit for the boron-rich samples, 0.03 for 16:54:30 and 0.08 for 20:40:40, but approaches nearly a quarter of the boron atoms in 15:25:60 (0.22) and 20:20:60 (0.28).

Comparison of the present structural results with the dissolution experiments shows a qualitative inverse relationship between the population of the B4s component and normalized silica release rates at pH 2. For the series 20:20:60 - 20:30:50 - 20:35:45, the increase of silicon release rates is correlated with a decrease of the fraction of boron atoms in silica-rich environments. However, the silica release rates sharply increase from 20:30:50 to 20:35:45 (Fig. 52), with small changes in the populations of boron structural units [e.g., $n(\text{B4s})$ decreases from 0.14 to 0.11], while the silica release rate from 20:20:60 to 15:25:60 decreases with decrease of $n(\text{B4s})$ from 0.28 to 0.22 and total B4 from 0.69 to 0.55. These findings indicate that additional structural factors control dissolution behavior in this pH region (pH 2). Further NMR efforts in this area should include use of those techniques capable of quantifying the concentration of non-bridging oxygens, such as ^{17}O NMR.

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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. C. M. Jantzen, *Glass Compositions and Frit Formulations Developed for DWPF*, memo to M. J. Plodinec, Savannah River Laboratory Report DPST-88-952 (1988).
5. *Defense Waste Processing Facility Waste Form Compliance Plan*, Westinghouse Savannah River Company Report WSRC-SW4-6, Rev. 1A (1992).
6. J. M. White and G. LaHaie, *Ultimate Fission Product Disposal, the Disposal of Curie Quantities of Fission Products in Siliceous Materials*, Atomic Energy of Canada, Ltd. Report CRCE-591 (1955).
7. U.S. Department of Energy, *Final Environmental Impact Statement, Defense Waste Processing Facility, Savannah River Plant, Aiken, SC*, U.S. DOE Report DOE/EIS-0082 (1982).
8. U.S. Department of Energy, *Final Environmental Impact Statement, "Long-Term Management of Liquid High-Level Wastes Stored at the Western New York Nuclear Service Center, West Valley, NY,"* U.S. DOE Report DOE/EIS-0081 (1982).
9. U.S. Department of Energy, *Final Environmental Impact Statement, "Disposal of Hanford Defense High-Level, Transuranic, and Tank Wastes,"* U.S. DOE Report DOE/EIS-0113 (1987).
10. U.S. Department of Energy, *The Evaluation and Review of Alternative Waste Forms for Immobilization of High-Level Radioactive Wastes, Report Number 2*, Alternative Waste Form Peer Review Panel, U.S. DOE Report DOE/TIC-11219 (1980).
11. T. A. Bernadzowski, J. S. Allender, J. A. Stone, D. E. Gordon, T. H. Gould, Jr., and C. F. Westberry, III, "High-Level Nuclear Waste Form Performance Evaluation," *Ceram. Bull.* 62(12), 1364-1390 (1983).

12. J. C. Cunnane, Ed., *High-Level Nuclear Waste Borosilicate Glass: A Compendium of Corrosion Characteristics*, in press (1994).
13. 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 (1990).
14. J. J. Mazer, *Temperature Effects on Waste Glass Performance*, Argonne National Laboratory Report ANL-91/17 (1991).
15. N. E. Bibler, "Leaching of Fully Radioactive SRP Nuclear Waste Glass in Tuff Ground Water in Stainless Steel Vessels," *Adv. Ceram.* 20, 619 (1986).
16. 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).
17. 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).
18. 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).
19. N. E. Bibler and C. M. Jantzen, *The Product Consistency Test and Its Role in the Waste Acceptance Process*, Savannah River Laboratory Report DP-MS-88-188 (1989).
20. N. E. Bibler, "Characterization of Borosilicate Glass-Containing Savannah River Plant Radioactive Waste," *Am. Chem. Soc. Symp. Ser.* 246, 359-372 (1983).
21. *JSS-Project Phase II: Final Report of Work Performed at Studsvik Energiteknik AB and at Swiss Federal Institute for Reactor Research*, Japanese, Swiss, Swedish Project Technical Report JSS-85-01 (1985).
22. 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).
23. 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).
24. 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 Nuclear Waste Glasses," *Nucl. Technol.* 104, 193-206 (1993).
25. B. E. Scheetz, W. P. Freeborn, S. Komarneni, S. D. Atkinson, and W. B. White, "The Role of Boron in Monitoring the Leaching of Borosilicate Glass Waste Forms," *Mater. Res. Soc. Symp. Proc.* 44, 129-134 (1985).
26. 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).

