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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 1991 - SEPTEMBER 1992**

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 1992 on the following tasks:

1. A compendium of the characteristics of high-level nuclear waste borosilicate glass has been written.
2. A critical review of important parameters that affect the reactivity of glass in an unsaturated environment is being prepared. The report on temperature effects has been published, the one on glass compositions has been drafted, and the others are in progress.
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.
4. The effect of radiation upon the durability of waste glasses at a high glass surface area-to-liquid volume (SA/V) ratio and a high gas-to-liquid volume ratio will be assessed. These tests address both vapor and high SA/V liquid conditions.
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.

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EXECUTIVE SUMMARY

This report is an overview of the progress during FY 1992 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 1992 on each of the technical tasks is summarized below.

Preparation of the Waste Glass Compendium

A review draft of the document entitled "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Characteristics" was prepared. 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. Informal review comments obtained from a steering group consisting of Drs. R. C. Ewing (University of New Mexico), A. A. Barkatt (The Catholic University of America), and D. M. Strachan (Battelle Pacific Northwest Laboratory) were utilized in guiding preparation of the review draft. The compendium will be published in FY 1993 after completion the review draft itself is reviewed.

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. We identified the need for a critical review as a task, which is currently underway.

A review for each critical parameter will be issued as a stand-alone document. They will be integrated into a compendium.

6. A series of natural analogue tests is being analyzed to demonstrate a meaningful relationship between experimental and natural alteration conditions.
7. 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.
8. A technical review of AEM results is being provided.
9. A study of water diffusion involving nuclear waste glasses is being performed.
10. A mechanistically based model is being developed to predict the performance of glass over repository-relevant time periods.

To perform this task, all known and pertinent sources of scientific literature have been assembled and carefully considered to glean the most up-to-date information on how each critical parameter affects nuclear waste glass reaction. The results obtained from different studies are being compiled, where possible, for making comparisons. All references used in the critical reviews have been collected into a computerized data base. A preliminary critical review had been performed previously to provide a foundation for the detailed reviews of each parameter.

The first individual review, detailing the effects of temperature on waste glass performance, has been completed and issued. This report concluded that reaction mechanisms for waste glass dissolution in water are complex and involve multiple simultaneous reaction processes. The temperature dependence of each of the individual reaction processes can be described by the Arrhenius equation, a relationship derived from empirical observations. In cases where the reaction mechanism changes as a function of time or temperature, which are the dominant reaction process changes, the Arrhenius equation is less useful in interpreting the temperature dependence of the overall reaction mechanism. Understanding the interplay of the reaction processes and their temperature dependences for nuclear waste glasses 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 in waste glass tests.

The second individual review concerns the effect of glass composition on glass durability. This report has been drafted and is undergoing review. Models of glass structure are being used to help understand how water may interact with glass.

Long-Term Testing of Fully Radioactive Glass

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 located in an unsaturated environment. Specifically, long-term test data will be generated such that (1) the reaction of fully radioactive glass can be compared with that of nonradioactive glass of the same 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 unsaturated disposal conditions so that glass performance models can be validated. To meet these goals, tests with fully radioactive glass (SRL 165/42, 131/11, and 200R compositions) and with simulated (nonradioactive glass) are being done in the following modes: batch, intermittent drip, and laboratory analogue.

To date, 126 of the planned 212 long-term tests have been completed. The longest tests have been in progress for more than 30 months. The solution analysis of all the completed tests is about 80% done and includes analyses on leachate pHs, cations, selected anions, total carbon, and actinides. The surface analyses on the terminated samples are in progress. These analyses consist of optical microscopy, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), secondary ion mass spectroscopy (SIMS), and analytical electron microscopy (AEM).

The data from long-term testing of both radioactive and simulated glass types for SRL 165, 131, and 200 frit compositions demonstrate that static tests at 340 and 2000 m⁻¹ for up to 720 days have shown little difference in reactivity between the two glass types. The same leach trends were also observed for both glass types. The differences in reactivity at 2000 m⁻¹ or below are neither large enough to alter the order of glass durability for the different compositions nor to change the controlling glass dissolution processes. The small differences in

reactivity between fully radioactive and the simulated glasses can be reasonably explained if the controlling reaction process and leachate pHs are accounted for. However, the simulated nuclear waste glass was found to leach faster than the corresponding radioactive glass by a factor of 40 when SRL 200-based glass compositions were tested at $20,000\text{ m}^{-1}$ for less than one year. The accelerated glass reaction with the simulated glass 200S is associated with the formation of crystalline phases such as clinoptilolite (or K-feldspar) and with a pH excursion. The radiation field generated by the fully radioactive glass reduces the solution pH. This lower pH, in turn, may retard the onset of increased reaction rate. These results suggest that the fully radioactive nuclear waste glass 200R may be substantially more durable than the simulated 200S if the lower pH in the 200R leachate can be sustained. The results also suggest that the ratio of glass surface area to leachate volume (SA/V) may, in certain circumstances, be a useful corrosion acceleration parameter since some of the data can be represented as a steady function of its product with time. Meaningful comparison tests between radioactive and simulated nuclear waste glasses should include long-term and high SA/V tests.

The ongoing static tests will be continued. Special attention will be placed on the tests of 200R at $20,000\text{ m}^{-1}$ to see whether the leach rate of the radioactive glass will eventually catch up to 200S. More emphasis will be placed on the analyses of the surface layers of the terminated samples (i.e., those from completed tests), especially on the radioactive samples. Data will be generated to compare the identities and sequences of the secondary phases between R and S glasses. The radionuclides will continue to be analyzed from all the available solutions. The solution data, combined with surface analysis results, will be utilized to further compare the reactivity of the radioactive and simulated glasses to provide a data base to validate glass performance models.

Effect of Radiation on Glass Reaction at Large SA/V

The objective of this task is to determine if there are any significant effects of radiation 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) glass reaction in a radiolytic field, and (3) the influence of radiation and radiolytic products on the formation and stability of glass alteration phases.

Gamma radiolysis blank tests run at 25, 90, and 200°C indicate that NO_3^- and NO_2^- yields vary inversely with temperature, with the 90°C yields being ~40% and the 200°C yields being ~10%, respectively of those that characterize the 25°C results. No differences in yield were noted during comparison runs of tests at dose rates of 50,000 vs. 3500 rad/hr (500 vs. 35 Gy/hr), and gas/liquid ratios of 100 vs. 10.

Glass wafers ~1 mm thick exposed to a gamma irradiation field at temperatures of 150 to 200°C have reaction layer thicknesses ~15 times thicker than their nonirradiated counterparts. In the irradiated tests, alteration layers appeared to form preferentially along fractures, producing altered zones that enveloped rounded and apparently unaltered glass cores. After 35 days of testing, the glass disks were completely altered, with the glass cores being replaced by a mottled or banded microcrystalline Si- and Fe-rich material. This inner material is overlaid by a banded clay-rich layer, a Ca-Si layer, and a heterogeneous crystalline surface layer. 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.

Cation release trends from irradiation tests with monoliths 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 pHs leveling out at ~9 after an early increase in values between 56 and 180 days. Most of the Am and Pu released from the altered glass samples plated-out on the stainless steel vessel walls, while the remainder was concentrated in the >50 Å fraction. Release of Np was dominated by the dissolved (<50 Å) fraction.

Relationship between High SA/V Experiments and MCC-1

Static leach tests are being conducted at various SA/V ratios to assess how it affects the rate and mechanism of the glass reaction. Test results over two years show the predominant effect of the SA/V to be the extent of dilution of the reaction products. The higher pHs and silicic acid concentrations that are attained at higher SA/V ratios influence the reaction rate: the higher pHs accelerate the dissolution of the silicate network, but the higher silicic acid concentrations tend to slow the reaction. A sudden increase in the reaction rate is observed under high SA/V conditions, which is attributed to the effects of secondary phase formation on the reaction.

Mechanistic Validation through the Study of Natural Analogues

It is not possible to experimentally demonstrate the durability of nuclear waste glass under projected repository conditions for repository lifetimes. Instead, the results of short-term laboratory experiments, performed under temperature-accelerated conditions, are extrapolated to repository lifetimes. For these extrapolations to be meaningful, a relationship between experiments and natural alteration conditions must be established.

The examination of natural silicate glasses that have existed in the geologic environment for up to millions of years has been proposed. These "natural analogues" may be helpful in understanding long-term nuclear waste glass durability. Natural glasses, especially basalt glasses, have a range of compositions that is somewhat similar to that of proposed nuclear waste glasses.

Studying how natural glasses alter in nature and in laboratory experiments will help determine the similarities between reaction paths and reaction mechanisms in nature in the laboratory and, consequently, determine whether results can be extrapolated from one set of conditions to another. This is especially useful for investigating whether any long-term reaction processes occur that are not observed in short-term laboratory tests. A process-oriented natural analog approach has focused on learning the processes by which glass is altered by water. The goal is to relate the reaction mechanisms found in the natural analogue to those found in nuclear waste glasses.

The first step is to develop a means of experimentally altering natural samples by the same reaction mechanism that occurs in nature. This usually must be performed at accelerated rates, so it is crucial to establish that the reaction mechanisms are identical. Careful comparison and interpretation of these test results form the basis for determining whether the reaction mechanisms in nature and in the laboratory are the same. Once experimental techniques for natural samples are developed, then they may be used on nuclear waste glasses of interest. Detailed surface characterizations and studies of the reaction kinetics for the nuclear waste glasses will provide information about durability under conditions experienced by the long-lived natural analogues. Although the compositions of the nuclear waste glasses and the natural analogues may be significantly different, the reaction processes by which water interacts with both of them are the same.

This study has focused on the alteration of tektite glass by water. Tektite is a silica-rich glass that has survived in nature for up to hundreds of millions of years. Laboratory studies have confirmed this excellent durability.

The first phase of this task was to determine the reaction mechanism for tektite glass under natural conditions. A sample of naturally altered indochinite, a type of tektite (0.7 Ma), was analyzed by AEM. The alteration layer was approximately 0.1 μm thick and consisted of several phases, including kaolinite, a mixture of 1:1 and 2:1 sheet silicates, and a mineral with features compatible with the clay glauconite (and other sheet silicates). Within the clays were also found infrequent occurrences of hematite ($\alpha\text{-Fe}_2\text{O}_3$), α -quartz (SiO_2), ilmenite (FeTiO_3), Fe-bearing rutile, and TiO_2 (B).

The same indochinite has been experimentally altered in vapor hydration experiments where limited amounts of water came into contact with tektite glass. Experiments had been conducted at 150, 175, 200 and 225°C for up to 400 days. Each sample was then cross-sectioned and analyzed optically for the formation of a birefringent strain layer. Birefringent layer formation has not been previously observed in tektite altered with water either in nature or in the laboratory. Our ability to induce birefringent layer formation in tektite demonstrates the importance of carefully controlling reaction conditions in laboratory experiments. In our analyses, the reaction of tektite with water initially involves the inward diffusion of water into the glass network and the subsequent formation of a birefringent layer. As the reaction proceeds, minerals nucleate and begin to precipitate within the hydrated layer that comprises the birefringent layer. The alteration layer on naturally altered tektite contains only mineral phases: there is no obvious birefringent layer. Over the time that the natural tektite has reacted, clay formation dominates the once-birefringent layer.

Our analyses of laboratory experiments examine the very early steps in the alteration process (molecular water diffusion and clay formation), while studying the naturally altered tektite allow us to determine the later long-term processes. A comparison of the minerals formed within the two sets of samples supports the contention that vapor hydration experiments reproduce the reaction mechanism by which tektite is altered in nature. Studying either set independently might have led to erroneous interpretation of the reaction mechanism. A similar study with basalt glasses, compositionally similar to most nuclear waste glasses, is currently in progress.

Analytical Electron Microscopy Support

This task includes the use of analytical electron microscopy (AEM), infrared spectroscopy (IR), and resonant nuclear profiling (RNP) to examine the structure of reacted glasses and the colloidal particles produced in such reactions.

The analytical support staff at ANL collaborates with other members of the Technical Support Program and scientists from other DOE laboratories to investigate and identify reaction products that are produced during glass corrosion. These structural studies provide the information necessary to understand the glass reaction processes and predict glass behavior. This year, in addition to examining reacted simulated glass layers, we started the AEM of fully radioactive reacted glass. The analysis of these samples has permitted direct microscopic comparisons of reaction products that form on the simulated glass and on fully radioactive glass. These studies contribute to the discovery of the effects of radiation on glass reaction processes. Brief examples of work done for several tasks are given. The AEM results were essential in monitoring the growth of the reaction layer and the formation of secondary phases.

Colloidal particles found in the leachates of waste glass tests have been examined by AEM. The major colloidal phase found in all tests was an alkali-rich dioctahedral smectite clay. The quantity and morphology of the clay colloids have been found to be dependent on the waste glass test parameters. In addition, discrete uranium-bearing colloids, carbonates, and transition metal oxides have also been identified in the leachates.

Technical Review of Analytical Electron Microscopy of Glass Reaction

AEM analysis of the reacted glass samples is an important component of the High-Level Nuclear Waste Technical Support Program at ANL. The objective of this project at the University of New Mexico (UNM) is to provide peer review input by performing AEM and SEM analyses of reacted glass samples to confirm the conclusions reached in the ANL program. This report covers the extensive AEM and SEM analyses performed on three reacted 131U samples at UNM.

Water Diffusion of Nuclear Waste Glass

Water uptake of three simulated nuclear waste glasses was measured using both dehydration and hydration methods at various temperatures, from which diffusion coefficients were determined. Two temperature ranges with different activation energies for diffusion have been observed. The effect of glass swelling on the water uptake was observed during hydration at low temperature under high water vapor pressure. The effect of water vapor pressure on the diffusion coefficient was also observed. The diffusion coefficient of water into the simulated nuclear waste glasses was estimated to be $\sim 2.0 \times 10^{-14} \text{ cm}^2/\text{s}$ at room temperature under low vapor pressure.

Chemical durability of glasses is strongly influenced by water content. Water can enter into glasses by diffusion process. However, the data on water diffusion into glass from the vapor phase are scarce, especially at low temperatures, in contrast to data on glass dissolution or leaching in solvents. This task is to obtain water diffusion data for the simulated nuclear waste glasses in order to evaluate chemical durability of the glasses. This report reviews the water diffusion study of the simulated nuclear waste glasses at the Rensselaer Polytechnic Institute (RPI) during the past year.

Modeling Tasks at Lawrence Livermore National Laboratory

The objective of this task is to develop a computer model for the behavior of nuclear waste glasses in a repository environment and to apply it. As part of the model development, we are performing experiments that are used to quantify parameters in the model. This information is fed directly into the glass dissolution model and used to perform simulations of site-specific tests (such as the PCT test), to model natural analogues, and to make performance assessment calculations of glass durability under repository conditions.

In FY 1992 we performed several series of flow-through tests of SRL 165U, SRL 202, SRL 131, and their simple analogues and determined the rate constant as a function of pH at 70°C for SRL 202 and SRL 131. We investigated the dissolution rates of SRL 165 analogue glass in our pH buffers that were doped with varying concentrations of Al, B, and Si to determine the effects of these dissolved species on glass dissolution rates. We also determined the effect on durability of adding incremental amounts of SiO₂ to SRL 202 analogue glass.

In our doped flow-through tests we found (1) that dissolved silica decreases the dissolution rate substantially at neutral-to-alkaline pHs, but has little effect at low pHs; and (2) that the opposite is true for aluminum, which has little effect at high pHs, but significantly decreases the rate at low pHs. These data agree with predictions of the pH dependence of dissolution rate for mixed oxides based on surface charge measurements. Our experiments aimed at quantifying the relationship between silica content and glass durability but were inconclusive due to experimental problems.

Plots of dissolution rate versus pH show a sharp v-shaped minimum that is not predicted by current dissolution kinetic theory. Theory predicts a less abrupt change in rate with pH at the minimum. We suspect it may involve surface charge on the glass at the zero point of charge (around pH 6). Although we cannot yet explain it, we believe this observation should give us more insight into the ultimate rate control for glass dissolution. We intend to collect surface titration data for these glasses and examine in more detail the relationship between surface charge, adsorbed metal species, and reaction rate in order to identify the cause for the observed behavior.

Using nuclear magnetic resonance (NMR) spectroscopy, we analyzed CSG (an SRL 165 analogue), S-202 (an SRL 202 analogue), and a series of Na-B-Si glasses in order to identify the molecular structure of these glasses. The NMR results tell us how various ions in the glasses are bonded, what their coordination numbers are, and to what extent clustering occurs in the glasses. This information is important for interpreting glass dissolution tests. The good resolution of the boron NMR spectra of the bulk glasses allowed us to determine the concentration of non-bridging oxygens (a good measure of glass durability) in each sample. For the S202-series glasses, we observed boron chemical shifts characteristic of borate-like environments, indicating that boron is not homogeneously distributed; instead it exists in the glass as clustered diborate units. Thus, some refinement of existing structural models of borosilicate glass may be necessary. In addition, boron and sodium may be preferentially leached from diborate clusters in the glass, which would explain why boron and sodium often share similar release rates in dissolution tests.

Modeling work in FY 1992 concentrated in two areas: (1) studying the effect of ion exchange on glass dissolution and implications for accelerating tests using high surface area-to-volume ratios; and (2) analyzing the affinity term in the rate equation. We found that $(SA/V) \cdot \text{time}$ scaling may apply to experiments having low SA/V ratios. However, at higher SA/V ratios, rapid early ion exchange causes the solution pH to rise so that glasses reacted at different SA/V ratios will follow different reaction paths instead of scaling. The cutoff in SA/V ratio above which the test results are not expected to scale will vary with glass composition and durability. Glasses with a high alkali content will reach relatively higher pHs than glasses with low alkali contents, and thus will deviate from good scaling behavior at lower SA/V ratios.

Our work on controlling glass dissolution rate by chemical affinity resulted in a modification of the affinity term in our glass dissolution rate equation. In future work on the model, we will aim at verifying our modified equation. The mathematical form of the affinity term is clearly of great importance in extrapolating our test results to long time periods. Currently, we cannot attach a physical significance to the modification of the affinity expression. However, it may become clear when we better identify the rate-controlling reaction on a microscopic level.

Modeling work in FY 1993 will concentrate on SRL 202 glass, which has the most diverse set of experimental results of the glasses tested. The experimental results will be obtained mainly from tests performed at ANL, although additional data are available from MCC and PCT tests from other laboratories. We will use our enhanced model to see if we can predict results from this wide variety of test types and conditions. The model results should allow us to

make predictions of long-term glass durability from results of short-term tests (e.g., the PCT test). We will now focus our experimental work in two areas: (1) measuring glass dissolution rates under near saturation conditions, the conditions that will control glass dissolution rates under most anticipated repository environments; and (2) continuing our systematic investigations of the effects of glass composition on glass durability.

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 1990 and 1991 [1,2]. 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 physical parameters or processes that are important for controlling glass reaction in an unsaturated environment include (1) glass composition, (2) radiation, (3) temperature, (4) surface area of glass/volume of liquid (SA/V), (5) the effects of unsaturated conditions on glass reaction, (6) the effect of alteration layers on glass reaction, and (7) 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.