27. E. Vernaz and N. Godon, *Examination of Ultrathin Cross Section Front R7T7 Glass Samples after 6 Months and 1 Year of Alteration in the WIPP*, European Atomic Energy Community Report EUR-12017, p. 15 (1989).
28. J.-C. Dran, J.-C. Petit, L. Trotignon, A. Paccagnella, and G. Della Mea, "Hydration Mechanisms of Silicate Glasses: Respective Role of Ion Exchange and Water Permeation," *Mater. Res. Soc. Symp. Proc.* 127, 25-32 (1989).
29. X. Feng, I. L. Pegg, Q. Yan, X. Mao, and P. B. Macedo, "Effects of pH on the Leaching Mechanism of Nuclear Waste Glasses," *Ceram. Trans.* 23, 95-104 (1991).
30. 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).
31. 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).
32. H. Vali and L. Bachmann, "Ultrastructure and Flow Behaviour of Colloidal Smectite Dispersions," *J. Coll. Interface Sci.* 126, 278-291 (1981).
33. J. K. Bates et al., *Annual Report to the Repository Technology Program*, submitted to the Repository Technology Program (1990).
34. J. E. Mendel (compiler), "Radiation Effects," in *Final Report of the Defense High-Level Waste Leaching Mechanisms Program*, Pacific Northwest Laboratory Report PNL-5157, pp. 5.0-5.18 (1984).
35. W. G. Burns, A. E. Hughes, J. A. C. Marples, R. S. Nelson, and A. M. Stoneham, "Effects of Radiation on the Leach Rates of Vitrified Radioactive Waste," *J. Nucl. Mater.* 107, 245-270 (1982).
36. 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).
37. 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).
38. J. K. Linacre and W. R. Marsh, *The Radiation Chemistry of Heterogenous and Homogenous Nitrogen and Water Systems*, AERE Report D-10027 (1981).
39. D. T. Reed and D. L. Bowers, "Alpha Particle-Induced Formation of Nitrate in the Cm-Sulfate Aqueous System," *Radiochim. Acta* 51, 119-125 (1990).
40. D. T. Reed and R. A. Van Konynenburg, "Effect of Ionizing Radiation on Moist Air Systems," *Mater. Res. Soc. Symp. Proc.* 112, 393-404 (1987).
41. 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).

42. D. J. Wronkiewicz and J. K. Bates, "Alpha and Gamma Radiation Effects on Air-Water Systems at High Gas/Liquid Ratios," submitted to *Nuclear Technology* (1994).
43. W. J. Weber, "The Effect of Radiation on Nuclear Waste Forms," J. Min. Metals and Mater. Soc., pp. 35-39 (July 1991).
44. G. L. McVay and C. Q. Buckwalter, "The Nature of Glass Leaching," Nucl. Technol. 51, 123-129 (1980).
45. 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).
46. W. J. Weber and F. P. Roberts, "A Review of Radiation Effects in Solid Nuclear Waste Forms," Nucl. Technol. 60, 178-198 (1983).
47. 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).
48. 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).
49. 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).
50. P. Van Iseghem, *Performance of Vitreous Waste Forms and Engineered Barriers under Clay Repository Conditions*, International Atomic Energy Agency Final Report (1988).
51. 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).
52. P. Van Iseghem, C. Cantale, M. Coquerelle, J. L. Dussossoy, G. Malow, and H. Roggendorf, "Corrosion Mechanisms of Vitrified High-Level Waste," in *Radioactive Waste Management and Disposal*, L. Cecille, Ed., Elsevier, New York, pp. 275-286 (1991).
53. L. L. Hench, D. E. Clark, and A. B. Harker, "Review Nuclear Waste Solids," J. Mater. Sci. 21, 1457-1478 (1986).
54. 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).
55. D. J. Wronkiewicz, L. M. Wang, J. K. Bates, and B. S. Tani, "Effects of Radiation Exposure on Glass Alteration in a Steam Environment," Mater. Res. Soc. Symp. Proc. 294, 183-190 (1993).
56. B. M. Biwer, J. K. Bates, T. A. Abrajano, Jr., and J. P. Bradley, "Comparison of the Layer Structure of Vapor Phase and Leached SRL Glass by the Use of AEM," Mater. Res. Soc. Symp. Proc. 176, 255-263 (1990).