To augment the Critical Review reports, "High-Level Nuclear Waste Borosilicate Glass: A Compendium of 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.

This year, in addition to the Compendium, reviews of each of the physical parameters continued, while testing and modeling were conducted to augment the reviews. In this report, progress in each active area is reviewed after a general background description applicable to all areas is presented.

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 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) "Mechanistic Validation through the Study of Natural Analogues,"
- (7) "Technical Review of Analytical Electron Microscopy of Glass Reaction,"
- (8) "Water Diffusion Study of Simulated Nuclear Waste Glasses," and
- (9) "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 glasses¹ 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

¹The 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.

several years and represent glasses developed as the process engineering matured. The base frits used in these glasses (131, 200, and 165) represent the expected durability range from least to most durable based on hydration theory [3]. The sludge from tanks 11 and 42 is rich in aluminum, and the final compositions of the 131/11 and 165/42 compositions 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) [4] 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 (LLNL), 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 an "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. However, the data presented in the subsequent sections of this report are based on the values in Table 1. A standard leachate, that 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

During this reporting period, a review draft of the document entitled "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Characteristics" was prepared. The content is a concise compilation 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 geological disposal. A brief summary of the scope, organization, and approach that was utilized in preparation of the review draft is presented here.

The document preparation effort started with a detailed annotated outline of the contents which was prepared and approved. In general, the scope covers information pertinent to understanding waste glass corrosion, weathering rates, and the associated release rates of individual radionuclides due to groundwater and/or water vapor contact. It also includes other waste glass alteration processes (e.g., cracking, phase transformations/devitrification, and radiation damage) that may influence the corrosion, weathering, and/or radionuclide release rates.

A key consideration that motivates the development of a sound understanding of waste glass alteration processes is the very long time period (extending to tens of thousands of years after emplacement in a repository) for which the effects of such alterations on radionuclide release have to be predicted. The intent of this document is, therefore, to communicate the current understanding of waste glass alteration processes using selected information from worldwide sources. The types of scientific information that are discussed include experimental testing data, data from natural and historical man-made glasses, interpretations of the data in terms of mechanistic understanding of the underlying physical and chemical processes involved, and mechanistic predictive modeling. The scope also includes a summary of waste glass production processes and descriptions of the waste glass products to be produced at Savannah River, SC, West Valley, NY, and Hanford, WA. The reasonably credible range of conditions to which the glass may be exposed during handling, storage, transportation, and eventual geologic disposal are summarized in order to identify the types of conditions for which an understanding of the alteration behavior is desired.

The document is organized into five major sections. In addition to describing the objectives, scope, and organization, the introduction includes background material on the history of glass as a waste form and an overview of the international experience with borosilicate glass waste. A description of the waste form and the environmental service conditions to which it might be exposed is provided in Section 2. Experimental observations on waste glass alteration are presented in Section 3. These experimental observations include laboratory corrosion and weathering results, materials interactions and field testing results, and observations from natural and historical man-made glasses. Waste glass modeling is discussed in Section 4 and a short summary of remaining uncertainties in understanding nuclear waste glass alterations is presented in Section 5.

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. Informal review comments obtained from a steering group consisting of Drs. R. C. Ewing (University of New Mexico), A. A. Barkatt (The Catholic University of America), and D. M. Strachan (Battelle Pacific Northwest Laboratory) were utilized in guiding preparation of the review draft.

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 to be hydrologically unsaturated and having possible air exchange with the neighboring biosphere. 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 the waste glass researchers. We identified the need for a critical review as a task, which is currently 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 alteration phases resulting from glass hydration. Detailed critical reviews of how each of these parameters affect waste glasses will be made as a part of this task.

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 will be integrated into a summary document, "High-Level Nuclear Waste Borosilicate Glass: A Compendium of Characteristics" [5]. The results from this Task will be used in support startup of the DWPF.

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 [6]. The first detailed report, which reviews the effects of temperature on waste glass performance, has been completed [7]. 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 that 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.

The parameter currently being reviewed is the effect of glass composition on waste glass durability. This report is nearly completed. This report is an expansion of the interim report and includes brief reviews of models of glass dissolution and glass structure to form a basis for later critically reviewing correlations of glass composition and glass durability.

E. Future Progress

The detailed reviews of the remaining parameters (radiation, SA/V ratio, surface layers, and unsaturated environments) are in progress, and drafts of each report will be completed in the upcoming year. A draft of the Compendium report has been prepared and will be revised, pending current review. This report is scheduled to be completed in June 1993.

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 analogues 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, supernate, 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 [8-13]. 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 [14]. 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 tests performed at high SA/V ratios and high SA/V flow tests done 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 [15] 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 [16].

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

1. Results and Discussion of Long-Term Static Tests

Table 3 shows the test matrix for the long-term static tests, which have been described in detail [17]. The matrix is divided into three sections based on the glass type (165/42, 131/11, and 200). The fully radioactive waste glass compositions (R glasses) were made in the SRL in-cell minimelter, using corresponding glass frits plus sludge from various high-level waste tanks at Westinghouse Savannah River Site. The simulated glass compositions (S glasses) were made to have the same compositions as the R glasses, but without radioisotopes. The tests are being performed at 90°C in EJ-13 water (repository groundwater equilibrated with tuff rock) at SA/V ratios of 340 m⁻¹ (monolith), 2000 m⁻¹ (powder), and 20,000 m⁻¹ (with glass 200 powders only). Most of the tests are done in duplicate. The test vessel is a 22-mL 304L stainless steel vessel with a copper gasket. The schedule allows for all long-term tests (>364 days) to be started at the same time, with to-be-determined (TBD) tests included to provide additional information where needed. Static tests are performed in batch mode so solids can be examined at each test period to document mass balance between the residual solids (reacted glass and secondary phases) and the solution composition. The tests are static, that is, no exchange of

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

[illegible]

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

Reaction Progress in terms of $SA/N \cdot t$ (units of $\text{day} \cdot \text{m}^{-1}$). No significance is implied to the use of this reaction progress indicator.

CTests are single tests.

^dTests are duplicate.

eThe underlined tests are terminated.

^fTBD represents to be determined.

leachant occurs, to promote conditions representative of an unsaturated site (little or no flow), and the reaction environment is disturbed as little as possible; thus, optimal conditions exist for secondary phase nucleation and growth.

The solution analyses of the terminated tests include leachate pH (at room temperature), cations, selected anions, and actinides. Analyses are done on solutions filtered through 0.45- and 0.005- μm filters. The errors associated with solution analyses are estimated to be less than 10%; the elemental concentrations of the major glass constituents from the duplicates are usually within 10%. The leached glass surfaces are examined optically and with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and secondary ion mass spectroscopy (SIMS).

a. Status

To date, 212 of the planned long-term static tests have been initiated, and 126 of these have been terminated. The longest tests have been in progress for more than 29 months. The solution analyses for the terminated tests are about 90% complete, and the surface analyses on the terminated samples are about 50% complete.

b. Results and Discussion

The emphasis of data interpretation from the static tests is to assess any differences in the leach behavior between radioactive and simulated waste glasses. This section is divided into the following: (1) comparison at 340 and 2000 m^{-1} , (2) comparison at 20,000 m^{-1} , (3) comparison of pHs in the leachates, (4) comparison of surface layers, (5) comparison through the acceleration parameter SA/V, and (6) conclusions.

(1) Comparison at SA/V Ratios of 340 and 2000 m^{-1}

The comparison of the normalized release based on 0.45- μm filtrate of B, Li, Na, and Si for all the glass compositions tested at 2000 m^{-1} is shown in Fig. 1. For 165/42 compositions at times of up to 560 days, the normalized Li and Si releases are similar for both R and S glasses. The B and Na releases from 165/42R are higher than those from 165/42S but by less than 150% (Figs. 1a and 1b). For 131/11 compositions at times of up to 280 days, the B, Li, Na, and Si releases from 131/11S are higher than those from 131/11R, with differences being less than 170% (Figs. 1c and 1d). For 200 compositions at times of up to 280 days, the B, Li, Na, and Si releases from 200S are higher than those from 200R, but by less than 90% (Figs. 1e and 1f). The solution result trends from testing each of these glasses at 340 m^{-1} (not shown here) are similar to these results at 2000 m^{-1} . While the differences that were measured for the reactivity of the R and S glasses are analytically significant, the absolute differences are relatively small and the trends in the data suggest that the same reaction processes are rate controlling for each glass type (R or S).

(2) Comparison at SA/V Ratio of 20,000 m^{-1}

The leach behavior of the 200-based composition at 20,000 m^{-1} indicates that there may be a large difference in the long-term reactivity between R and S glasses. Figure 2 shows that the glass dissolution for 200S glass at 20,000 m^{-1} is greatly accelerated between 182 and 364 days. The acceleration was verified with two TBD tests which were terminated at 300 and 390 days. The normalized release in terms of B, Na, Li, and Si increased by a factor of 35, 23, 9, and 10, respectively, from 182 to 364 days. The solution pH increased from 11.82 to 12.27 (Fig. 2c). The 100- to 200-mesh glass powder of 200S was fused into a

Fig. 1. Comparison of Leach Behaviors of S and R Glasses at 2000 m^{-1} in Terms of B, Li, Na, and Si Release: 165/42, (a) and (b); 131/11, (c) and (d); 200, (e) and (f).

Fig. 2.
Comparison of Leach Behaviors of
200S and 200R Glasses at
 $20,000 \text{ m}^{-1}$ in Terms of (a) B and
Na Release, (b) Li and Si Release,
and (c) pH

material that caked to the walls of the test vessel, and a large quantity of white crystalline precipitated material formed on top of the glass powder. The examination by both SEM and AEM of the reacted surface layers on the glass samples revealed rapid thickening of the surface layers with abundant crystalline phase formation. This is discussed in more detail in the next subsection. 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 at $20,000 \text{ m}^{-1}$ increased by a factor of 13 after the acceleration. This is somewhat surprising owing to the basic pH of the leachates. The increased U in solution may be a result of the higher concentration of anions in the glass leachate. During acceleration, the concentration increases are 22 times for F^- (7 to 147 mg/L), 21 times for Cl^- (9 to 187 mg/L), 13 times for HPO_4^{2-} (77 to 950 mg/L), and 70 times for SO_4^{2-} (165 to 11,550 mg/L). The retention of actinides or rare earth elements by the glass has been found to decrease dramatically when the glass is tested in brine and other solutions that contain high concentration of anions [18,19].

On the other hand, the release rate for 200R at $20,000 \text{ m}^{-1}$ showed almost no increase at all during the same interval, and the slow reaction trend has extended up to 560 days (Fig. 2). The leachate pH of the 560-day test of 200R was 11.64, similar to the pH at 15 days. The various anion concentrations for 200R were almost constant throughout the 364-day period. At 364 days, the leach rate of 200S is 39, 31, 16, and 9 times higher than 200R in terms of B, Na, Si, and Li release, respectively. The pH of 200S is 0.6 unit higher than the corresponding pH of 200R at 364 days.

(3) Comparison of pHs in the Leachates

Figure 3 shows the difference in pHs between leachates of radioactive and simulated waste glasses, which is due to the effect of radiation of the R glasses [20]. In general, the leachate pH of a radioactive glass is usually lower than that of a simulated glass because nitric and other acids are formed in the leachate of a radioactive glass when the test is done in the presence of air. This condition occurs for the 200 and 131/11 glass compositions. However, if the dominant glass reaction process is an ion-exchange reaction (e.g., $\text{Glass-O-Na}^+ + \text{H}_2\text{O} = \text{Glass-O-H} + \text{OH}^- + \text{Na}^+$), the release of alkali will counter the radiation effect. In some cases, the pH increase due to ion exchange will overcome the pH decrease caused by radiation, which is the case for the 165/42 compositions.

The lower leach rates of 200R compared with 200S, at SA/V values of 340 and 2000 m^{-1} and time periods less than 330 days at 20,000 m^{-1} , have been attributed to the lower solution pH because of the radiation effect [21]. For example, the dominant glass dissolution process for both 131/11 and 200 compositions is network hydrolysis. This process is enhanced by high solution pH values; thus, when the leachate pH in the R glass tests is lowered due to the radiation effect, the reaction is slower than that observed for the S glasses (Fig. 1). On the other hand, ion exchange is the dominant reaction process for the 165/42 compositions during the time periods examined. Ion exchange occurs more readily in 165/42R than in 165/42S because of its lower initial pH (Fig. 3c). As the ion-exchange reaction continues, the solution pH increases, which, in turn, promotes the network hydrolysis reaction. This reaction sequence explains why 165/42R is slightly more reactive than 165/42S in terms of B and Na release.

Fig. 3.
Comparison of Leachate pHs of R
and S Glasses at 2000 m^{-1} for
(a) 131/11, (b) 200, and (c) 165/42

The acceleration of the glass reaction for 200S at $20,000 \text{ m}^{-1}$ can also be correlated with solution pH, since the pH of the solution increases from 11.82 to 12.29 during acceleration. The leach rates of both 200S (before rate acceleration) and 200R (up to 560 days) decrease with time while the reaction rate of 200S greatly increases with time when the leachate pH value exceeds 12.0. pH is already known to be one of the dominant effects on nuclear waste glass reaction [22,23]. The leach rate for 200R at $20,000 \text{ m}^{-1}$ is lower than the corresponding reaction for 200S (Fig 2); also, the corresponding leachate pH for 200R is always lower than that for 200S. The 200S glass leachates had pH values of 11.82 ± 0.05 after 15, 56, 98, and 182 days of reaction, while the 200R had pH values of 11.65 ± 0.13 between the 15 and 560 days. The pH of 200R leachate at 560 days is still similar to its pH at the beginning of the test (Fig. 2c) and shows no sign of a pH excursion. This lower pH of 200R may retard the onset of increased glass reaction rate. No reaction acceleration would be expected for 200R if the radiation effect can maintain the leachate pH below 11.8. The consequences of the pH effect are important because in a repository setting, where minimal water can contact with the glass, may enhance the effect of radiation.

If pH is the only controlling parameter, it is difficult to understand why the 200 glass composition is "stable" at pH values of approximately 11.82 (25°C) for 200S up to 182 days and 11.65 (25°C) for 200R up to 560 days. A pH value of 11.82 is higher than the pK_2 value of 11.77 of H_4SiO_4 (25°C) and the pK of 11.20 of H_3AlO_3 (25°C). Another possible explanation for the observed rate acceleration is the formation of a suite of crystalline phases, which is discussed in the next section.

(4) Comparison of Surface Layers

The surface layers are significantly different before and after acceleration. The surface layer of 200S at $20,000 \text{ m}^{-1}$ before acceleration is a single-layer structure, as shown in Figs. 4d and 4e. The layer thickness grows slowly with time, being about 150 nm thick (Fig. 4d) at 98 days, and about 300 nm (Fig. 4e) at 182 days. After acceleration, the surface layers increased to about 6500 nm in thickness with two distinct regions: a crystalline region of about 2000 nm thick and a large amorphous alteration region more than 4500 nm in thickness below it. (See Fig. 4f.)

Several types of phases have been identified in the crystalline region. A dominant phase consists of elongated prism-shaped crystals with a composition of Si, 61.5; Al, 22.8; K, 9.0; Ca, 4.0 (element wt%). The composition shows significant variations in the amounts of K and Ca. The electron diffraction pattern of the phase shown in Table 4 matches well with the crystal spacing of a clinoptilolite [24]. The typical oxide formula for this zeolite phase is $(\text{Na}_2, \text{K}_2)\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 8\text{H}_2\text{O}$ (Ca and Mg also present; $\text{Na}, \text{K} \gg \text{Ca}$) [24]. However, the composition, d-spacings, and the morphology are also consistent with a K-feldspar phase. Formation of K-feldspar from zeolite has been well documented [25]. Since the phase observed was extremely sensitive to electron irradiation, an indication water present in the structure, the phase is more likely to be the zeolite. The other phases are an Fe-rich clay phase (Fig. 3d through 3g), an almost pure amorphous Si phase that was both isolated from and in close vicinity with the clay phase, and a Si-Ca phase that is a button-like mass.

Figure 4g is a TEM micrograph of 200R glass reacted for 364 days. The surface layer is 150-300 nm thick, which is similar to that of 200S at 182 days. The composition of the surface layer in the 364-day sample of 200R is also similar to the layer composition of 200S before acceleration.

Fig. 4. Surface Layer Examination on Reacted 200 Glass Compositions at $20,000 \text{ m}^{-1}$. SEM micrographs were taken of the top surface views on 200S samples reacted for (a) 98 days, (b) 182 days, and (c) 364 days. TEM micrographs were made of cross-sections of 200 S samples reacted for (d) 98 days, (e) 182 days, and (f) 364 days, and of 200 R samples (g) reacted for 364 days of 200R.

Table 4. Comparison of Electron Diffraction Patterns of White Precipitates of 200S at 20,000 m⁻¹ with Clinoptilolite^a

d/Å	Error Estimate	Clinoptilolite
		8.97
		7.89
6.71	0.3	6.78
5.96	0.2	5.93
5.08	0.2	5.100
		5.244
4.76	0.1	5.050
4.64	0.1	4.651
		4.229
		3.974
3.87	0.09	3.915
3.76	0.09	3.711
		3.698
		3.555
		3.461
3.42	0.08	3.421
		3.391
		3.123
3.08	0.05	3.070
3.01	0.06	3.038
		2.974
2.91	0.06	2.854
2.78	0.05	2.796
2.70	0.05	2.732
2.63	0.05	2.725
2.50	0.05	2.550
		2.464
		2.457
		2.346
2.24	0.04	2.362
2.18	0.04	2.208
2.10	0.04	2.110
2.09	0.04	2.093
2.08	0.03	
1.98	0.03	1.975
		1.931
1.84	0.03	1.870

^aFrom Gude [24].

As the glass reaction progresses, the solution concentration increases. The increased solution concentration lowers the glass reaction affinity [26], and glass reaction rate decreases with time before acceleration. When the solution concentration reaches the solubility limits of selected secondary phases and the nucleation barrier is overcome, the formation of secondary phases reduces solution concentration (activity) and increases the glass reaction affinity, resulting in glass reaction acceleration. Figures 4a to 4c show the gradual increase in the formation of surface precipitates. At 98 days (Fig. 4a), there are few surface precipitates. The amount of surface precipitation increases at 182 days (Fig. 4b), and the surfaces are fully covered with white precipitates (Fig. 4c) at 364 days. (Note that Fig. 4b and 4c are at the same magnifications.) The dominant zeolites phase (e.g., clinoptilolite), which may be a main contributor to the acceleration, observed in the 330-, 364-, and 390-day samples are not present in the 182-day sample.

The reduction in glass reaction affinity results from the decrease in solution concentration (activities) of the secondary-phase-forming species. However, the direct cause for the concentration reduction is usually difficult to assess directly from the concentration measured. This is because many factors besides secondary-phase formation, such as solution pH, ionic strength, and glass dissolution, influence solution activities. Table 5 is a list of concentrations of the relevant species for the formation of a clinoptilolite (or K-feldspar) before and after acceleration of 200S at $20,000 \text{ m}^{-1}$. In general, the boron and alkali concentrations continue to increase with time and have a large increase during acceleration. The Al concentration decreases about ten times during acceleration. (Note there is variance in the duplicate 364-day tests due to onset and extent of phase nucleation.) The Si concentration also decreases in one of the duplicate 364-day tests (364B in Table 5) and further decreases from 8000 mg/L at the peak concentration to a level of 600 mg/L at 390 days. This decrease in Si concentration occurs even though the pH is the highest at 390 days and Si is normally projected to be more soluble at higher pH values. The reduction in observed concentrations of Si and Al may correlate with the formation of the zeolite phases and serves as evidence for the reaction affinity control.

H_4SiO_4 has been proposed [27] to be the only species to be accounted for when evaluating glass reaction affinity. However, the data from this study do not seem to support this hypothesis. First, the glass reaction rate of 200S at $20,000 \text{ m}^{-1}$ before acceleration is relatively slow, although the concentration of the undissociated silicic acid, H_4SiO_4 , is expected to be very low. This is because the leachate pH values for 200S are approximately 11.8 (25°C), which is higher than the pK_2 of silicic acid (11.77). This low silicic

Table 5. Leachate Concentrations of 200S at $20,000 \text{ m}^{-1}$
Before and After Acceleration^a (mg/L)

Days	B	Li	K	Al	Si
98	499 ± 1	107 ± 5	191 ± 1	4.7 ± 0.1	608 ± 3
182	642 ± 14	117 ± 16	287 ± 11	3.4 ± 1.1	833 ± 12
300	6,389	439	1,783	1.1	2,421
364(A)	23,148	1,130	4,809	9.4	8,289
364(B)	22,275	1,071	4,467	0.8	1,444
390	20,924	1,190	4,706	0.4	661

^aThe values with errors are calculated from the duplicate tests and the remaining values are from a single test that has an analytical error of less than 10%.

acid concentration (activity) should have resulted in a high reaction rate instead of the low rate observed before acceleration. Second, the glass reaction was greatly accelerated between 182 and 364 days, while the total Si concentration also increased (Table 5). If silicic acid were the only species to affect the affinity, one would expect that the acceleration would occur only when the silicic acid concentration is low. While it is believed that Si should be one of the major species which influences glass reaction affinity, it is likely that other species also have an influencing role.

(5) Comparison through Acceleration Parameter SA/V

The data given above for the comparison tests done at 340 and 2000 m^{-1} show little difference up to 560 days in reactivity between radioactive and simulated glasses of 165/42, 131/11, and 200 compositions. On the other hand, the accelerated tests at high SA/V of 20,000 m^{-1} show a difference of up to a factor of 39 in leach rates between 200R and 200S glasses within 364 days. This demonstrates the need of long-term tests at high SA/V for the comparison studies. Figure 5 shows that the data for 200S and 200R at S/V of 340, 2000, and 20,000 m^{-1} at various times can be well represented by a single curve when plotted against the product of SA/V and $t^{0.5}$. The scaling of SA/V and t has been used to simulate long-term glass corrosion during a short period [28,29]. For example, if the empirical relationship shown in Fig. 5 is applied to the present data, the observed rate acceleration of 200S at 20,000 m^{-1} at 330 days would correlate with a similar acceleration for this glass tested after 90 years at 2000 m^{-1} . If the $(\text{SA}/V) \cdot t^{0.5}$ scaling holds, no difference in the reaction rates of 200S and 200R glasses would be observed following the current test matrix.

Note that the present data cannot be represented by a steady function of product of SA/V and t^1 (Fig. 6), as has been suggested by several studies [28,29]. The successful scaling of waste glass dissolution data by the product of SA/V and $t^{0.5}$ has been recently suggested by Grambow et al. [30] and Van Iseghem et al. [31] as evidence for a diffusion-controlled dissolution mechanism. This explanation requires collaboration from the investigation of the integrity of the surface layers and the adherence of the layers to bulk glass. However, our preliminary results from examination of the reacted glass surfaces indicates that these surface layers are very porous and usually loosely attached to the bulk glass. In fact, the surface layers are very thin (about 300 nm on 200S 182-day samples, as shown in Fig. 4e) before reaction acceleration but thicker than 6500 nm after acceleration. It is difficult to explain why the very thin layers formed on the glass surfaces before acceleration can act as diffusion barriers to slow down glass reaction, while the surface layers with 20 times more thickness and with similar porosity and adherent properties are associated with the highest observed glass reaction rates.

(6) Conclusion

Static tests at 340 and 2000 m^{-1} for up to 560 days on three SRL nuclear waste glass compositions have shown that there is little difference in reactivity between radioactive and simulated nuclear waste glasses with similar chemical compositions. A large difference in reactivity (up to a factor of 39 in leach rates of boron) has been observed between 200R and 200S when tested at SA/V of 20,000 m^{-1} for up to one year. The accelerated glass reaction rate with the simulated glass 200S is associated with the formation of crystalline phases such as a clinoptilolite (or potassium feldspar) and a pH excursion. The radiation field generated by the fully radioactive glass reduces the solution pH. This lower solution pH, in turn, may retard the onset of increased reaction rate. These results suggest that radioactive glass 200R may be much more durable than the corresponding simulated glass 200S 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 discussed above, that influence glass reaction

Fig. 5. Leachate Concentration Plotted as a Steady Function of the Product of SA/V and $t^{0.5}$ for 200S (a-d) and 200R (e-h). The lines are a guide for the eye.

Fig. 6. Leachate Concentration Plotted as a Steady Function of the Product of SA/V and t for 200S (a-d) and 200R (e-h). The lines are a guide for the eye.

must be accounted for to make adequate long-term predictions. The data presented here indicate that the reaction progress for both 200S and 200R can be represented empirically as a steady function of the product of SA/V and $t^{0.5}$. The SA/V in some situations may be a useful reaction correlation parameter, but to be viable, a mechanistic basis for the correlation must be established. Meaningful comparison tests between radioactive and simulated nuclear waste glasses should include long-term and high SA/V tests.

c. Future Progress

The ongoing static tests will be continued. Special attention will be placed on the tests of 200R at $20,000 \text{ m}^{-1}$ to see whether the leach rate of the radioactive glass will eventually mirror that of 200S. It is noted that the anion concentrations such as phosphate and sulfate in the leachate of 200S at $20,000 \text{ m}^{-1}$ had doubled before the rate acceleration took place (i.e., at 182 days). The anion concentrations in 200R leachates at 560 days are twice as high as those at 364 days, which may indicate that the acceleration of glass reaction in 200R is imminent. The TBD tests will be utilized to verify any glass reaction acceleration. More emphasis will be placed on the analyses of the surface layers of the terminated samples, especially on the radioactive samples. Data will be generated to compare the identities and sequences of the secondary phases between R and S glasses. The radionuclides will continue to be analyzed from all the available solutions. This analysis is expected to be enhanced by the newly available technique of ICP-MS. The solution data, combined with surface analysis results, will be utilized further to compare the reactivity of the radioactive and simulated glasses to build a data base for validating glass performance models.

2. Long-Term Intermittent Flow Tests at High SA/V

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 [15,32]. 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 6. There are two sets of five replicate tests and one blank test. The test periods have been modified from the matrix presented in last year's report [2] to collect more solution for analyses.

The first set of five tests 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 . It could also occur in a vapor environment if a breach occurs at a temperature

Table 6. Test Matrix for Long-Term Intermittent Flow Tests at High SA/V Ratios

Test No.	Test Type ^a	Components ^{b,c}	Test Duration, weeks							
			0	18	55	85	105	135	165	195
N4-1	Batch	4-week-aged glass & 304L SS holder	—	—	—	—	—	—	—	—
-2	Continuous	4-week-aged glass & 304L SS holder	—	✓	✓	✓	✓	✓	✓	✓
-3	Batch	2-week-aged glass & 304L SS holder	—	—	—	—	—	—	—	—
-4	Continuous	2-week-aged glass & 304L SS holder	—	✓	✓	✓	✓	✓	✓	✓
-5	Continuous	2-week-aged glass & 304L SS holder	—	✓	✓	✓	✓	✓	✓	✓
-6	Batch	glass, 304L SS holder	—	—	—	—	—	—	—	—
-7	Batch	glass, 304L SS holder	—	—	—	—	—	—	—	—
-8	Continuous	glass, 304L SS holder	—	✓	✓	✓	✓	✓	✓	✓
-9	Continuous	glass, 304L SS holder	—	✓	✓	✓	✓	✓	✓	✓
-10	Continuous	glass, 304L SS holder	—	✓	✓	✓	✓	✓	✓	✓
-11	Continuous	blank	—	✓	✓	✓	✓	✓	✓	✓

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

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

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

below $\sim 95^{\circ}\text{C}$ 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.

The second set of five tests is being performed with unaged or as-cast glass, and the results will be comparable with previous test series using the Unsaturated Test method [32]. 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.

Sampling was done at the 18- and 55-month periods, and two tests (N4-1 and N4-6) were terminated at the 55-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 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.

The results of the solution analyses are shown in Tables 7 and 8. 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 pHs 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 in solution at levels several hundred times greater for the aged glass than for as-cast glass. 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 using the rationale used in analyzing the long-term test results of drip tests on SRL 165 [32], more meaningful information regarding solution chemistry and its effects on radioactive distribution is provided by describing the elemental concentrations, as presented in Table 7.

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

Table 7. 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 ⁼	SO ₄ ⁼	C ₂ O ₄ ⁼
8	1	7.97	3	3	4.6	<0.5	7.5	5.2	3.3	<1	104	2.8
	2	8.26	2	5	7.6	a	14	15	2.5	<1	38	11
9	1	8.12	2	4	9.3	<0.5	9.4	9.0	4.0	<1	10	<0.7
	2	7.94	3	3	8.5	a	20	23	4.3	<1	60	11
10	1	8.60	4	5								
	2	8.55	3	7	5.3	a	5.2	6.7	2.4	<1	18	10
6	terminated	8.45	2	7	5.7	a	10	13	1.9	<1	81	7.8
2	1	11.28	29	4			167	<15	<25	193	5660	<50
	2	11.27	22	1	11	a	71	<15	42	169	781	56
4	1	11.37	21	4			211	<15	<25	397	9870	<50
	2	11.13	23	2	11	a	47	<15	40	168	815	60
5	1	11.33	35	0			256	<15	<25	334	8840	66
	2	11.43	19	1	13	a	36	<15	44	197	886	<50
1	terminated	11.09	25	3	29	a	58	<15	74	286	2376	59

^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.

Table 8. Total Elemental Release^a to Solution in Drip Tests (ppm)

Test #	Sampling Period	B	Li	Na	Si
8	1	2	9	160	60
	2	33	17	410	70
9	1	3	6	27	10
	2	29	8	220	20
10	1	81	21	300	100
	2	60	28	700	190
6	terminated	96	52	800	200
2	1	42000	2400	85000	2200
	2	22000	1600	61000	12600
4	1	39000	2200	82000	2800
	2	19000	1200	50000	5700
5	1	33000	1600	64000	24100
	2	70000	1400	70000	2000
1	terminated	53000	3400	151000	4800

^aThe amount of each cation in the leachate as reported has not been corrected for the amount in the EJ-13 water.

potential for anions to complex radionuclides [33] adds significance to their concentrations in the leachates. As is presented in Table 7, the concentrations of $\text{SO}_4^{=}$, Cl^- , and $\text{HPO}_4^{=}$ in the leachates from the aged glass tests are in the 500 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.

There is also a marked difference in the organic carbon content between the test types, as measured by both carbon and anion analyses. The increase in organic carbon in the aged glass leachates is due to increased concentration of formate (CHO_2^-) and oxalate ($\text{C}_2\text{O}_4^{=}$). Both species are known to complex actinides in solution [33] and thus have the potential for affecting the solubility of the transuranic elements in solution.

The measured amount of actinides in solution is given in Table 9. The values presented are order of magnitude levels, provided to indicate differences between release from the two test types. Alpha 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. The actinide content in the solutions has both truly dissolved and particulate fractions. The truly dissolved fraction passes through the final filter, which nominally has a pore size of 50 Å. While all of the material measured in solution was suspended in solution (the aliquots were taken from the middle of the

Table 9. Preliminary Actinide Release^a from Drip Tests (ppm)

Test No.	Sampling Period	$^{238}\text{Pu}/^{241}\text{Am}^b$	^{239}Pu	^{244}Cm
8	1	2E-8	2E-7	2E-9
	2	5E-10		2E-11
9	1	1E-8	1E-7 ND	9E-10
	2	ND ^c		ND
10	1	2E-8	-- ^d	6E-10
	2	2E-8	--	5E-10
6	terminated	4E-9	--	7E-11
2	1	3E-7	--	9E-10
	2	1E-9	--	--
4	1	1E-7	--	--
	2	4E-9	--	--
5	1	1E-6	--	2E-10
	2	2E-9	--	--
1	terminated	4E-9	--	2E-11

^aReported values are based on alpha spectroscopy of original test solution. Because of attenuation of the spectra for samples 2, 4, 5, and 1, the data are only order-of-magnitude estimates.

Additional analyses are being performed to improve these values. Concentration of all material detected in solution is reported, including both truly dissolved and suspended fractions.

^bThe ^{238}Pu and ^{241}Am alpha energies were not resolved: thus, all values are reported as being produced by ^{238}Pu . Additional analyses may be able to distinguish between the ^{238}Pu and ^{241}Am fractions.

^cND = none detected.

^dIf a value is left blank, attenuation of the alpha spectra obscured the peak of interest.

test solutions), it is possible that over time the larger particles may settle out of solution and not be transportable. Thus, it is important to know the size distribution of the particles. The general trend noted in the filtration experiments is that greater than 90% of the transuranic component measured in the as-cast solutions was filtered by either the 5- or 1- μm filters, while it is estimated that more than 75% of the actinides in the aged glass solutions are truly dissolved in solution. Thus, for the aged glass, the release of Pu is generally several orders of magnitude greater than from the as-cast glass, and the Pu is also dissolved in solution.

Some indication of the types of colloids in the as-cast glass leachates is obtained by examining the particles that were isolated on the performed carbon grids. The solutions from tests N4 6, -8, -9, and -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 could not be wicked effectively through the grid, and were rinsed with deionized water in the hope that some particles may remain on the grid.

Test N4-6 is typical of the as-cast glass samples and shows evidence of eight different particulate phases, including a smectite-type clay, Mg silicate, Ti oxide phase, Al-rich phases, two types of K-Al-silicate phases, a Mn-iron phase, and a Mg-K-Al-silicate phase. All tests show the presence of Mn-rich clay minerals.

Electron diffraction and compositional data were obtained from all of these phases. CBED was used during investigations of a number of the particles. Recently, Zhou and Möllenstadt [34] used CBED to study mica with a 60 kV accelerating potential. These experiments were repeated but CBED of smectite phases results in almost immediately amorphization and even kaolinite stands up little better. Mica does produce satisfactory convergent beam patterns (see Fig. 7). Figure 8 shows a CBED pattern down a major zone axis of rutile.

The Mn-Fe phase is of particular interest. Figure 9e shows the EDS of a clay colloid that demonstrates the high Mn content. Oxides of Fe and Mn are typical constituents of many clays and are formed by the oxidation of Mn^{2+} contained in low-temperature solutions or in hypogene minerals. Birnessite ($\text{Na}_4\text{Mn}_14\text{O}_{27} \cdot 9\text{H}_2\text{O}$) is a mineral commonly found in soils that consists of alternately stacked sheets of MnO_6 octahedra linked through oxygen ions and water molecules that occupy the interlayers. The phase was identified in leached layers of a 131 glass [35]. The major clay phase revealed a double diffraction rink for the hk-lines, which is possibly a saponite. Electron diffraction (Figs. 9b, 9c, and 9d) of colloids from these tests shows a steady progress in complexity and crystallinity. In N4-9 the ordering of the Mn phases within the layers is such that a Kikuchi pattern can be observed. Figure 10 shows the structure of the mixed clay phase.

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 6, and tests N4-3 and N4-7 will be terminated after approximately two years of reaction. 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 terminations have been effected and the samples analyzed, the results from these tests will be compiled in a Topical Report.

Fig. 7. CBED Pattern (a) and Composition from EDS (b) of Mica Showing Pseudo-hexagonal Symmetric

Fig. 8. CBED Pattern as Seen Down a Major Zone Axis of Rutile

Fig. 9. Electron Diffraction Patterns and Composition of Colloids in the N4 Series of Tests. A double-ring pattern can be seen (a) that is possible evidence of saponite. The increase in ordering of a Mn phase within the colloids is shown (b-d). EDS (e) was used to demonstrate this Mn-rich phase. Some regions were found to be rich in iron. The rest of the colloids were a K-Al silica.

Fig. 10. Mixed Clay Phase: (a) Micrograph Showing Its Structure, (b) Electron Diffraction Pattern of Selected Area, and (c) EDS

3. Long-Term Repository Environment Tests

The laboratory analogue test [36] 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 those 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. 11. The tuff core and WPA are assembled, and an unsaturated flow of water is forced through the core by using a vapor pressure slightly above ambient.

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

a. Status

On December 19, 1991, two analogue 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 52 weeks, and the water that passes through the cores is collected. The tests are being run at two different flow rates: the unaged glass has a flow rate of 0.02 mL/hr and the aged glass a flow rate of less than 0.005 mL/hr. The effluent has been collected and periodically checked for gross radioactivity. To date, no indication of activity in the solution has been detected. After one year of testing, the solutions will be condensed by evaporation and analyzed with alpha and 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.

Fig. 11. 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).

VI. EFFECT OF RADIATION ON GLASS REACTION AT LARGE SA/V

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 causing damage to solid materials and by interacting with air, water vapor, or liquid water to produce a variety of radiolytic products that may be reactive towards 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^+), hydroxyl ($\bullet OH$), and hydroperoxyl ($HO_2\bullet$) ions; hydrogen atoms ($H\bullet$); 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 [37].

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 [8,38-40]. 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 [41,42]. 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 [41-44].

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 [38,41,42,44]. Burns et al. [38,39] formulated an equation to predict the molar concentration of nitric acid accumulating in water using values determined for $G(NO_3^-)$, the concentration of N_2 in the atmosphere, gas/liquid ratio, dose rate, and exposure time. These calculated pH values can then be used to predict the reaction behavior of glass samples in irradiated systems.

The 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 [45] 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 [40,46,47]. 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 [39,48]. 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 the transuranic-doped glass. Glass samples that were gamma-irradiated prior to being immersed in DIW did not display any increase in release rates, indicating that solid-phase gamma-irradiation does not have any 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 [8,49,50]. Hench et al. [51] 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 on the glass surface. In this environment, radiolytic products may rapidly concentrate in this water. In such a high SA/V environment, the bicarbonate present in the small volume of leachate may be quickly overwhelmed by nitric acid produced in radiolysis reactions [44]. 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 sequester elements from the leachate and lower the activity of certain ions in solution, thereby promoting additional dissolution of the glass [42].