57. D. J. Wronkiewicz, C. R. Bradley, and J. K. Bates, "A Comparison of Alteration Paragenesis between High-Level Nuclear Waste Materials and Geologic Analogues," Geol. Soc. Am. Abst. with Program A-185 (1993).
58. M. Utada, "Zonal Distribution of Authigenic Zeolites in the Tertiary Pyroclastic Rocks in Mogami District, Yamagata Prefecture," Sci. Papers Coll. Gen. Educ. Univ. Tokyo 15, 173-216 (1965).
59. R. L. Hay, "Geologic Occurrence of Zeolites," in *Natural Zeolites - Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, Eds., Pergamon Press, New York, pp. 135-143 (1978).
60. R. C. Surdan and R. A. Sheppard, "Zeolites in Saline, Alkaline-Lake Deposits," in *Natural Zeolites - Occurrence, Properties, Use*, L. B. Sand and F. A. Mumpton, Eds., Pergamon Press, New York, pp. 145-174 (1978).
61. C. E. Chapin, New Mexico Bureau of Mines and Mineral Resources, personal communication (1993).
62. 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).
63. 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).
64. 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).
65. 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).
66. W. L. Ebert, and J. K. Bates, "Comparison of Glass Reaction at High and Low SA/V, PCT vs. MCC-1," Proc. Third Int. Conf. on High-Level Radioactive Waste Manage., Vol. 1, Las Vegas, NV, pp. 934-942 (1992).
67. 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).
68. 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).
69. B. Grambow, "Geochemical Approach to Glass Dissolution," in *Corrosion of Glass, Ceramics and Ceramic Superconductors. Principles, Testing, Characterization and Applications*, D. E. Clark and B. K. Zaitsev, Eds., Noyes Publications, Park Ridge, NJ, pp. 124-152 (1992).
70. J. P. Bradley and J. K. Bates, "Leached Nuclear Waste Glasses: Ultramicrotomy and Analytical Electron Microscopic Characterization," Proc. of the 12th Int. Congress for Electron Microscopy, Seattle, WA, August 13-17, 1990, pp. 444-445 (1990).
71. J. K. Bates, J. P. Bradley, A. Teetsov, C. R. Bradley, and M. ten Brink Buchholtz, "Colloid Formation during Nuclear Waste Glass Reaction: Implications for Nuclear Waste Disposal," Science 256, 649-651 (1992).

72. E. C. Buck, J. K. Bates, J. C. Cunnane, W. L. Ebert, X. Feng, and D. J. Wronkiewicz, "AEM Study of Colloids from Nuclear Waste Glass Reaction," Mater. Res. Soc. Symp. Proc. 294, 199-206 (1993).
73. X. Feng, E. C. Buck, C. Mertz, J. K. Bates, and J. C. Cunnane, "Study of Colloids Generated from High-Level Nuclear Waste Glasses," Proc. Waste Management '93, Vol. 2, pp. 1015-1021 (1993).
74. X. Feng, E. C. Buck, J. K. Bates, C. Mertz, J. C. Cunnane, and D. Chaiko, "Colloid Formation during Nuclear Waste Glass Dissolution," to be published in *Radiochim. Acta* (1994).
75. G. Cliff and Lorimer, "Thin Film Analysis," J. Microsc. 103, 203-207 (1975).
76. A. J. Garrett-Reed, "Microanalysis of Nanostructures by STEM," presented at the Fall Material Research Society Meeting, Boston, MA, November 29-December 3, 1993.
77. O. L. Krivanek and M. K. Kundmann, Int. Conf. Electron Micros., Beijing, China, p. 390 (1991).
78. D. E. Newbury, "Trace Analysis of Nanoscale Materials by Analytical Electron Microscopy," presented at the Fall Material Research Society Meeting, Boston, MA, November 29-December 3, 1993.
79. R. D. Leapmann, Microscopy Society of America Annual Meeting, Cincinnati, OH, August 5-12, 1993.
80. E. C. Buck and J. K. Bates, "Identification of Uranium-bearing Colloids from the Dissolution of Spent Fuel and UO₂," Proc. of GLEMA'93, J. Electron Microsc. Technol. (1993).
81. I. P. Jones, "Chemical Microanalysis using Electron Beams," The Institute of Materials, Bourne Press Limited, Bournemouth (1992).
82. P. E. Batson, "Simultaneous STEM Imaging and Electron Energy Loss Spectroscopy with Atomic Column and Sensitivity," Nature 366, 727-728 (1993).
83. C. R. Bradley, Argonne National Laboratory, personal communication (1993).
84. 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).
85. X. Feng, J. K. Bates, C. R. Bradley, and E. C. Buck, "Does Fully Radioactive Glass Behave Differently Than Simulated Waste Glass?," Mater. Res. Soc. Symp. Proc. 294, 207-214 (1993).
86. 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 Nuclear Waste Glasses," Nucl. Technol. 104, 193-206 (1993).
87. G. Gottardi and E. Galli, *Natural Zeolites*, Springer-Verlag, Berlin, p. 326 (1985).