Glass waste forms will exhibit temporal variations in both types and intensities of radioactivity. During the first 500 years of repository operation, radiation emissions are expected to be dominated by beta and gamma radiation from ^{137}Cs , ^{90}Sr , and other fission product sources with relatively short half-lives. Alpha particle-emitting actinides generally have much longer half-lives (from hundreds to tens of thousands of years) and thus will become the dominant radiation source at longer times. Because of their low penetrating ability in solids, the alpha and beta particles can interact with the surrounding environment only after the waste container has been breached and the air/water environment of the repository comes in direct contact with the glass. Gamma radiation can penetrate the waste canister walls and interact with the environment surrounding the waste package. However, the relatively short half-lives of gamma-emitting sources lessen their importance as the waste glass becomes older [45].

B. Objectives

The overall purpose of this task is to determine if there are any significant effects of radiation 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). The second objective 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 objective 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 is displayed in Table 10. A minimum of two tests were carried out for each configuration, although in some instances up to four identical tests were performed. These duplications allow the precision of the testing method to be evaluated. For tests utilizing glass monoliths, the composition of the initial glass frit is given in Table 1. The composition of the EJ-13 solution used in batch leach tests is given in Table 2.

Blank experiments have been carried out in several sample configurations, with each test conducted in duplicate. Base-line gamma blank tests were conducted in 22-mL stainless steel Parr test vessels, with enough DIW added to achieve a gas/liquid ratio of 100 L/L at 25°C. These tests will be used to compare NO_3^- yields in a high SA/V environment, which is expected for an unsaturated environment, to results previously obtained at lower SA/V ratios (0.1 to 18) [41]. The present experiments also allow any differences in NO_3^- yield that result from the use of a gamma-radiation source with the present tests instead of the neutron-dominated source of the Linacre study to be evaluated. The matrix of gamma blank tests includes external gamma dose rates of 3×10^3 to 1×10^5 rad/h (30 to 1000 Gy/h); temperatures of 25, 90, and 200°C; and gas/liquid ratios of 10 and 100 (Table 10a).

Alpha blank tests utilized a 1500- μCi ^{241}Am foil attached to either a Lucite or stainless steel support rod. The measured dose rate from these samples is $\sim 3 \times 10^3$ rad/h (30 Gy/h) (Table 10a). This assembly was inserted into a 1.9-liter glass vessel with enough DIW added to achieve a gas/liquid volume ratio of 100 and sealed. Results correlated with gamma-blank tests from this study and the neutron-source tests of Linacre and Marsh [41] allow a comparison of the effects of different types of ionizing radiation on radiolytic production formation. Sample aliquots were taken for anion analysis from both gamma and alpha blank tests, while additional samples for pH and carbon analysis were taken from the alpha blank tests. The surfaces of the test vessels and components from both test types were next sprayed with DIW to collect any condensed radiolytic products. Aliquots of this rinse solution were also analyzed for pH, carbon, and anions.

Experiments with glass monoliths were also performed in the same type of 22-mL stainless steel test vessels used in the gamma blank tests. The glass samples for these tests were cut into $\sim 1 \times 10$ mm wafers. Several different glass compositions were tested, including uranium-doped SRL 131 and 202 compositions and actinide- plus Tc-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 10a. "Effects of Radiation" Sampling Matrix: Alpha and Gamma Blank Tests

Expt. Number	Radiation Type Alpha/Gamma	Temp. (°C)	Test Length (days)	Dose Rate (MR/hour)	Gas/Liquid Ratio (L/L)
IV9000	Gamma	25	7, 14, 28, 56, 120	0.05	100
IV9000	Gamma	25	34, 56, 126	0.003	100
IV1000	Gamma	90	49, 85, 122, 150, 171	0.003	100
IV2000	Gamma	200	49, 122, 156, 171, 180	0.003	100
IV9000	Gamma	25	56, 120	0.003	10
IV9000	Alpha-Lucite Support	25	22, 31, 65	0.003	100
IV9000	Alpha-SS Support	25	14, 33, 45, 60, 63, 110, 129	0.003	100

Table 10b. "Effects of Radiation" Sampling Matrix: Saturated Batch Leach Tests

Expt. Number	Glass Type	Temp. (°C)	Water Type	Test Length (days)
IV9202A	202A	90	EJ-13a	14, 28, 56, 91, 180, 360, 540, 720
IV9165A	165A	90	EJ-13	91, 180, 360, 720
IV9131A	131A	90	EJ-13	14, 28, 56, 180, 360, 720

^aReference groundwater for the Yucca Mountain Site Characterization Project.

Table 10c. "Effects of Radiation" Sampling Matrix: Vapor Hydration Tests

Expt. Number	Glass Type	Temp. (°C)	Water Type	Test Length (days)
IVE202A	202A	200	DIW ^a	7, 14, 21, 35, 56
IVE202U	202U	200	DIW	7, 14, 21, 35, 56
IVE165A	165A	200	DIW	7, 14, 21, 35, 56
IVE131A	131A	150	DIW	7, 14, 21, 35, 56
IVE131U	131U	150	DIW	3, 5, 7, 14, 28, 56, 91, 182, 362, 728

^aDeionized water.

Two types of SA/V tests were conducted on glass monoliths. 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 10b). 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 aliquots to be collected to complete all desired analyses. As with the gamma blank tests, these experiments were exposed to an external gamma source of $\sim 3 \times 10^3 \text{ rad/h}$ (30 Gy/h). Solution aliquots were taken from these tests for analyzing pH, carbon, cation, anion, and filtered size distributions of actinides. Results from these irradiated tests will be directly comparable to 340 m^{-1} nonirradiated tests from the SA/V task (Section VII).

The second type of SA/V test involves exposing glass disks to an irradiated vapor-rich 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 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 surface 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 sample. The experimental temperatures ranged from 150 to 200°C (Table 10c). The elevated temperatures of these experiments are used to accelerate the glass reactions to reasonably short experimental time frames. Previous testing [53] indicates that the glass reaction mechanism and the sequence of secondary phases produced will not change under the range of temperatures examined.

The actinide-and-Tc-99-doped samples were exposed to an external gamma dose rate of $\sim 3500 \text{ rad/h}$ (35 Gy/h), which subjected them to an internal alpha-beta and external gamma source. This 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 time period. Cumulative gamma exposures for the 56-day tests were $\sim 5 \times 10^6 \text{ rads}$ ($5 \times 10^4 \text{ Gy}$). Irradiated and nonirradiated samples were suspended via Pt-Rh and Teflon wires, respectively. Because of the small amounts of solution present in these tests, it was not possible to take aliquots for analysis. Instead, extensive solid phase characterizations were made of altered surface material by utilizing optical microscopy SEM/EDS, XRD, and AEM techniques.

All experiments for the Radiation Effects Task have been completed. Remaining efforts will focus on surface analyses of the reacted glass monoliths from 340 m^{-1} and vapor hydration tests. Efforts will also be directed towards summarizing results into a topical report and several open literature publications.

D. Results and Discussion

1. Blank Tests

Significant amounts of nitrogen acids were produced in the test vessels of all irradiated blank tests. Nitrate and nitrite were concentrated in the surface rinse fraction, indicating that irradiation of an air atmosphere saturated with water vapor results in the concentration of nitrogen acids into thin films of water covering solid surfaces in the test vessel.

Tests run at 25°C with an alpha radiation source indicate a $G(\text{NO}_3^- + \text{NO}_2^-)$ value of 2.4 ± 1.1 . This value is less than the 3.2 ± 0.7 determined for the gamma blank tests at the same temperature. The cause for the lower alpha blank values is probably related to partial attenuation of the alpha particles in the thin film of water contacting the ^{241}Am foils. A large degree of data scatter for most test results may also reflect variable attenuation rates of alpha particles or uncertainties in dose fluxes for individual foils.

Gamma radiolysis blank tests run at 25, 90, and 200°C measure the formation of radiolytic products as a function of temperature. Results indicate that NO_3^- production varies inversely with temperature, with the lowest quantities being detected for the higher temperature experiments (Fig. 12). $G(\text{NO}_3^-)$ values for the 25, 90, and 200°C experiments are 3.2 ± 0.7 , 1.3 ± 1.0 , and 0.4 ± 0.3 , respectively. The 90°C yields are comparable to the $G(\text{NO}_3^-)$ values of 1.9 obtained by Linacre in tests conducted at 80°C. The results indicate that NO_3^- yields for the 90°C experiments are ~40%, while the 200°C yields are ~10% of those that characterize the 25°C results, respectively. These trends are important in that the highest gamma dose rates will occur when the repository temperature is also the highest. Thus, the elevated temperatures expected early on in the repository may reduce the radiolytic effect of greatly lowering the pH.

Gamma radiolysis tests run at high (~50,000 rad/h) and low dose rates (~3500 rad/h) indicate little variation in nitrogen acid yields. G values were 3.2 ± 0.4 for the high dose rate tests at 25°C, while the low dose rate yields were 3.4 ± 0.9 . A comparison of 90°C tests run at different gas/liquid ratios (G/L) also suggest little variation in yields, although there is a considerable degree of data scatter. Tests run at $G/L = 100$ had G values of 1.3 ± 1.0 , while tests at a $G/L = 10$ had a G value = 1.6 ± 0.7 .

Fig. 12. Average NO_x ($\text{NO}_3^- + \text{NO}_2^-$) Production as a Function of Cumulative Exposure and Temperature in Gamma Blank Experiments. Rinse fraction represents total NO_x production for each test. Experimental conditions are the following: temperatures of 25, 90, and 200°C; dose rate is ~3500 rad/h; gas/liquid ratio is 100. The 80°C line is from Linacre and Marsh [41] with $G(\text{NO}_x) = 1.9$.

2. Tests with Glass Monoliths

The second objective of these experiments examines the cumulative effects of radiolytic product formation on the alteration of a simulated borosilicate waste glass. To examine these parameters, glasses of near-identical compositions were reacted under variable SA/V conditions in both gamma radiation and nonradiation fields. The gamma irradiated test samples were also doped with ^{99}Tc and transuranic isotopes (^{237}Np , ^{239}Pu , and ^{241}Am).

a. 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 studies 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 that formed as the solution contacting the glass became saturated with leached components.

1. Layer formation

The irradiated 202A monoliths had completely reacted through their 0.7- to 0.9-mm thicknesses within the first 14 days of testing, suggesting a glass reaction rate that locally exceeded $30\ \mu\text{m}/\text{day}$. The alteration layer progressed nonuniformly into these samples with rapidly developed alteration fronts occurring along preferential zones, which may be fractures, that completely enveloped rounded and apparently unaltered glass cores. In some regions the remnant cores remained intact; in others they were highly fractured, but otherwise appeared unaltered during optical examinations. It is not known whether the fracturing is related to release of thermal stresses incorporated during sample casting (the glasses were annealed prior to testing) or to stresses induced by water diffusion into the glass, or whether it is a result of radiation damage to the glass. Radiation damage appears to offer the least plausible explanation because damage zones would be expected to be uniformly distributed throughout the samples and the cumulative $\sim 10^6$ rads (10 Gy) these samples received is two to three orders of magnitude less than that generally required to cause structural damage [54,55].

After 35 to 56 days, the remnant glass cores in the 202A tests were completely replaced by a mottled or banded, microcrystalline, Si- and Fe-rich material (Fig. 13a). Up to three additional layers, some of which were also banded, enveloped this Si-Fe core. The layer immediately overlying the Si-Fe core was a brownish gel that was lighter in color at its base and displayed numerous dissolution pits at its surface. Its composition is consistent with presence of nontronite and saponite clays. Overlying this brown layer is a thin sheet of white, fine-grained, ameboid shaped, Ca-Si crystals. This thin Ca-Si layer was, in turn, overlain by a heterogeneous mixture of crystalline material that had intergrown to an extent where it behaved as a cohesive layer. A number of individual crystalline phases were identified in this layer, including tobermorite, adularia, haiweeite, Na-weeksite, and a fine-grained material with a morphology and composition consistent with smectite or mixed-layer smectite/illite clay.

Fig. 13. SEM Photomicrographs of SRL 202 Glasses Reacted for 35 Days in a Saturated Vapor Environment at 200°C. Horizontal white bars on photos (a) and (c) are artifacts of photography. (a) Secondary electron image (SE) of auto-fractured section of 202A glass shows banded textured Si-Fe core material (200X). (b) Backscattered electron image (BSE) of polished cross section of 202U glass shows (from bottom to top) unaltered glass, inner smectite layer, outer illite layer, and precipitate cover (1000X). (c) BSE image of reacted 202A glass surface displays large stellate weeksite, large trapezo-hedron, and dimpled analcime (deposits on Pt-Rh wire running from lower left to upper right), bright BSE images of fine-grained Na-weeksite phase (bright linear and curved BSE features result from Ag mounting medium that has impregnated fractures 50X). (d) SE image of reacted 202U glass surface displays large dimpled analcime, fine-grained adularia buttons, Ca-Si rosettes, and Si-K-Ca-S-Al-Na needles (100 X).

The 202U samples reacted without external radiation developed a ~130- μm alteration layer only after 56 days of reaction. Two separate layers were identified on 202U glasses. An *in situ* layer of smectite was detected on the surfaces of all 202U samples terminated prior to 21 days of testing. This layer was depleted in Na, Mn, and K, but contained more Mg, Ti, Fe, and Ca than the unaltered glass [56]. Major d-spacings measured from selected area diffraction patterns combined with the compositional analyses indicate that this layer is composed of nontronite and ferroan saponite clays. After 35 days, the smectite was blanketed with a layer of high-albedo clay material (Fig. 13b). Compositional and XRD analyses identified this layer as illite. Small amounts of illite were also detected on the support wires for these samples indicating that this phase precipitated from solution in contact with the glass surface. A comparison of the rate of alteration layer development between irradiated and nonirradiated tests indicates that layer development may be accelerated by a factor of ~15 due to radiation exposure at high SA/V conditions.

Optical surveys of SRL 131 and SRL 165 glasses also indicate that the irradiated samples are more extensively altered than their nonirradiated counterparts. The 165A glasses also displaying localized mounds of altered material that suggest internal voids may have developed during testing. More detailed examinations of these samples will be performed in the future.

2. Surface precipitates

Alteration patterns for both the irradiated and nonirradiated SRL 202 glasses were characterized by the formation of a variety of zeolite, clay, Ca-Si, and alkali or alkaline earth uranyl silicate phases. Faster glass alteration rates are observed in an irradiated vapor-rich environment as evidenced by the greater abundance of secondary precipitates on the sample surfaces (Figs. 13c and 13d). A comparison of the paragenetic sequences for both test types indicates that secondary mineral formation has also been accelerated in the irradiated tests relative to the nonirradiated tests (Fig. 14). For example, analcime, weeksite, phillipsite, and adularia were detected after shorter reaction times in tests with 202A than with the 202U glass. The transient phase herschelite formed early in the 202U tests, but was not detected on any of the 202A samples, although it is possible that herschelite first precipitated and then dissolved before the first samples were collected at seven days. A number of secondary precipitates were also observed only on the 202A samples, the most notable being the uranyl silicates Na-weeksite, boltwoodite, and haiweeite.

Electrons accelerated to 30 kV were also utilized during SEM/EDS analysis to excite the L-shell electrons of the transuranic elements. Transuranic elements were not detected in any of the secondary phases examined, suggesting that these elements were retained at concentrations below detectability within the *in situ* alteration layers (~0.5 wt %). More sensitive autoradiography techniques will be employed in future studies to better characterize the distribution of transuranics within altered glass profiles.

Optical examinations of irradiated 165A glasses displayed a relatively simple mineralogical sequence with the precipitation of analcime, weeksite, adularia, and the unidentified Ca-Si rosette phase. The mineralogical sequence developed on the 165U glasses was similar to that of the 165A samples, except that tobermorite and calcite were identified on the former. Optical examinations of irradiated 131A glasses were characterized by the development of weeksite, herschelite, phillipsite, analcime, and several unidentified phases. Secondary phases on the 131U glasses include herschelite, analcime, calcite, and a number of unidentified phases.

Fig. 14. Alteration Mineral Paragenetic Sequence Identified for SRL 202 Glasses. Solid lines represent 202U samples while dotted lines represent 202A glass reactions.

b. Batch Leach Tests

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 and for time periods ranging from 14 to 720 days. Results from solutions in contact with the glass samples show invariant temporal paths for the anions F⁻, Cl⁻, SO₄⁼, COOH⁻, and C₂O₄⁼. These trends suggest that the presence of reacting glass in the tests at this SA/V 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. 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 [41]. 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. 1 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 2 also demonstrates that increased NO₂⁻ stability may be influenced by catalytic decomposition of radiogenic H₂O₂ by Fe- and Mn-oxides forming on the altered glass surface [51].

Analyses of 202A and 131A samples show that their pHs appear to have leveled out at ~9 after displaying an early increase between 56 and 180 days (Fig. 15). 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 and alkaline earths are released from the glass in concentrations greater than that necessary to neutralize the H⁺ ions dissociated from radiolytic acids. In longer term tests, a buildup of radiolytic acids in the leachate results from a decrease in the rate of ion exchange with the glass. An examination of cation solution results for tests up to 360 days indicates a decrease in the rates of Na, Li, K, and B release to solution after 180 days [2]. While these decreased release rates in themselves are not *a priori* evidence for decreased glass reaction rates (i.e., sequestering of elements by secondary alteration phases may also decrease element concentrations), their decrease after 180 days coincides with the timing of the pH change, thus supporting the contention that a change in the rate of the ion exchange process occurs.

The 165A glass samples continued to display increasing pH values throughout the duration of the tests (Fig. 15). This trend probably reflects that this glass composition exhibits relatively greater resistance to alteration than the 131A and 202A glasses, and that the ion-exchange reaction is the dominant reaction process over the term of the test. This glass appears to continually release alkalis in more than sufficient quantities to reduce buildup of radiolytic acids, thereby allowing for continued increases in pH of the test solution.

Fig. 15. Solution pH Results from 340 m^{-1} Batch Leach Tests at 90°C . SRL 202A, 165A, and 131A samples were doped with $23 \mu\text{Ci/g}$ alpha radiation source and exposed to external gamma dose rate of $\sim 3000 \text{ rad/h}$. SRL 202U samples (dotted line) represent average value for U-238 doped glass reactions without any external gamma exposure.

Alpha counting results for unfiltered, $50 \text{ \AA}$ -filtered, and test vessel acid strip aliquots from the 340 m^{-1} batch tests have been compiled for all results up to one year in duration. Data trends indicate that the Am and Pu released from the glass samples is concentrated predominantly by the acid strip component. The portion of Am and Pu recovered from the $<50 \text{ \AA}$ fraction is negligible for most time periods (Figs. 16a and 16b). These data indicate that most of the Am and Pu released from the glass subsequently plate out on the stainless steel vessel walls, while the remainder of the released fluid component is dominated by particulates $>50 \text{ \AA}$. These results are of interest because they indicate that (1) stainless steel waste canisters may adsorb Am and Pu from solution and thus may retard the release of Am and Pu from the repository and (2) Fe-oxide particulates and colloids present in natural groundwaters may serve as carriers for actinide migration.