88. H. W. Zandbergen, "High Resolution Electron Microscopic Study of the Growth of Denser Phases on Zeolite Y and Zeolite L," *Mater. Res. Soc. Symp. Proc.* 111, 135-140 (1988).
89. D. J. Wronkiewicz, C. R. Bradley, and J. K. Bates, "A Comparison of Alteration Paragenesis between High-Level Nuclear Waste Materials and Geologic Analogues," presented at the Geological Society of America Annual Meeting, Boston, MA, October 25-28, 1993.
90. E. C. Buck, Argonne National Laboratory, unpublished results (1993).
91. M. Kawano and K. Tomita, "Formation of Allophane and Beidellite during Hydrothermal Alteration of Volcanic Glass below 200°C," *Clays and Clay Miner.* 40, 666-674 (1992).
92. E. C. Buck, J. K. Bates, and X. Feng, "Characterization of Colloids Formed during the Reaction of SRL200 Glass," presented at the American Ceramic Society Annual Meeting, Indianapolis, IN, April 24-28, 1994.
93. B. E. Viani, S. I. Martin, and M. ten Brink, presented at the Yucca Mountain Characterization Project: Colloid Workshop, Santa Fe, NM, May 3-5, 1993.
94. J. D. F. Ramsey, "Role of Colloids in the Release of Radionuclides from Nuclear Waste," *Radiochim. Acta* 44/45, 165-170 (1988).
95. T. M. Ahn, C. G. Interrante, and R. A. Wellar, "A Justification for the Use of Data from Accelerated Leach Tests of Glass," *Mater. Res. Soc. Symp. Proc.* 294, 599-604 (1993).
96. V. A. Drits, *Electron Diffraction and High Resolution Electron Microscopy of Mineral Structures*, Springer-Verlag, New York (1983).
97. F. V. Chukhrov, A. I. Gorshkov, E. S. Rudnitskaya, V. V. Beresovskaya, and A. A. Sivitsov, "Manganese Minerals in Clays: A Review," *Clays and Clay Miner.* 28, 346-354 (1980).
98. H. Vali and L. Bachmann, "Ultrastructure and Flow Behaviour of Colloidal Smectite Dispersions," *J. Coll. Interface Sci.* 126, 278-291 (1988).
99. M. Pan and P. A. Crozier, "Low Dose High Resolution Electron Microscopy of Zeolite Materials with a Slow Scan Camera," *Ultramicroscopy* 48, 332-340 (1993).
100. W. L. Bourcier, S. A. Carroll, and B. L. Phillips, "Constraints on the Affinity Term for Modeling Long-Term Glass Dissolution Rates," *Mater. Res. Soc. Symp. Proc.* 333, 507-512 (1994).
101. H. Bethke, *The Geochemist's Workbench: A Users Guide to Rxn, Act2, Tact, React, and Gtplot*, Univ. of Illinois Press (1992).
102. P. Aagaard and H. C. Helgeson, "Thermodynamic and Kinetic Constraints on Reaction Rates among Minerals and Aqueous Solutions. I. Theoretical Considerations," *Am. J. Sci.* 282, 237-285 (1982).