An accurate determination of the aliquot concentrations of Np is complicated by the relatively small ^{237}Np peak heights and an overlap of the ^{237}Np with the ^{239}Pu spectra. Despite this caveat, the release of Np is dominated by the $<50 \text{ \AA}$ fraction (Fig. 16c). Recovery of a plate-out fraction of Np is generally negligible, although some increase is noted in the 360-day tests. These trends indicate that Np release is dominated by a soluble or fine colloidal ($<50 \text{ \AA}$) suspension in these tests.

Fig. 16. Actinide Release from 340 m^{-1} Batch Leach Tests. Data presented in total ng released as a function of time. (a) Am release, (b) Pu release, and (c) Np release.

Optical examinations have also been completed on all 202A, 165A, and 131A batch leach samples completed thus far. The altered surfaces are characterized by the progressive development of a white clay-like layer that progressively thickens with time. After one year of reaction, the alteration layer had increased in thickness to a point where it masked the presence of the original sample polishing surface scratches. All sample surfaces were characterized by the development of thin alteration layers, with the surfaces from the 202A samples also showing some evidence for delamination of the altered layers for samples run for 1.5 and 2 years in duration.

E. Future Progress

More detailed interpretation of solution results will be made as remaining analytical results are received and evaluated. Detailed surface analyses of glass monoliths will continue to be performed, with results being integrated with the solution analyses. Surface investigations will include detailed SEM/EDS, XRD, and AEM investigations. Results will be compiled into a series of papers to be published in the open literature.

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

A. Introduction and Background

Static leach tests are being used to measure the durabilities of borosilicate glasses that may be used in the vitrification of high-level waste and will be used to measure the product consistency of glass produced by the Defense Waste Processing Facility (DWPF). The ranges of many test variables used for testing glasses destined for use in waste disposal are defined by factors in the anticipated repository environment (e.g., temperature, pressure, and groundwater chemistry) or by testing constraints at the processing facility. The effects of test variables on the measured response need to be understood before using their results of such tests to assess the durability of waste glass in various environments.

An important test variable in static leach tests is the glass surface area/leachant volume ratio (SA/V). Its major effect on the glass reaction is through dilution of the reaction products: tests at low SA/V have larger volumes of solution per unit area of glass than do tests at higher SA/V and thus dilute reaction products to a greater degree. The solution concentrations of tests at lower SA/V will, therefore, change at a lower rate per unit mass of glass reacted than those of tests at high SA/V. Since the rate of glass reaction is known to depend on the solution chemistry, the response of a glass in tests at different SA/V may be different because of the difference in dilution and both the dominant reaction step and the rate of glass reaction measured in a leach test may change as the SA/V is varied.

Two static leach tests used to measure the durability of glass produced for the purpose of high-level nuclear waste disposal are the MCC-1P test, which measures the response of glass monoliths at an SA/V of 10 m^{-1} , and the Product Consistency Test (PCT), which measures the response of powdered glass at an SA/V of about 2000 m^{-1} . Both tests are usually performed at 90°C with DIW as the leachant for short time periods (usually 7 to 28 days). Because of the different SA/V used in these tests, the leachates in the PCT will become concentrated at a greater rate than the leachates in the MCC-1P test as the glass reacts. Differences in the resulting solution chemistries may then affect both the mechanism and the rate of glass reaction. It is necessary to understand changes in the reaction which occur as the SA/V changes in order to relate the glass durabilities measured in tests at different SA/V.

The results of static leach tests have also been used to derive the algorithm to describe the glass reaction kinetics for computer models used to predict long-term glass behavior under potential repository environments. These models often rely on rate parameters that are regressed from experimental data. The parameters used in computer simulations must be demonstrated to apply to tests other than those from which they were derived. Because it is the long-term reactivity of glass that is of interest, laboratory tests that accelerate the glass reaction are preferred for comparison to model predictions. Performance of tests at high SA/V has been suggested as an experimental means of accelerating the glass reaction progress to simulate long-term behavior wherein tests performed at equivalent products of SA/V and the reaction time are assumed to produce equivalent extents of glass reaction. Before tests at high SA/V can be used to model long-term reaction behavior, it must be demonstrated that the reaction mechanism is the same in laboratory tests at high and low SA/V ratios, that similar reaction paths are followed at different SA/V, or that differences can be accounted for in the model.

B. Objectives

The objective of this task is to assess the effects of the SA/V of a static leach test on the mechanism and rate of the glass reaction. Tests are designed to monitor changes in both the leachate and the reacted glass surface as a function of the SA/V, the reaction time, and the leachant solution. The results of these tests will provide insight into comparison of tests performed at different SA/V, including the MCC-1 and PCT tests, the influence of the SA/V on the secondary phase assemblage, and the use of SA/V as an accelerating parameter for static leach tests.

C. Technical Approach

Static leaching experiments were performed at 10, 340, 2000, and 20,000 m⁻¹ at 90°C for up to two years using two simulated high-level nuclear waste glass compositions representative of the waste form to be produced by the DWPF. Tests were performed to compare the reaction in a dilute leachate solution generated under the MCC-1 test condition of 10 m⁻¹ to that in a more concentrated solution generated under PCT conditions at 2000 m⁻¹. Other tests were performed at 340 and 20,000 m⁻¹ using monoliths or powdered glass. Tests were performed with DIW and with a modified J-13 groundwater, which is a reference groundwater of the Yucca Mountain Project, to assess the effects of the SA/V under site-relevant conditions, and with DIW. Reaction times were selected to demonstrate the temporal reaction trends and to compare data obtained from tests run for equivalent products of (SA/V)•time. The leachate solutions and reacted solids were analyzed to compare the mechanism and kinetics of the glass reaction at different SA/V ratios. These tests were performed to provide detailed solution results with accompanying solids analyses for future comparison with computer simulations.

Samples were prepared from SRL 131 and SRL 202 glass provided by Westinghouse Savannah River Company (WSRC). The glass was doped with Tc, U, Np, Pu, and Am, and then cast into bars. These actinide-doped glasses are referred to as SRL 131A and SRL 202A. Another glass, which is referred to as SRL 202U, was made by doping SRL 202 with U only. Cores approximately 1 cm in diameter were drilled from the bars and sectioned into disks approximately 0.9 mm thick. All surfaces of the disks were then ground to a final 600-grit finish. The remaining glass in the bars were crushed and sieved to separate the -100+200 mesh (74-149 µm) fraction for use in tests at 2000 and 20,000 m⁻¹. Both the monolith and powdered samples were washed to remove fines, and representative samples were surveyed in an SEM to verify acceptability prior to use and to assure that no measurable alteration had occurred during sample preparation. The surface area of the powdered glass was approximated using the average mesh openings of the sieves; assuming cubic particle geometry, it was calculated to be 2×10^{-2} m²/g. This nominal particle size was confirmed using an SEM. The geometric surface areas of the monolith samples were measured directly.

Tests with SRL 131A and SRL 202A glass were performed in 304L stainless steel vessels in a constant temperature circulating air oven; those with SRL 202U glass were performed in Teflon vessels in a constant temperature water bath. A nominal SA/V of 10 m⁻¹ was achieved by placing one monolith disk in about 17 mL of leachant. Ratios of 2000 and 20,000 m⁻¹ were achieved by placing 1 or 5 g of powdered glass in 10 or 5 mL of leachant, respectively. This provided sufficient leachate for solution analysis after each test. The leachates from tests with powdered glass were filtered through preheated 0.45-µm filters while still near the reaction temperature to remove any suspended glass particles prior to analysis. This filtrate and the unfiltered leachate from tests with monoliths were analyzed for pH, anions, and cations, including actinides. The steel reaction vessel was stripped using a nitric acid

solution to measure the amounts of transuranics sorbed onto the vessel. Solutions from tests with glasses doped with transuranics were further filtered through 6 nm filters to remove colloidal material, and the filtrate was analyzed for transuranics. Enough solution was filtered through 6-nm filters in some tests to allow additional cation analyses.

The reacted solids were rinsed gently with DIW and allowed to dry before analysis. Representative samples were analyzed using SEM with X-ray emission analysis to characterize the surface alteration and the secondary phases that were formed. Samples were also fixed in epoxy resin and cross-sectioned to characterize the structural and compositional changes accompanying reaction, and to measure the depth of alteration. Some samples were thin-sectioned using an ultramicrotome and analyzed by AEM to characterize the altered glass surface or to identify other secondary phases that may have formed.

D. Results and Discussion

1. Leachate pH

The leachates from tests at 10 m^{-1} and the filtrates from tests at 2000 and 20,000 m^{-1} were allowed to cool to room temperature before analysis. The pH values were measured using a combination electrode. The average pH of duplicate tests with SRL 131A and SRL 202A reacted in EJ-13 are plotted versus the reaction time in Figs. 17a and 17b. Differences in duplicate tests were generally within about 0.2 pH units, except for tests at 10 m^{-1} reacted 232 or 600 days, where the results differed by about 0.6 pH units. The higher pH values of these tests are plotted. The curves are drawn in the figures to show the trends of the pH increases and do not represent an analytical fit to the data. The measured pH in tests with both glasses at 2000 and 20,000 m^{-1} are significantly higher than the pH of the initial leachant (i.e., 8.15) at all reaction times. Tests at 20,000 m^{-1} attain higher pH values than tests

Fig. 17. Leachate pH vs. Reaction Time of Tests with SRL 202A and SRL 131A Glass at (•) 10, (□) 2000, and (◇) 20,000 m^{-1}

at 2000 m^{-1} at all reaction times. The pH increases only slightly above the initial leachant pH in tests at 10 m^{-1} . Leachates from tests with SRL 131A generally had higher pH values than tests with SRL 202A at the same SA/V after the same reaction time. The pH values increase slightly with time in all tests, although several small incremental increases are evident. Tests with SRL 202A glass show increases between about 140 and 280 days at 2000 m^{-1} and between 182 and 364 days at $20,000\text{ m}^{-1}$. Tests with SRL 131A show increases between 140 and 280 days at 2000 m^{-1} and between 98 and 232 days at 10 m^{-1} . The pH values of tests before and after these increases are nearly constant. Tests with SRL 131A at $20,000\text{ m}^{-1}$ show a nearly constant pH at all times tested.

2. Elemental Release

The leachate and filtrate solutions were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and fluorescence spectroscopy. Figures 18 and 19 show the normalized elemental mass losses of several glass components from SRL 131A and SRL 202A glass at 10 , 2000 , and $20,000\text{ m}^{-1}$ that were computed from the leachate (10 m^{-1}) and from $0.45\text{ }\mu\text{m}$ -filtered solutions (2000 and $20,000\text{ m}^{-1}$). The normalized mass loss of an element is simply the measured solution concentration of that element less the amount present in the initial leachant divided by the product of the test SA/V and the mass fraction of that element in the original glass. The release of different glass components from SRL 131A and SRL 202A can be compared directly using this function. Figures 18 and 19 show that the release of Li, Na, K, B, Si, and U from both glasses into solution is nonstoichiometric with respect to the glass composition at all SA/V ratios tested. Table 11 shows the relative release rates of these elements for the two glasses at the three SA/V ratios. The order given is that measured at the longest time tested. The order varies with the reaction time under some test conditions. For example, lithium is initially released to the greatest degree in tests with both glasses at 2000 m^{-1} and in tests with SRL 202A at $20,000\text{ m}^{-1}$ and then decreases at longer reaction times.

The reaction rate also varies with the reaction time. Consider the boron release to represent the glass reaction rate and the data for SRL 202A reaction at 2000 m^{-1} in Fig. 19b. Initially, the boron concentration increases at a high rate through about 56 days, but the release slows as the reaction progresses. (This occurs in tests with both glasses and at all SA/V, but is seen most clearly in Fig. 18b.) The normalized boron release varies approximately as the square root of time over the reaction progress. As the reaction progresses under several test conditions, however, the boron release rate suddenly increases and becomes nearly linear with time. This occurs in tests with SRL 202A and SRL 131A at $20,000\text{ m}^{-1}$ after about 182 days and in tests with SRL 131A glass at 2000 m^{-1} after about 140 days. Tests with SRL 131A at 10 m^{-1} may also show an acceleration of the boron release, but the data increase with a nonlinear time dependence. Most likely, the release trend over 600 days is slowly decreasing with the 98-day data being anomalously low. The releases of sodium and potassium appear to be accelerated at the same time, but at a slower rate than boron. The lithium release shows more complicated behavior: it increases linearly in tests with SRL 202A at $20,000\text{ m}^{-1}$, but appears to reach maximum concentrations in tests with SRL 131A glass at 2000 and $20,000\text{ m}^{-1}$.

The silicon concentrations are only slightly increased when boron shows accelerated release in tests at 2000 and $20,000\text{ m}^{-1}$. In tests with SRL 131A at 10 m^{-1} , however, the silicon concentration is near the initial leachant concentration at reaction times through 98 days; then it increases significantly at 232 and 600 days.

Fig. 18.
Normalized Elemental Mass Loss
from SRL 202A Glass. Tests were
run at (a) 10, (b) 2000, and
(c) 20,000 m⁻¹, for (■) Li, (▲) Na,
(●) B, (◆) K, (○) Si, and (□) U.

Fig. 19.
Normalized Elemental Mass Loss
from SRL 131A Glass. Tests were
run at (a) 10, (b) 2000, and
(c) 20,000 m⁻¹, for (■) Li, (▲) Na,
(●) B, (◆) K, (○) Si, and (□) U.

Table 11. Relative Elemental Release Rates from SRL 131 and SRL 202A at Three SA/V Ratios

Glass	SA/V		
	10 m ⁻¹	2000 m ⁻¹	20,000 m ⁻¹
SRL 131	Na > B > Li > K > Si > U	B > Na > K > Li > Si > U	B > Na > K > Li > Si > U
SRL 202A	Na > Li = B = K > Si > U	Li > Na > B > K > Si > U	B > Na > K > Li > Si > U

3. Effect of Filtration

Further filtration of the leachate through 6-nm filters resulted in decreases in the concentrations of some components in tests at 2000 and 20,000 m⁻¹. Components with high solubilities were not reduced by filtration beyond the analytical error limits, which were about $\pm 10\%$. Filtration did not affect the boron, alkali metal, and silicon concentrations, but it reduced the concentrations of other glass components. Reductions in the concentrations were measured for tests with SRL 202U, SRL 202A, and SRL 131 glasses at all SA/V ratios tested. Table 12 shows the measured concentrations of aluminum, iron, silicon, and boron in the 0.45- μm and 6-nm filtrates of tests with SRL 202U glass in EJ-13 at 20,000 m⁻¹. Notice in Table 12 that the aluminum and iron concentrations in the 0.45- μm filtrates increase with the reaction times through 14 days, but then decrease to low values at longer times. The silicon and boron concentrations increase with the reaction time at all times tested. Large increases in the silicon and boron concentrations are measured in both the 0.45- μm and 6-nm filtrates after 364 days of reaction, indicating an acceleration of the reaction. This is consistent with the increased rate of reaction of SRL 202A glass in Fig. 19c.

4. Transuranic Release

The amounts of transuranics that were suspended and dissolved in the leachate or sorbed onto the vessel walls were measured using alpha-spectroscopy. The aqueous fraction was measured using the 0.45- μm filtrate to ensure that no suspended glass particles were included in the aliquots. The concentrations of dissolved transuranics were obtained by further filtering the solutions through 6-nm filters. The sorbed fraction was determined by analyzing the nitric acid solution used to strip the vessel. The amounts of Np, Pu, and Am measured in tests with SRL 131A and SRL 202A glasses at 2000 and 20,000 m⁻¹ are plotted against the reaction time in Figs. 20 and 21. In tests with SRL 131A glass at 2000 m⁻¹, very little of the plutonium or americium released from the glass stays in solution either dissolved or suspended. Rather, they are sorbed onto the steel vessel. Neptunium levels in the leachate increase at short reaction times, but decrease as the reaction progresses; little of it is sorbed onto the vessel. At 20,000 m⁻¹, the solution levels of all transuranics are very low, and most of the released Np, Pu, and Am is sorbed onto the steel vessel walls.

The solution levels of the transuranics released from SRL 202A glass at 2000 m⁻¹ reach near-constant values after short reaction times. The amounts of Pu and Am sorbed onto the vessel increase with the reaction time, but Np is not sorbed to the vessel. At 20,000 m⁻¹, the amounts of the three transuranics in solution increase initially, but then decrease to very low values after about 56 days, while the amounts of all three sorbed onto the vessel increase with the reaction time.

Table 12. Effect of Filtration on Leachate Analysis for 202U Glass in EJ-13 Water at 20,000 m⁻¹

Test No.	Reaction Time (days)	pH ^a	Al, ppm		Fe, ppm		Si, ppm		B, ppm	
			0.45 µm ^a	6 nm ^b	0.45 µm	6 nm	0.45 µm	6 nm	0.45 µm	6 nm
1	3	10.86	5.23	1.26	25.7	0.38	276	243	75.3	73.5
2	3	10.89	5.42	1.25	26.8	0.38	283	243	77.0	75.0
3	7	11.03	9.18	1.31	44.2	0.30	351	267	93.8	85.9
4	7	11.01	8.33	-	38.2	-	338	-	92.8	-
5	14	11.23	11.5	-	51.7	-	411	-	111	-
6	14	11.28	12.1	<2.5	54.9	0.75	417	323	111	107
7	28	11.37	6.05	1.80	18.5	0.28	361	360	119	127
8	28	11.38	3.85	1.93	8.37	<0.19	350	362	121	128
9	56	11.37	1.55	-	0.50	-	381	-	148	-
10	56	11.41	1.52	-	0.37	-	385	-	149	-
11	91	11.40	<1.3	<1.1	0.66	<0.23	429	440	177	182
12	91	11.38	2.33	1.70	0.24	<0.23	436	446	180	181
13	182	11.63	1.12	<1.64	0.173	<0.328	562	532	246	230
14	182	11.66	1.21	<1.72	0.173	<0.345	567	539	244	229
15	364	11.75	<2.86	1.3	1.43	0.602	1064	971	3489	3400

a) Filtrate solution from 0.45-µm filtration.

b) Filtrate solution from approximately 6-nm filtration.

Fig. 20. Amounts of Np, Pu, and Am Released from SRL 202A in Tests at 2000 m⁻¹ and at 20,000 m⁻¹. (●) Total mass release into solution, (■) total mass dissolved into solution, and (▲) total mass sorbed onto steel vessel.

Fig. 21 Amounts of Np, Pu, and Am Released From SRL 131A in Tests at 2000 m⁻¹ and at 20,000 m⁻¹. (●) Total mass release into solution, (■) total mass dissolved into solution, and (▲) total mass sorbed onto steel vessel.

5. Solids Analysis

The reacted glass surface was analyzed using SEM and AEM. Figure 22 shows the altered layer formed on the surface of SRL 202U glass reacted in EJ-13 for 14, 182, and 364 days. The layer is crystalline, even after only 14 days. Note that the layer has separated from the underlying glass after 14 and 182 days. The layers were depleted in sodium and enriched in transition metals and alkaline earths at all reaction times. The layers are also presumed to be depleted in lithium and boron. Longer reaction times through 182 days result in an increase in the thickness of the layer, but no significant change in morphology or composition. After 364 days, a large increase in the thickness of the layer and a change in the morphology of the layer can be seen. Energy dispersive X-ray spectroscopy (EDS) analyses of the inner and outer portions of the layer give similar compositions. The outer portion of the layer appears similar to the layers formed at shorter reaction times, but the inner portion is different. Selected area electron diffraction (SAED) of the outer and inner parts of the layer formed after 364 days shows that both are smectite clay (which is consistent with the composition), but that the inner portion of the layer has smaller domain size and is more randomly oriented. Notice that there is a sudden transition between the inner and outer portions of the layer and that the inner portion of the layer has not separated from the underlying glass. This is in contrast to the layers formed at shorter times, which were separated from the glass.

AEM analysis of the reacted solids has also shown the presence of weeksite, clinoptilolite, and an amorphous silicon phase. The two latter phases have only been seen in tests that have been accelerated, and may be responsible for the acceleration. Computer modeling of the long-term glass reaction has shown that secondary phases which form during the reaction may reduce the silicic acid concentration in solution. Because the reaction rate is controlled primarily by the silicic acid concentration, the formation of these phases accelerate the reaction rate. Work is in progress to relate changes in the measured solution composition to changes in the reaction rate and the formation of secondary phases.

6. Discussion

The test results allow the comparison of glass samples with different compositions (SRL 131 vs. SRL 202), with the presence and absence of doped transuranics (SRL 202A vs. SRL 202U), with different glass surface preparations (polished monoliths vs. fractured crushed glass), and with different surface area/leachant volume ratios (10, 340, 2000 and 20,000 m⁻¹). The different comparisons are discussed separately.

The preponderant physical effect of the SA/V used in a test is through the dilution of the reaction products. This is seen clearly to affect the leachant pH values that are attained. The pH increases as alkali metals in the glass exchange ions with protons from water molecules. The reaction generates hydroxide, which may be released into the solution. Tests with high SA/V have less solvent to dilute hydroxide generated by ion exchange reactions than tests at lower SA/V; therefore, the pH may increase to high values after very little hydroxide is produced. That is, if the same amount of hydroxide is produced by the glass reaction in tests at 2000 and 20,000 m⁻¹, the pH of the tests at 20,000 m⁻¹ will be one pH unit higher due to the difference in dilution. Of course, the pH will affect the glass reaction rate so that the rate of hydroxide generation will be different in tests at different SA/V even at short reaction times. As seen in Fig. 17, the difference in the pH in tests with SRL 202A glass at 2000 and 20,000-m⁻¹ at long reaction times is greater than 1 unit. The difference in tests with SRL-131A at 2000 and 20,000 m⁻¹ is initially greater than 1 unit, but is less than 1 unit at longer times. Tests at 10 m⁻¹ are expected to have pH values about 2.3 pH units lower than tests at 2000 m⁻¹, based solely on dilution effects. Tests with SRL 131A glass at 10 and 2000 m⁻¹ differ by about 2.3 units, but the difference is less in tests with SRL 202A glass.

Fig. 22. Photomicrographs of Cross-Sectioned Reacted Glass Surfaces of SRL 202U Reacted in EJ-13 for (a) 14, (b) 182, and (c) 364 days

Differences in SA/V also affect the release of other glass components. The results plotted in Figs. 18 and 19 show that the normalized elemental mass losses are affected by the SA/V. The values plotted have been normalized to the SA/V to account for differences in dilution, although the surface area is assumed to remain constant throughout the reaction period. If the reaction rates are the same in tests at different SA/V ratios, then the normalized released rates should also be the same. However, the results in Figs. 18 and 19 show that the normalized release rates are different at different SA/V ratios. These results demonstrate that the glass reaction rate and/or mechanism is affected by the different solution chemistries. For each glass composition, the normalized elemental mass losses measured in tests at different SA/V ratios can be compared directly. The initial and final rates can be approximated by the results of the shortest and longest test durations. The measured reaction rates are given in Tables 13 and 14 for the short-term and long-term tests. The component showing the greatest release to solution was used to measure the rate. SRL 131A glass shows the long-term reaction to be fastest at 10 and 20,000 m^{-1} and slowest at 2000 m^{-1} , while the long-term reaction of SRL 202A glass is fastest at 20,000 m^{-1} and slowest at 2000 m^{-1} . The short-term rates are greatest at 10 m^{-1} for both SRL 131A and SRL 202A glasses. The long-term reaction rate of SRL 202U is similar to that of SRL 202A and is similar in EJ-13 and DIW at 20,000 m^{-1} .

Instead of plotting the normalized elemental mass loss against time, as in Figs. 18 and 19, the measured concentrations can be plotted against the product of the reaction time and the SA/V of the test. The product $(\text{SA/V}) \cdot t$ has been suggested to be a single parameter that can be used to measure the extent of glass reaction, meaning that tests at different SA/V ratios but equivalent $(\text{SA/V}) \cdot t$ products should yield the same extent of glass reaction. The boron data for SRL 131A and SRL 202A glass are plotted against $(\text{SA/V}) \cdot t$ in a log-log plot (Fig. 23). Data from replicate tests are plotted to show the scatter in the data and any differences in reactivity that may be masked by plotting average values. Tests at 2000 and 20,000 m^{-1} performed for equivalent $(\text{SA/V}) \cdot t$ products clearly do not generate equivalent solution compositions for either glass. Tests with SRL 131A show a larger difference than tests with SRL 202A. Although duplicate tests at 10 m^{-1} show significant scatter, some tests at 10 m^{-1} have boron concentrations similar to those in tests at 2000 m^{-1} .

Table 13. Measured Reaction Rates (Short-Term/Long-Term)
at Different SA/V Ratios

Glass	SA/V, $\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$		
	10 m^{-1}	2000 m^{-1}	20,000 m^{-1}
SRL 131A ^a	1.0(Na) ^b /0.05(Na)	0.40(Li)/0.02(B)	0.86(B)/0.04(B)
SRL 202A ^a	1.1(Na)/0.02(Na)	0.35(Li)/0.001(Li)	0.06(Na)/0.03(B)
SRL 202U ^a			0.07(Li)/0.04(B)
SRL 202U ^c		0.14(Li)/0.001(Li)	0.06(Li)/0.04(B)

^aReacted in EJ-13 solution.

^bComponent on which rate is based.

^cReacted in DIW.

Table 14. Measured Reaction Rates (Short-Term/Long-Term) at Different SA/V Ratios Based on Boron Release

Glass	SA/V, g•m ⁻² •d ⁻¹		
	10 m ⁻¹	2000 m ⁻¹	20,000 m ⁻¹
SRL 131A ^a	0.14/0.051	0.25/0.02	0.86/0.04
SRL 202A ^a	0.10/0.01	0.03/0.0005	0.01/0.03
SRL 202U ^a			0.05/0.04
SRL 202U ^b		0.10/0.0008	0.05/0.04

^aReacted in EJ-13 solution.

^bReacted in DIW.

Fig. 23 Log([B]) vs. Log((SA/V)•t) for Tests with SRL 202A Glass and SRL 131A Glass at (●) 10, (■) 2000, and (♦) 20,000 m⁻¹. Lines drawn with slope of 1 through data at 20,000 m⁻¹.

The data plotted in Fig. 23 can be further interpreted based on the current model of the glass reaction rate, which can be written as

$$[B] = (SA/V) k (1 - Q/K)t + R_f \quad (3)$$

or

$$\log([B]) = \log[k (1 - Q/K)] + \log[(SA/V) \cdot t] + \log(R_f) \quad (4)$$

where k is the forward reaction rate coefficient, $(1 - Q/K)$ is the reaction affinity, and R_f is the "final rate." The affinity term is generally written with Q as the silicic acid concentration in solution and K as the saturation concentration of silicic acid. The final rate, R_f , is the rate when the solution is saturated (i.e., when $Q = K$). According to the above equation, the short-term data in a plot of $\log([B])$ vs. $\log[(SA/V) \cdot t]$ will yield a slope of 1 and a y-intercept equal to the log of the rate coefficient times the reaction affinity. The short-term data represent the forward rate of glass reaction under dilute conditions where the reaction affinity term is near one (i.e., $Q = 0$). Longer-term data are expected to deviate negatively from the line fit to the short-term data as the silicic acid concentration increases, the affinity term decreases, and the reaction rate decreases until a minimum rate is reached. The glass reaction then continues at a low, constant rate after saturated conditions are achieved and the affinity term remains near zero. The y-intercept of the line of unit slope drawn through the long-term data represents the final dissolution rate under saturated conditions. The above analysis assumes that the rates of reaction under the dilute conditions of the forward rate and the saturated conditions of the final rate are both constant and linear in time. The effects of the leachate pH on the reaction rate (both in k and R_f) are implicitly included in the analysis because the experimental data at short and long durations are used to determine the rates under the achieved conditions. Other rate laws, such as those for diffusion-limited reactions, may not be amenable to this analysis.

Lines with a slope of 1 are shown in Fig. 23a for the data of tests run at $20,000 \text{ m}^{-1}$ with SRL 202A glass. Short-term data do not show a constant reaction rate; instead the rate decreases with the reaction progress. A line with a slope of 1 is therefore drawn through the data point of the test run for the shortest time. This line has a y-intercept (at $\log[(SA/V) \cdot t] = \text{zero}$) of about $\log[B] = -3$. Dividing this value by the atomic fraction of boron in SRL 202A glass, which is 0.0248, the initial rate (based on the boron release) is about $0.04 \text{ g/m}^2/\text{day}$. This represents a minimum approximation of the forward rate for tests with SRL 202A at $20,000 \text{ m}^{-1}$. Another line is drawn through the intermediate-term data which has a y-intercept of about -4. This corresponds to a rate of about $0.004 \text{ g/m}^2/\text{day}$, which is the minimum rate achieved in tests with SRL 202A glass at $20,000 \text{ m}^{-1}$ at intermediate reaction times. The longer-term data in Fig. 23a fall close to the line describing the initial reaction rate, indicating a reacceleration of the reaction. Similar lines can be drawn for tests at other SA/V ratios. It can be seen in Fig. 23a that tests with SRL 202A glass at 2000 m^{-1} have not yet reached a constant, final dissolution rate, but the reaction rate after 560 days is already lower than the lowest rate attained in tests at $20,000 \text{ m}^{-1}$. From Table 13, the final dissolution rate at 2000 m^{-1} is expected to be less than $0.0005 \text{ g/m}^2/\text{day}$. Tests at 10 m^{-1} appear to be reacting at a constant rate similar to the (minimum) forward reaction rate of tests at $20,000 \text{ m}^{-1}$, although some duplicate tests showed much less reactivity.

Similar analysis of the SRL 131A data for tests at $20,000 \text{ m}^{-1}$ in Fig. 23b gives a forward rate of about $1 \text{ g/m}^2/\text{day}$ and a final dissolution rate of about $0.1 \text{ g/m}^2/\text{day}$. Long-term data of tests with SRL 131A glass at $20,000 \text{ m}^{-1}$ show that reaction continues at the final dissolution rate throughout the times tested. Tests with SRL 131A glass at 2000 m^{-1} react at a

final dissolution rate near $0.03 \text{ g/m}^2/\text{day}$ after about 140 days of reaction. Tests at 10 m^{-1} react at a rate near the final dissolution rate of tests at $20,000 \text{ m}^{-1}$ when reaction times exceed about 14 days.

The above analyses show that the apparent final dissolution rates vary with the SA/V of the test for both glass compositions. Differences can be attributed in part to the leachate pH: at high SA/V ratios, the higher pH values accelerate the hydrolysis reaction to release boron from the glass. Tests with SRL 131A glass at 2000 and $20,000 \text{ m}^{-1}$ both reach saturation conditions and proceed at a constant rate at long reaction times, but the higher pH values of tests at $20,000 \text{ m}^{-1}$ lead to a higher final dissolution rate. Likewise, the minimum rate observed for tests with SRL 202A glass at $20,000 \text{ m}^{-1}$ is greater than that achieved in tests at 2000 m^{-1} , which may decrease at longer reaction times.

Because alkali metals continue to be released into solution as the glass reacts, the leachate pH may continue to increase at all SA/V ratios. The pH does increase in tests with SRL 131A at 2000 m^{-1} after these tests attain the final dissolution rate, when the solubility limit of silicon in solution increases. Thus, the measured silicon concentration continues to increase while the glass dissolves at a nearly constant rate. The pH of tests with SRL 131A at $20,000 \text{ m}^{-1}$ does not increase measurably after the first few days of reaction, and the silicon concentration in solution increases only slightly at long reaction times.

The results of tests with SRL 131A glass at 10 m^{-1} reflect the early stages of the glass reaction where ion-exchange reactions dominate the glass dissolution. Alkali metals in the glass structure are exchanged for protons from water, which results in the release of alkali metal ions into solution and the generation of hydroxide ions. The hydroxide ions may then participate in the hydrolysis of bridging oxygen bonds, such as Si-O or B-O bonds. Hydrolysis of terminal $-\text{OSi}(\text{OH})_3$ or $-\text{OB}(\text{OH})_2$ groups may result in the release of silicic or boric acid into solution. From the results in Fig. 18, the release of boric acid occurs at near the same rate as alkali metal release. Silicon is not released into solution in significant quantities until after about 232 days of reaction, after the glass has been leached of alkali metals and boron. Silicon and uranium are then released at rates similar to the alkali metals at long terms.

Tests with SRL 202A at 10 m^{-1} also show the alkali metals and boron to be leached at short times. The short-term data shows only sodium to be leached, but the differences in the releases seen at 232 days and longer are due to preferential leaching at short times. The pHs of leachates from SRL 131A and SRL 202A glasses at 10 m^{-1} do not exceed the pK_{a1} of silicic acid (which is about 9.1 at 90°C), so only the nondissociated acid is expected to be present in solution in appreciable quantities. The maximum silicon concentrations measured were 97 and 63 ppm for tests run 600 days. These concentrations are only slightly greater than the silicon level in the initial leachant, which was about 45 ppm. It is unlikely that the tests have attained the final dissolution rates within the times tested. Instead, the nearly constant rates seen in Fig. 23a are probably the forward rates of the hydrolysis reaction of these glasses, and what is measured prior to about 232 days is the rate of ion exchange that releases the alkali metals. The scatter in the data of tests run at 10 m^{-1} is due to differences in the reaction step that is dominating the glass reaction: tests with low boron releases are dominated by ion exchange and tests with high boron releases are dominated by hydrolysis. Tests with low boron release also had lower leachate pH values. (The higher pHs attained are plotted in Fig. 17, and the higher boron concentrations are plotted in Figs. 18 and 19.) The change from an ion-exchange-dominated system to a hydrolysis-dominated system is usually assumed to occur due to the increase in the leachate pH. Ion-exchange reactions consume protons and are favored under acidic conditions while hydrolysis reactions consume hydroxide and are favored

under alkaline conditions. The change from ion-exchange to hydrolysis domination is usually found to occur at a pH of about 9. Above this pH, the rate of silicic acid release becomes greater than the rate of ion-exchange, which shows only a weak pH dependence. From Fig. 17, the pH values of tests with SRL 131A are greater than those of tests with SRL 202A at 232 days or more. This results in a much greater extent of reaction at these times in tests with SRL 131A. From Figs. 18 and 19 and Table 12, the long-term rate of SRL 131A is more than 3 times that of SRL 202A.

Tests with both glasses at 2000 and 20,000 m^{-1} attain pH values well above 9 at all times tested, and the glass dissolution is expected to be dominated by the hydrolysis reaction in all tests. The ion exchange that occurred within the first 3 days is partly responsible for the nonstoichiometry of the leachate composition seen in Figs. 18 and 19. Secondary phase formation may also affect the leachate composition; the lithium and uranium concentrations are probably affected by secondary phases.

Several insights can be gained from the change in the gross morphology of the layer before and after the rate increases. Through 182 days in tests with SRL 202A at 20,000 m^{-1} , the layer forms separate from the glass because it is crystalline and the glass is noncrystalline. As the glass dissolves, more clay is formed in the layer. The inner surface of the layer does not bond to the glass surface. Instead, the glass continues to dissolve and crystallize in the layer. Before the glass reaction accelerates, the glass dissolves slowly and the clay crystals are well-formed. Upon accelerated reaction, the glass dissolves faster than the clay crystallizes, so small clay particles crystallize on the existing clay surface, effectively filling in voids in the original clay structure. Continued glass reaction results in the crystallization of many small clay crystals. Because these microcrystallites of clay form faster as the glass reacts, they do not become separated from the underlying glass and appear to form an interface with the reacting glass surface.

E. Future Progress

Several long-term tests remain in progress. Detailed analysis of the reacted solids are in progress and will represent the focus of upcoming effort. Results of tests available to date will be compared to the results of tests in other Tasks and to computer calculations. Insights gained to the effects of the SA/V ratio and the glass reaction mechanism and rate will be incorporated into a description of the glass reaction mechanism.

VIII. MECHANISTIC VALIDATION THROUGH THE STUDY OF NATURAL ANALOGUES

A. Introduction and Background

One of the regulatory requirements of the repository program is the projection of radionuclide release during the repository lifetime. Unfortunately, experimentally demonstrating nuclear waste glass durability under projected repository conditions for repository lifetimes is impractical. Instead, the results of short-term laboratory experiments, performed under accelerated conditions, are extrapolated (through modeling) to repository lifetimes. For these extrapolations to be meaningful, a relationship between experiments and natural alteration conditions must be established.

The natural occurrence of silicate glasses in the geologic environment for up to millions of years forms the basis for proposing that these "natural analogues" may help in understanding long-term nuclear waste glass durability. Natural glasses, especially basalt glasses, have a range of compositions that is somewhat similar to that of proposed nuclear waste glasses.

Studying how natural glasses alter in nature and in laboratory experiments will allow the development of a methodology for understanding whether results can be extrapolated from one set of conditions to another. It can also help determine the similarities between reaction paths and reaction mechanisms in nature in the laboratory. This is especially useful for investigating whether any long-term reaction processes are not observed in short-term laboratory tests. Natural analogue studies can also help develop public confidence in the capability of a glass waste form to isolate radionuclides from the biosphere. The very existence of natural analogues provides an instantly identifiable and readily appreciated demonstration of the durability of glass in an unengineered environment.

B. Objectives

The objective of the Natural Analogue Task is to relate the long-term alteration of naturally occurring glasses to the reaction of borosilicate nuclear waste glasses expected in the projected geologic repository.

C. Technical Approach

The technical approach used to achieve the objectives of this task has been to develop a natural analogue approach for relating natural glasses to glass waste forms. This is accomplished through a detailed experimental study of reaction mechanisms. This process-oriented natural analogue approach has focused on understanding the processes by which glass is altered by water. The goal is to relate the reaction mechanism found in the old natural analogue to that found in nuclear waste glasses. Two criteria are employed in understanding reaction mechanisms: (1) comparison of reaction products and (2) comparison of reaction kinetics. The approach is graphically illustrated in Fig. 24.