103. B. Grambow, *Nuclear Waste Glass Dissolution: Mechanism, Model and Application*, Japanese, Swiss, Swedish Project Technical Report JSS 87-02 (1987).
104. L. R. Pederson, C. Q. Buckwalter, G. L. McVay, and B. L. Riddle, "Glass Surface Area to Volume Ratio and Its Implications to Accelerated Leach Testing," *Mater. Res. Soc. Symp. Proc.* 15, 47-54 (1983).
105. 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).
106. 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).
107. A. C. Lasaga, "Transition State Theory," in *Kinetics of Geochemical Processes*, A. C. Lasaga and R. J. Kirkpatrick, Eds., Mineralogical Society of America, Chelsea, MI, pp. 135-169 (1981).
108. K. G. Knauss, W. L. Bourcier, K. D. McKeegan, C. I. Merzbacher, S. N. Nguyen, F. J. Ryerson, D. K. Smith, H. C. Weed, and L. Newton, "Dissolution Kinetics of a Simple Nuclear Waste Glass as a Function of pH, Time, and Temperature," *Mater. Res. Soc. Symp. Proc.* 176, 371-381 (1990).
109. T. Advocat, J. L. Crovisier, B. Fritz, and E. Vernaz, "Thermokinetic Model of Borosilicate Glass Dissolution: Contextual Affinity," *Mater. Res. Soc. Symp. Proc.* 176, 241-248 (1990).
110. W. L. Bourcier, *Geochemical Modeling of Radioactive Wasteglass Dissolution using EQ3/6: Preliminary Results and Data Needs*, Lawrence Livermore National Laboratory Report UCID-21869 (1989).
111. S. S. Jørgensen, "Solubility and Dissolution Kinetics of Precipitated Amorphous Silica in 1 M NaClO₄ at 25°C," *Acta Chem. Scand.* 22, 335-341 (1968).
112. U. Svensson and W. Dreybrodt, "Dissolution Kinetics of Natural Calcite Minerals in CO₂-Water Systems Approaching Calcite Equilibrium," *Chem. Geol.* 100, 129-145 (1992).
113. K. L. Nagy, A. E. Blum, and A. C. Lasaga, "Dissolution and Precipitation Kinetics of Kaolinite at 80°C and pH 3: The Dependence on Solution Saturation State," *Am. J. Sci.* 291, 649-686 (1991).
114. T. E. Burch, K. L. Nagy, and A. C. Lasaga, "Free Energy Dependence of Albite Dissolution Kinetics at 80°C, pH 8.8," *Chem. Geol.* 105, 137-162 (1993).
115. J. D. Rimstidt and H. L. Barnes, "The Kinetics of Silica-Water Reactions," *Geochim. Cosmochim. Acta* 44, 1683-1699 (1980).
116. P. V. Brady and J. V. Walther, "Kinetics of Quartz Dissolution at Low Temperature," *Chem. Geol.* 82, 253-264 (1990).

117. S. Carroll-Webb and J. V. Walther, "A Surface Complex Reaction Model for the pH-Dependence of Corundum and Kaolinite Dissolution Rates," *Geochim. Cosmochim. Acta* 52, 2609-2623 (1988).
118. G. Furrer and W. Stumm, "The Coordination Chemistry of Weathering: I. Dissolution Chemistry of δ -Al₂O₃ and BeO," *Geochim. Cosmochim. Acta* 50, 1847-1860 (1986).
119. B. Zinder, G. Furrer, and W. Stumm, "The Coordination Chemistry of Weathering: II. Dissolution of Fe(III) Oxides," *Geochim. Cosmochim. Acta* 50, 1861-1869 (1986).
120. E. Wieland, B. Wherli, and W. Stumm, "The Coordination Chemistry of Weathering: III. A Generalization on the Dissolution Rates of Minerals," *Geochim. Cosmochim. Acta* 52, 1969-1981 (1988).
121. C. Armheim and D. Suarez, "The Use of a Surface Complexation Model to Describe the Kinetics of Ligand-Promoted Dissolution of Anorthite," *Geochim. Cosmochim. Acta* 52, 2785-2794 (1988).
122. A. Blum and A. C. Lasaga, "The Role of Surface Speciation in the Dissolution of Minerals," *Nature* 331, 341-343 (1988).
123. P. V. Brady and J. V. Walther, "Controls on Silicate Dissolution Rates in Neutral and Basic pH Solutions at 25°C," *Geochim. Cosmochim. Acta* 53, 2823-2830 (1989).
124. P. V. Brady and J. V. Walther, "Surface Chemistry and Silicate Dissolution at Elevated Temperatures," *Am. J. Sci.* 292, 639-658 (1992).
125. S. A. Carroll and J. V. Walther, "Mechanisms of Kaolinite Dissolution at 25, 60 and 80°C," *Am. J. Sci.* 290, 797-805 (1990).
126. L. Chou and R. Wollast, "Steady State Kinetics and Dissolution Mechanisms of Albite," *Am. J. Sci.* 285, 963-993 (1985).
127. K. G. Knauss and T. J. Wolery, "Dependence of Albite Dissolution Kinetics on pH and Time at 25° and 70°C," *Geochim. Cosmochim. Acta* 50, 2481-2497 (1986).
128. M. Tole, A. C. Lasaga, D. Pantrano, and W. White, "The Kinetics of Dissolution of Nepheline," *Geochim. Cosmochim. Acta* 50, 379-392 (1986).
129. K. G. Knauss and T. J. Wolery, "The Dissolution Kinetics of Quartz as a Function of pH and Time at 70°C," *Geochim. Cosmochim. Acta* 52, 43-53 (1988).
130. P. Dove and D. A. Crerar, "Kinetics of Quartz Dissolution in Electrolyte Solutions using a Hydrothermal Mixed Flow Reactor," *Geochim. Cosmochim. Acta* 54, 955-969 (1990).
131. P. M. Dove and S. F. Elston, "Dissolution Kinetics of Quartz in Sodium Chloride Solutions: Analysis of Existing Data and a Rate Model for 25°C," *Geochim. Cosmochim. Acta* 56, 4147-4156 (1992).
132. P. W. J. G. Wijnen, T. P. M. Beelen, J. W. DeHaan, L. J. M. Van de Ven, and A. Van Santen, "The Structure Directing Effect of Cations in Aqueous Silicate Solutions. A Si-29 NMR Study," *Coll. Surf.* 45, 255-268 (1990).