The first step is to develop methods to experimentally alter natural samples by the same reaction mechanism that occurs in nature. This is necessarily performed at accelerated rates, so it is crucial to establish that the reaction mechanisms are identical. In our approach, we check this by investigating both the alteration products and the reaction kinetics. Careful comparison and interpretation of these test results form the basis for determining that the reaction mechanisms in nature and experiments are the same. Once experimental techniques for natural samples are developed, then nuclear waste glasses of interest can be experimentally altered

Fig. 24. Graphic Depiction of a Natural Analogue Approach (see text for details)

using the same experimental techniques. Detailed surface characterizations and studies of the reaction kinetics for the nuclear waste glasses then provide information about durability under conditions experienced by the long-lived natural analogues. The compositions of the nuclear waste glasses and the natural analogues may be significantly different. However, when the natural analogue approach is used, the observations and conclusions made for natural analogues are applicable to nuclear waste glasses, since the reaction processes by which water interacts with glasses are the same.

D. Results and Discussion

The alteration of tektite glass with water has been the focus of the natural analogue task. Tektite is a silica-rich glass that has survived in nature for up to hundreds of millions of years [57]. This long-term durability has been duplicated in laboratory studies [58-61]. The first phase of this task was to determine the reaction mechanism for tektite glass under natural conditions. A naturally altered tektite, indochinite, (0.7 Ma) was analyzed by AEM. The chemical composition of the unreacted glass was determined by acid dissolution and ICP analysis (see Table 15).

The alteration layer was approximately 0.1 mm thick and consisted of several phases. The dominant phase is an aluminosilicate clay with a 7-Å basal spacing and a SAED pattern consistent with kaolinite. The EDS analysis of this mineral found average elemental ratios of 1.00 Si : 0.625 Al: 0.125 Mg; 0.094 Fe; 0.63 K. This formula probably indicates a mixture of 1:1 and 2:1 sheet silicates. The other major component of the alteration layer is a mineral with a 10-Å basal spacings and a SAED pattern that includes strong 4.55-Å spacings (see Fig. 25). These features are compatible with the clay glauconite and other sheet silicates. This material could not be analyzed with EDS due to its small domain sizes. Within the clays were also found infrequent occurrences of hematite (α -Fe₂O₃), α -quartz (SiO₂), ilmenite (FeTiO₃), Fe-bearing rutile, and TiO₂ (B). Each of these phases were identified and characterized with EDS and SAED.

Table 15. Composition of Indochinite as
Determined from Acid Dissolution/ICP Analysis

Oxide	wt %
SiO ₂	74.4
Al ₂ O ₃	12.17
Fe ₂ O ₃ (total)	5.02
K ₂ O	2.61
Na ₂ O	1.32
CaO	1.52
MgO	1.85
TiO ₂	0.76
MnO(total)	0.11

Fig. 25. AEM Photograph of the Outermost Portion of the Alteration Layer for an Experimentally Hydrated Indochinite. The average composition of the poorly crystalline material is presented in the text.

The same indochinite was experimentally altered in vapor hydration experiments where limited amounts of water come into contact with tektite glass [62]. Polished 1-cm x 1-cm x 1-mm monoliths were suspended from a stainless steel support with Teflon thread inside a sealed stainless steel vessel. Enough distilled and deionized water was added to provide a relative humidity of 100% at the test temperature. Experiments were conducted at 150, 175, 200 and 225°C for up to 400 days [62]. The experimental conditions are presented in Table 16.

Each sample was cross-sectioned and analyzed optically for the formation of a birefringent layer. Birefringent layer formation on silica-rich glasses is attributed to the inward diffusion of water molecules and is believed to reflect the resultant strain in the glass structure [63-65]. Table 16 presents the average birefringent layer thickness measured on each sample. As shown in Fig. 26, these data form a linear trend when plotted as a function of the square root of time. Linear regression fits to these data were used to derive reaction rate constants (see Table 17). The temperature dependence of the reaction was examined by plotting the logarithm of the rate constant as a function of reciprocal absolute temperature, Fig. 27. This analysis results in an activation energy of 91 kJ/mol.

Birefringent layer formation has not been previously observed in tektite altered with water in nature [64,68] or in the laboratory [58,61]. Our ability to induce birefringent layer formation in tektite demonstrates the importance of carefully controlling reaction conditions in laboratory experiments. In our experiments, tektite reaction with water initially involves the inward diffusion of water into the glass network and the formation of a birefringent layer. As the reaction proceeds, minerals nucleate and begin to precipitate within the hydrated layer that comprises the birefringent layer. The alteration layer on naturally altered tektite only contains mineral phases; there is no obvious birefringent layer. This is because over the time that the natural tektite has reacted, clay formation dominates what was once the birefringent layer.

Table 16. Vapor Hydration Experiments Performed on Indochinite at 100% Relative Humidity

Sample #	Temp (°C)	Duration (days)	Average Rim Thickness (μm)
IC2210-01	225°C	4	1.71
IC2210-02	225°C	10	2.52
IC2210-03	225°C	18	3.40
IC2210-04	225°C	48	4.83
IC2010-01a	200°C	36	2.59
IC2010-02	200°C	10	1.34
IC2010-03	200°C	23	2.11
IC2010-05	200°C	120	4.27
IC1710-01a	175°C	22	1.22
IC1710-02a	175°C	81	2.20
IC1710-03a	175°C	128	2.16
IC1510-03a	150°C	71	0.87
IC1510-04	150°C	120	1.01
IC1510-05	150°C	256	2.03
IC1510-06	150°C	400	2.11

Fig. 26. Graph of the Measured Birefringent Layer Thickness vs. $t^{0.5}$ at (△) 150, (◆) 175, (○) 200 and (●) 225°C for Indochinite in Hydration Experiments at 100% Relative Humidity

Fig. 27. Arrhenius Plot of the Temperature Dependence of the Hydration Rate Constants Presented in Table 17. A linear regression fit to data corresponds to an activation energy of 91 kJ/mol.

Table 17. Experimentally Determined Tektite Hydration Rates^a

Temp (°C)	Hydration Rate ($\mu\text{m}/\text{days}^{1/2}$)	N ^b	Correlation Coefficient
225	0.697	4	0.994
200	0.390	4	0.997
175	0.208	3	0.981
150	0.096	3	0.997

^aThese values were calculated from linear regression fits to the data presented in Table 16.

^bN = number of tests performed at this temperature.

Our laboratory experiments allow us to study the very early steps in the alteration process (molecular water diffusion and clay formation), while study of the naturally altered tektite allow us to study the later long-term processes. A comparison of the minerals formed within the two suites of samples is presented in Table 18. The close correspondence supports the contention that vapor hydration experiments reproduces the reaction mechanism by which tektite alters in nature. Study of either suite of samples independently may have led to erroneous interpretation of the reaction mechanism.

E. Future Progress

Basalt glass is compositionally similar to most nuclear waste glasses [66-71]. A set of vapor hydration experiments at 150, 175 and 200°C, using the aforementioned techniques, have been performed previously for up to 500 days. Samples from these experiments will be analyzed with AEM. Samples of natural basalt glass artifacts with associated radiocarbon dates have been obtained from the Bishop Museum in Hawaii. These two suites of samples will comprise the samples used to establish a correlation between laboratory and natural reaction for basalt glasses.

Basalt glass alteration with water under vapor hydration conditions is known to be more complex than that of rhyolitic glasses [e.g., 72]. Thus, it appears that a direct extrapolation of the results of our tektite experiments to basalt glass alteration is not appropriate. Preliminary results of AEM analyses with basalt glasses indicate that the high-temperature laboratory reaction mechanism is dominated by concurrent network hydrolysis and clay and zeolite formation [73].

Table 18. Comparison of Secondary Minerals Found on Laboratory and Naturally Altered Indochinite (0.7 Ma) and Haitian Tektites (65 Ma)

	Experimentally Altered Indochinite	Naturally Altered Indochinite	Haitian K/T Clay
Glaucony	X		X
Smectite	X (tr)		X
Kaolinite		X	X
Goethite			X
Hematite		X	X
Pyrite			X
α -quartz		X	
Fe-Rutile, Ilmenite		X	
Feldspar			X

IX. ANALYTICAL ELECTRON MICROSCOPY SUPPORT

A. Introduction and Background

Analytical electron microscopy (AEM) is a combination of transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), selected area electron diffraction (SAED) and convergent beam electron diffraction (CBED). Point-to-point resolution for images obtained with the TEM approaches 3 Å, and the smallest region that can be investigated using electron diffraction, energy dispersive spectroscopy, and electron energy loss spectroscopy is about 200 Å. The AEM is a very powerful tool for investigating inhomogeneous samples because it can handle very small inclusions, small crystallites, colloidal-size particles, and thin reaction layers.

Samples for AEM studies must be extremely thin (500 to 800 Å) to be electron transparent. Considerable effort is required to prepare the required specimens. Fully radioactive TEM samples have been produced by ultramicrotoming.

B. Objectives

The Analytical Support staff collaborates with other members of the High-Level Waste Technical Support Program to investigate and identify reaction products produced from the corrosion of nuclear waste forms during simulations of expected environmental conditions. These structural studies provide information on the reaction processes, and thus they contribute to the development of the models needed to predict glass behavior.

C. Technical Approach

Work is concerned with reaction layers formed on the surfaces of reacted glasses. These layers are frequently 50 µm or more thick and are extremely fragile. In order to identify secondary phases using AEM, extremely thin self-supporting samples are needed. Transverse cross-sections of these reaction layers are prepared by ultramicrotomy, thin sectioning of small particles mounted in epoxy blocks using a diamond knife. This is a difficult process and often requires several attempts to achieve success. After the particles are sectioned, each grid is surveyed in the electron microscope. The micrographs produced are used for interpreting the glass dissolution mechanism and possibly for use in publications. If a secondary phase, other than a smectite clay, is observed in the layers during the survey, EDS composition information and SAED and, on occasions, CBED data are obtained to characterize the phase. The most intact TEM sections from a particular reacted glass sample will be returned to for further detailed analysis.

In addition to the analysis of reaction layers, colloidal particles present in the leachate, some of which may carry radionuclides, have been examined. Colloidal samples have been collected by wicking the leachate through with ethanol onto a perforated carbon grid. These grids are coated with specially prepared carbon films approximately 200 Å to 400 Å thick and perforated with very small holes. The solution passes through these holes leaving the particulate matter dispersed on the film, where they can be analyzed with the AEM. Examination of colloids present in the leachate has permitted identification of colloidal phases and furnished a picture of colloidal particle formation in the leachate.

D. Ongoing Tasks

A short description of the work being performed in support of the program tasks along with selected results is given in this section. More extensive discussions, interpretation, and correlation with other techniques is presented in sections devoted to each task.

Tables 19 through 23 present an overview of the results of samples surveys this year. The aim of the survey is to obtain publication-quality micrographs and data on the mechanism of glass reaction, and to select best samples produced, which undergo further detailed analysis. The samples are identified by Task Plan number and further information related to the test conditions can be obtained from the Task Plan.

1. Analysis of Long-Term Testing Task Glass

The Long-Term Testing Task seeks to determine the long-term performance of fully radioactive glass and to compare this performance with that of nonradioactive glasses with the same nominal composition. The test matrix is designed to allow investigation of several variables that may effect glass reaction including; SA/V•t scaling, glass composition, and inclusion of radionuclides in the glass [6,74]. Samples have been prepared of all nonradioactive tests terminated to date in this matrix and sections of several radioactive samples have been produced. Detailed analyses have been performed on many of the samples which have been terminated. Colloidal particles have been collected from the leachates of these glasses and detailed analysis of these particle assemblages has been performed and is discussed elsewhere in this report.

The surveys from the reacted layers of the Long-Term Testing Task are shown in Table 19. 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 (Section V). Samples of 131/11S, 165/42S, and 200S glass reacted at 2000 m^{-1} and 340 m^{-1} have been analyzed; analysis of $20,000\text{ m}^{-1}$ samples has begun. The alteration layer in most samples examined to date is a poorly crystallized smectite (Table 24). Samples from longer term reactions give diffraction and compositions that match well with montmorillonite/nontronite. Samples reacted for shorter periods of time give much weaker diffraction suggesting that the layer is largely amorphous although the compositions are similar. Reaction layers on the 131/11S and 200S glasses are thicker than those found on 165/42S glass reacted for the same lengths of time at the same SA/V ratio. Results of short term tests of the slowly reacting 165/42S glass are consistent with montmorillonite/nontronite, but are inconclusive. Identification of the clay phase developing on the 165 glass is based on the results from the longer term tests.

The analyses performed to date shows that the reaction layers are only poorly crystallized; diffraction is extremely weak, and lattice fringe images rarely show more than five or six consecutive fringes. Diffraction in "standard conditions," although, weak displays the qualitative behavior expected. Samples which have been reacted for longer periods of time and samples of more reactive glasses usually have stronger diffraction patterns.

In addition to the identification of clays developed on the outer surface of the glass compositional variations in the underlying glass as a function of depth was investigated. In some samples (longer term tests with pitting) variations of Ca, Mn, and Mg with depth were observed (see Fig. 28). This technique complements SIMS investigations and is particularly valuable for $20,000\text{ m}^{-1}$ samples (powder samples), which cannot be profiled with SIMS. Even in those situations where SIMS can be readily applied, it is useful to examine the surface with the AEM in order to ascertain whether any compositional inhomogeneities are responsible for

Table 19. Results of Sample Surveys for "Long-Term Testing" Task Glass

Test	Comments	Blocks Prepared
DP9	The total layer thickness was 300-500 nm. Etch pits were visible underneath the outer layer.	511, 512, 518, 519
DP17	The outer layer was 150 nm thick (occasionally >200 nm) and there was an etched region underneath the clay layer.	524, 525
DP23 (131/11S 280 days, 2000 m ⁻¹)	Radiation damage was easily produced in this glass. The layer was 100 nm thick though in some areas it was 150-250 nm thick. Etch pits were visible along the interface. Some good samples.	419, 420
DP180 (200S, 20,000 m ⁻¹ 182 days)	The layer was 150-300 nm thick. The layer appeared to be disordered and in some regions >0.5 μ m thick.	427, 428, 429
DP81 (165/42S 560 days)	The layer was very thin in the order of 40-70 nm thick. All the specimens of DP81 were of good quality.	436, 437, 438
DP106 (200S, 340 m ⁻¹ 56 days)	Much of the specimen was intact. The epoxy has infused between the layer and glass in many regions. The fringe layer was 100-150 nm thick. Glass particles were 5 μ m wide and 40-50 μ m in length.	411
DP107 (200S, 340 m ⁻¹ , 56 days)	The layer was 150 nm thick and in some regions as much as 300 nm. Cracks were occasionally seen in the glass and these had undergone alteration.	439, 440
DP109 (200S, 340 m ⁻¹ , 180 days)	The outer layer was 100-150 nm thick and on occasions extended 0.5 μ m.	457, 558, 459
DP110 (200S, 340 m ⁻¹ , 364 days)	The outer layer was 200 nm thick and the alteration layer was 0.5 μ m thick. Uranophane crystallites were observed on occasions.	589, 590, 592, 593, 594, 595
DP111 (200S, 340 m ⁻¹ , 364 days)	The outer layer was 0.5 μ m thick, sometimes extending 2 μ m.	596, 597, 598, 599, 600
DP144	The 200-300 nm thick layer possessed a backbone structure.	508
DP145	The layer was ~1 μ m thick.	509, 510
DP164 (200R)	A 200 nm thick layer was present.	678
DP183 (200S, 20,000 m ⁻¹ , 364 days)	Two types of secondary phases were observed in the reacted layers of these samples apart from smectite clay. A zeolite phase (highly unstable in the electron beam) and a silicon rich phase. The layer was >5 μ m thick, the outer layer was ~0.5 μ m thick.	613, 614, 615, 616, 617, 618, 619, 620, 622, 623, 625
DP188 (200S, 20,000 m ⁻¹ , 330 days)	A zeolite phase identified as clinoptilolite was found. The alteration layer was 5-7 μ m thick.	606, 607, 608, 609, 610, 611, 612
DP189S (200S, 20,000 m ⁻¹ , 390 days)	A potassium aluminum silicate (zeolite) was observed.	673, 674
DP189b (200S, 20,000 m ⁻¹ , 390 days)	~1 μ m thick outer layer was found. As well as a zeolite phase a silicon rich phase was also found.	668, 669, 670, 671, 672

2 of 3

Table 20. Results of Sample Surveys for "Effects of Radiation" Task Glass

Test	Comments	Blocks Prepared
IV202U-7-16	It was found to be extremely difficult to generate a decent sample from this test. Samples were remounted and resectioned a number of times in order to produced some good samples.	412, 413, 414
New Embedding Resin Used	Layer was estimated to be 500 nm thick. Lattice fringes were easily visible. No interface was visible between the glass and the layer.	434, 435
IVE202U-7-16	The total layer thickness was 2 μm . The layer glass interface was intact. A number of good sections.	463, 464, 465, 466
202U35-2a	In one block there was a multiband alteration layer was at least 50 μm thick. It was for the most part totally intact. Only one band had been plucked out. Each band had a different morphology, though most appears to be clay one of the outer bands was a uranium silicate.	454, 468, 469, 473, 474
IVE202U-21-1a	Lattice fringes visible from a very thin layer. Pits were visible underneath this layer.	475, 476, 477
131-3-2b	Most sections were intact. The alteration layer was 1-1.3 μm thick and the outer clay layer 200-500 nm thick.	555
131U-5-2b	The outer layer was thicker and better crystallized than the previous test (131U-3-2b). It was 400-500 nm thick with an alteration layer of 1.5 μm . Reasonable samples.	559, 560
131U-7-1b	The alteration layer and the outer layer were intact.	563, 564
131U-14-2a	The alteration layer was 3.5 μm thick.	565, 566, 569
IV202U-35-20	Nothing intact	