133. D. L. Dugger, J. H. Stanton, B. N. Irby, B. L. McConnell, W. W. Cummings, and R. W. Maatman, "The Exchange of Twenty Metal Ions with the Weakly Acidic Silanol Group of Silica," *J. Phys. Chem.* **68**, 757-760 (1964).
134. R. K. Iler, *The Chemistry of Silica*, John Wiley and Sons, New York (1979).
135. B. C. Bunker, G. W. Arnold, E. E. Day, and P. J. Bray, "The Effect of Molecular Structure on Borosilicate Glass Leaching," *J. Non-Cryst. Solids* **87**, 226-253 (1986).
136. B. C. Bunker, D. R. Tallant, T. J. Headley, G. L. Turner, and R. J. Kirkpatrick, "The Structure of Leached Sodium Borosilicate Glass," *Phys. Chem. Glasses* **29**, 106-120 (1988).
137. B. C. Bunker, D. R. Tallant, R. J. Kirkpatrick, and G. L. Turner, "Multinuclear Nuclear Magnetic Resonance and Raman Investigation of Sodium Borosilicate Glass Structures," *Phys. Chem. Glasses* **31**, 30-46 (1990).
138. M. Kinoshita, M. Harada, Y. Sato, and Y. Hariguchi, "Percolation Phenomenon for Dissolution of Sodium Borosilicate Glasses in Aqueous Solutions," *Am. Ceram. Soc.* **74**, 783-787 (1991).
139. X. Feng, I. L. Pegg, A. Barkatt, P. B. Macedo, S. J. Cucinell, and S. Lai, "Correlation between Composition Effects on Glass Durability and the Structural Role of the Constituent Oxides," *Nucl. Technol.* **85**, 334-345 (1989).
140. G. L. Turner, K. A. Smith, R. J. Kirkpatrick, and E. Oldfield, "Boron-¹¹ Nuclear Magnetic Resonance Spectroscopic Study of Borate and Borosilicate Minerals and a Borosilicate Glass," *J. Magn. Reson.* **67**, 544 (1986).
141. A. Samoson, E. Kundla, and F. Lippmaa, "High-Resolution MAS-NMR of Quadrupolar Nuclei in Powders," *J. Magn. Reson.* **49**, 350-361 (1982).
142. Y. H. Yun and P. J. Bray, "Nuclear Magnetic Resonance Studies of the Glasses in the System Na₂O-B₂O₃-SiO₂," *J. Non-Cryst. Solids* **27**, 363 (1978).
143. D. Massiot, C. Bessada, J. P. Coutures, and F. Taulelle, "A Quantitative Study of Al-27 MAS NMR in Crystalline YAG," *J. Magn. Reson.* **90**, 231-241 (1990).
144. W. J. Dell, P. J. Bray, and S. Z. Xiao, "¹¹B NMR Studies and Structural Modelling of Na₂O-B₂O₃-SiO₂ Glasses of High Soda Content," *J. Non-Cryst. Solids* **58**, 1 (1983).

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