Table 21a. Results of Sample Surveys for "Effects of SA/V" Glass at 20,000 m⁻¹

Test	Comments	Blocks Prepared
<i>Reacted in DIW</i>		
TZ6 (14 days)	50 nm outer clay layer. The layer was at least 400 nm thick in some regions. The etched glass contained numerous crystallites. Some good samples.	361,384, 384,385
TZ8 (28 days)	Layer around 50 nm thick. Good specimen were produced.	372, 371, 373
TZ10 (56 days)	Layer was 50 nm thick sometimes extending 150-200 nm. A backbone structure was seen to be developing.	365, 368, 369, 370
TZ12 (91 days)	In some regions the layer was around 600 nm thick, in other 100 nm. There was a gap between the layer and glass in nearly all sections.	421, 422, 423
TZ13 (182 days)	The layer consisted of a single backbone with 100-150 nm of clay lattice fringes visible either side of it. The layer has separated from the glass and this gap has infused with epoxy.	481, 482, 483, 484, 486
TZ16R (364 days)	Weeksite and clay present.	639, 640, 641, 642, 643
TZ16 (364 days)	The outer layer was 300-500 nm thick and the alteration layer was ~2 μ m thick. A calcium phosphorous silicon phase identified as Nagelschmidtite as well as weeksite were found in the layers.	644, 645, 646, 647, 648
<i>Reacted in EJ-13</i>		
TZ36 (14 days)	Blocks had a variable layer thickness (40-120 nm thick layer). Good samples.	362, 274, 375
TZ38 (28 days)	The layer was 30-50 nm thick.	366, 380, 381
TZ40 (56 days)	The layer was 50-90 nm thick with some etched and pitted areas with 150-200 nm thick clay layers.	367, 376, 377
TZ42 (91 days)	The layer was around 100-200 nm thick and a backbone structure was visible.	424, 425, 426
TZ44 (182 days)	The layer was 100-200 nm with a backbone structure, etch pits were visible.	478, 479, 480, 485
TZ46S (364 days)	The clay layer was 2-3 μ m thick plus a 400 nm thick fringe layer. The phase nagelschmidtite was observed.	649, 650, 652

Table 21b. Results of Sample Surveys for "Effects of SA/V" Glass at 2000 m⁻¹

Test	Comments	Blocks Prepared
TY2 (3 days)	30-60 nm layer with a backbone visible in some regions. Some sections were well intact.	363, 382, 383
TY3 (7 days)	The layer was 50-70 μm thick and consisted of an outer a layer, a 'gel' like layer and a darker (Z-contrast) band underneath this.	570, 571
TY5 (14 days)	A 100 nm thick layer possessed an iron-rich stain within the alteration layer.	572, 573, 574
TY7 (30 days)	The layer was 250 nm thick and had a backbone structure. Uranium titanium precipitates were observed.	575, 576, 577
TY9 (70 days)	The outer fringe layer was 100-150 nm thick and the alteration layer was 100 nm thick. The uranium phases were visible.	578, 580
TY11 (140 days)	The layer was 150 nm thick. Though one area had a very thick layer which was at least 2 μm thick. A darker band was visible underneath the outer layer. Electron diffraction of the clay layer was consistent with montmorillonite. A good sample.	447, 448
TY12 (140 days)	Layer was 100-150 nm thick. In some regions the layer was 300 nm thick. A backbone structure was visible. This backbone was 20 nm thick and had darker contrast.	449, 450
TY13 (280 days)	The layer was 400 nm thick and possessed a clear backbone.	581, 582, 583

Table 21c. Results of Sample Surveys for "Effects of SA/V" Glass at 340 m⁻¹

Test	Comments	Blocks Prepared
<i>Reaction in DIW</i>		
TW1A (14 days)	In some areas the layer was thin (~40 nm thick) and in other areas slightly thicker (50-70 nm). One block (388) had a 500 nm thick layer in some regions.	386, 388
TW3A (28 days)	The layer was on average 100-200 nm thick extending to 500 nm in some regions.	389, 390, 391
TW5A (56 days)	A 150-200 nm thick layer with a backbone structure was visible in some blocks.	392, 393, 394, 395
TW7A (91 days)	Backbone visible. Outer clay layer was 120-200 nm thick. The section also revealed an alteration layer around 500 nm thick.	487, 488, 489, 490
<i>Reacted in EJ-13</i>		
TW31A (14 days)	The layer consisted of 70-100 nm of clay fringes and a further 100-200 nm of etched glass. Some good specimens.	400, 401, 402, 403
TW33A (28 days)	Fringes were 50-100 nm in length with the layer extending 150 nm in some parts.	396, 397, 398, 399
TW37A (91 days)	The layer had a variable thickness from 100-200 nm. A backbone structure was visible in some areas. Some sections were well intact. One crystalline phase was found consisting of Ca, Mg and O (dolomite). Precipitates were observable. These seemed to be amorphous and were composed of a fairly high concentration of uranium.	494, 495, 496, 497, 498, 499
TW39A (180 days)	A CaCO ₃ phase was identified. The layer was 100-150 nm thick. Lattice fringes were clearly visible.	491, 492, 493

Table 22. Results of Sample Surveys for Fully Radioactive Glass
for "Effects of SA/V" Task

Tests	Comments	Blocks Prepared
<i>202A Glass</i>		
BZ7 (202A glass 20,000 m ⁻¹ , EJ-13, 28 days)	The layer was 50-100 nm thick. Etching was visible. A crystalline Fe, Ca, Ti silicate phase was identified by CBED as garnet, probably a devitrification product as it had a shared interface with the fresh glass.	455, 456, 454
BZ13	The outer layer was 150 nm thick (occasionally 200 nm fringes extended above the main layer), the glass was etched.	451, 452, 453
BZ15 (202A glass 20,000 m ⁻¹ , EJ-13, 364 days)	Fully radioactive sample. The layer consisted of a number of bands. The visible alteration layer was 0.5 μ m thick, on top of this was an ordered 600 nm clay layer possessing a backbone structure and finally an outer fringe layer extending 2-3 μ m. A crystalline iron silicate phase was visible similar to that in BZ7.	514, 515, 516, 517
BY-13 (202A glass 20,000 m ⁻¹ , EJ-13, 182 days)	The outer layer was not as beam sensitive as the clay observed in BZ-15. This might suggest that it is a different clay. The layer was 150-200 nm thick. No etched region underneath this was observed. The layer was sometimes disordered and 400 nm thick.	526, 527, 528
<i>131A Glass</i>		
PY14		538, 539, 540, 541
PY15 (131A glass 2000 m ⁻¹ , 280 days)	The sections consisted of a 350 nm outer layer and 4-5 μ m thick alteration layer. Complete layer structure was visible. In one block the sections consisted of a kaolinite phase which had within it small titanium oxide phases scattered about. A precipitated uranium silicate phase was found.	542, 543, 544, 545, 546

Table 23. Results of Sample Surveys for "Natural Analogue" Glass

Tests	Comments	Blocks Prepared
JT-8	The layer had an etched appearance. The outer layer extended 0.5 μm and the alteration layer 1.2 μm .	603, 604, 602, 605
T-44	Analcime was identified in the reacted layers.	637, 638
HB1710-02	Barite phase found in layers and a clay with a high Al/Si ratio.	707, 708, 709, 710, 711, 712
HB1510-01	The outer layer was 500-800 nm thick.	663, 664, 665, 666, 667
NBG-9	Silicon-rich (quartz) regions were observed as well as a highly crystalline iron magnesium titanium oxide phase identified by SAED as belonging to the spinel group. The layer was 500 nm thick.	701, 702, 703, 704, 705, 706
BE-04	An Al/Si ratio >1 was found in one phase. Iron magnesium aluminum silicate and a less crystalline calcium aluminum silicate were observed in the layers.	659, 660, 661, 662, 657

Table 24. Alteration Layers on "Long-Term Testing" Samples

Glass	SA/V (m ⁻¹)	Reaction Time (Day)	Layer Thickness (nm)	Clay & Secondary Phases Observed
131/11S	340	28	50	smectite
		91	70 to 100	smectite
		364	400	smectite
	2000	30	50 to 90	smectite
		70	80 to 120	smectite
		140	120 to 160	smectite
		280	250 to 310	smectite
165/42S	340	28	none	a
		91	50 to 70	a
		364	80 to 200	smectite
	2000	30	0 to 40	smectite
		70	0 to 45	smectite
		140	0 to 45	smectite
		280	40 to 80	smectite
		560	50 to 80	smectite
200RS	340	14	120	smectite
		56	150 to 250	smectite
		182	250 to 300	smectite
	2000	3	40 to 80	smectite
		14	65 to 145	smectite
		70	200 to 240	smectite
	20,000	56	125 to 180	smectite

^aNo clay layer or development too primitive to identify.

Fig. 28.
Composition as a Function of Depth
into the Sample along a Remnant
between Two Etch Pits: (a) Ca,
(b) Mn, and (c) Mg). The sample is
a 131/11S glass reacted for 364 days
at 340 m^{-1} . The concentration
reaches the bulk composition about
1 mm into the sample.

observed gradients. The Ca profile observed in the 340 m^{-1} 364-day 131 glass was restricted to remnants of glass which remained between etch pits "stringers". Most samples examined in this matrix do not show significant differences in concentration between glass and near surface glass.

In some samples there is a backbone structure (Fig. 29) with clay crystallites growing out from both sides of the backbone. Composition above, below, and on the backbone was investigated and no significant differences have been observed.

Discrete secondary phases were not found on the earlier samples in the matrix but in studies of samples terminated near the end of this reporting period discrete phases have been found and are discussed elsewhere in this report (Section V).

2. Analysis of Effects of Radiation Task Glass

A limited number of surveys were performed from the Effect of Radiation on Glass Reaction at Large SA/V Task. These were 131 and 202U glasses reacted for various times in a radiation field (see Table 20). The reacted layers developed rapidly, and there was some problem in obtaining a completely intact section.

Fig. 29. A Backbone Structure with Clay Crystallites Growing Outward into the Solution and Down toward the Glass. The composition above, below, and on the backbone was investigated in these samples and no significant differences have been observed.

3. Analysis of Effects of SA/V Task Glass

Survey results for the Effects of SA/V Task are shown in Table 21. A detailed analysis of a 202A glass reacted in EJ-13 for 364 days at $20,000 \text{ m}^{-1}$ was completed. In summary, sections of this sample contained three clay layers with different morphologies but essentially the same composition and electron diffraction. The different morphologies suggest different deposition environments and rates. Figure 30 is a low magnification micrograph of the layers on this sample. In this case sectioning (preparation of the $500 \text{ \AA}$ thick samples required for analysis) has resulted in some disruption of the layers. However, three layers are clearly present: an outer layer that looks like an assembly of individual particles floating just above the surface (floaters); next, an "oriented" layer, with the clay platelets growing perpendicular to the surface; and a "web-like" inner layer.

The floaters displayed extremely weak diffraction but composition and occasional lattice fringes are consistent with a smectite intermediate between montmorillonite and nontronite. Since diffraction from this region is extremely weak it is clear that crystal growth is not very far advanced. The composition and electron diffraction of the oriented layer

Fig. 30.
A Low-Magnification Micrograph of the Layers Which Have Developed on the 202A 20,000 m⁻¹ EJ-13 364-Day Sample. In this case sectioning (preparation of the 500 Å thick samples required for analysis) has resulted in some disruption of the layers. Clearly present are an outer layer which looks like an assembly of individual particles floating just above the surface, an oriented layer with the clay platelets growing perpendicular to the surface, and the inner "web-like" layer.

match with a smectite intermediate between montmorillonite and nontronite. The web-like layer has a very similar composition and diffraction is also about the same as that from the oriented layer.

The material in both the web-like layer and the oriented layer is a smectite with a composition between montmorillonite and nontronite but with a significantly different morphology. This different morphology suggests that growth conditions were different in the two regions. Material that crystallizes in the web-like layer is nucleating in many locations with random orientation. Figure 31 is a micrograph of a glass layer interface which suggests this type of development. The oriented layer is probably the same crystal growing epitaxially into the solution.

Fig. 31. The Web-Like Layer Appears to be Nucleating in Many Locations with Random Orientation. The oriented outer layer has the same composition and diffraction and is probably the same phase growing epitaxially into the solution.

Observations of the sodium concentration in the glass below the clay layer have considerable spread due to beam damage effects. Sodium is present but concentrations are indeterminate. Excluding Na, K, and U (which cannot be quantified reliably), the observed composition matches that of the bulk glass.

4. Analysis of Natural Analogue Task Glass

Several samples of reacted natural analogues (see Table 23 for surveys) were examined to provide input for a presentation at the Mars Surface and Atmosphere Through Time (MSATT) meeting [75]. These samples were basalt glasses reacted in vapor conditions at 200°C for 14, 50, and 60 days and one sample reacted at 150°C for 100 days. In all cases an oriented layer of smectite clay either montmorillonite or saponite (Table 25) was observed on

Table 25. Secondary Phases Observed on "Natural Analogue" Samples

Sample	Outer Layer	Inner Layer	Deeper Layer	
200°C 14 day	smectite (saponite, or montmorillonite)	Backbone smectite	amorphous mottled area	
200°C 50 day	Trioctahedral smectite (saponite)	mottled layer smectite		Large precipitate analcime
200°C 60 day	Trioctahedral smectite (saponite)	smectite		
150°C 100 day	Trioctahedral smectite (saponite)	crystalline particles 10 nm in diameter		

the outer surface of the glass, and in the higher temperature reactions a layer of smaller crystalline regions embedded in an amorphous layer was observed beneath this outer layer. A large single crystal of analcime was observed in sections taken from the 50-day 200°C sample.

5. Colloid Formation During Nuclear Waste Glass Reaction: AEM Investigations

During this reporting period we have continued to use the AEM in characterizing colloidal material from the leachates of waste glass tests. There is great interest in the role of colloids in nuclear waste management and whether colloids will increase or decrease the release of radionuclides into the environment [76-68]. Most studies have concentrated on pre-existing colloids in the groundwater as possible vectors for radionuclide transport. The investigation of the leachates from waste glass tests has demonstrated the presence of a new source of colloids [79].

Recently, it has been shown that colloidal particles can be produced as a direct result of the alteration of the waste glass itself. By using small particle handling techniques and autoradiography, Bates et al. [80] have shown that particles formed during simulated weathering of nuclear waste glass (drip tests) can adsorb americium and plutonium. Leachates from related tests were passed through a series of filters, alpha spectroscopy, and light-scattering measurements were performed in order to determine the actinides present and the size distribution of colloids associated with this activity. Neptunium was not found to be associated with colloids but americium and plutonium were [81].

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," "Effects of Radiation," and "Effects of SA/V." Colloids from other glass tests were also examined.

As previously described [2], clay colloids can be readily identified in the TEM, as they often produce oblique textured electron diffraction patterns (OTED) when tilted (Fig. 32). However, it is known that the electron microscope environment often reduces clay c-axis spacings to approximately 10 Å [82]. This means that any determination of c using OTED patterns would lead to this erroneous result. Results show that such spacings have been identified during colloidal particle analysis, which is in contrast to the sample preparation technique used to analyze the layers forming on reacted glasses. As the samples are embedded

Fig. 32. OTED Patterns of Clay Colloids from a 200R Glass Leachate. (a) The pattern at 0° tilt displays hKO reflections and (b) at 35° tilt the turbostratic OTED pattern, which is characteristic of smectites [83] is observed. The hk- indices are listed on the patterns.

in an epoxy then ultramicrotomed, the c-axis spacings are preserved. During the studies of the various leachate tests by AEM, differences were found both in intensity and spacings of these clay diffraction rings. The pattern of rings is seldom altered; thus, the rings from the central spot can be indexed, as shown in Fig. 32a. These are the hk0 lines. For the more crystalline clay colloids, a number of weaker rings are visible, which are due to the $00l$ (where l is an integer) reflections. For a monoclinic unit cell, typical of a smectite clay, the hk0 spacings will be uneven (i.e., the reflections are not equally spaced along the minor axis of the ellipse).

The initial aim of this study was to identify and characterize colloidal material. Data on size distributions was not possible with the specimen preparation technique used. However, qualitative estimates of amounts of colloidal material were possible. This colloid study is therefore broken into two parts based on the information obtained; part one is devoted to examination of the conditions for stable colloid development and part two examines the use of the AEM in identifying phases. In addition, two other sections have been included on some other aspects of colloidal particle analysis with the AEM; the first examines the use of EELS during colloidal particle investigations and the second explores a possible electron channeling effect.

a. Formation of Colloids in Waste Glass Leachates

From the Long-Term Testing Task a number of experiments were run with a 200 glass at various SA/V ratios and reaction times; however, samples from many of the tests run earlier were not taken and it has, therefore, been difficult to see any trends except in a few samples.

The leachates of 200R glass reacted at 340 m^{-1} showed a steady increase in complexity and amount of clay colloidal material between 56 and 364 days. At 56 days no clay material was found, but there were a number of salts and a few amorphous silicates

containing potassium (probably also salt material). By 182 days, the leachate had a few crystalline clay colloids (see Fig. 33). These were so thin that EDS composition data was difficult to obtain. The clay was found to be an iron aluminum silicate. There were also uranium-bearing colloids, calcium phosphate phases, and kaolinite in the 182-day test. At 364 days the material was so crystalline that electron diffraction information on the 001 lines was obtained. High-resolution lattice fringe images were also possible, and the phase was identified as montmorillonite. The composition was basically the same as that in the 182-day test. As the clay colloids become more crystalline, the colloids started to overlap and no longer settled onto the carbon film in a textured manner.

The 200S glass reacted at $20,000 \text{ m}^{-1}$ displayed mainly amorphous sodium rich silicate colloids after 300 days. The reacted layers of these tests after 360 days were well over $5 \mu\text{m}$ thick and precipitates such as zeolite were observed (see Table 19), whereas the leachates showed very little material. The presence of the silica-rich material in the leachate may be an indication that aluminum is being removed for zeolite formation. A more in-depth comparison between reacted layers and colloids is being undertaken to answer these questions. The precipitated clay material observed on the surface of the ordered outer clay layer on 200S glass is probably derived from colloidal material. The increase in colloidal complexity appears to be due to different modes of particle association (see Fig. 34). The first few clay colloids only undergo face-to-face association (i.e., the colloids are well dispersed). As reaction time increases, there is a rise in the amount of edge-to-edge association (flocculation) and partial aggregation, which permits the c-axis spacings to be observed during high resolution imaging.

A more systematic study on formation of leachate colloids in SRL 202U glass tests (Effects of SA/V Task) has been performed. Experiments were conducted in DIW and equilibrated tuff groundwater (EJ-13) at $20,000 \text{ m}^{-1}$, 2000 m^{-1} , and 340 m^{-1} for various times. (See Fig. 35.)

Fig. 33. Development of Clay Colloids in a 200R Glass Leachate Reacted at 340 m^{-1} from 182 Days to 364 Days.

Fig. 34.
Schematic Diagram Showing the
Development of Leachate
Colloids with Time and Their
Modes of Particle Association

These experiments show colloidal particle development depending strongly on the test parameters. In general, a smaller amount of colloidal material was found in tests run at the larger SA/V. The number of colloidal particles increased with time and reached a maximum which was dependent on the SA/V. For example, in the 2000 m^{-1} tests at 14 days, very little, if any, real colloidal material could be seen. Most of the material was an unidentified calcium silicate, which may have been a contaminant. At 30 days a trace amount of clay-like material was observed. Reasonable electron diffraction was possible. By 70 days, clay colloids were clearly visible and some of these had uranium rich regions in them. Uranium particles were found by looking for Z contrast, darker contrast in the TEM due to backscattering electrons out of the objective aperture. When an EDS probe was applied to these colloids, they were found to contain uranium and titanium, the same composition as that found in the reacted layer. (See Table 21.) The uranium-titanium phases were observed in the layers by 30 days, while they were only found in colloids at 70 days. This evidence supports spalled-off layers forming uranium-bearing colloids in this glass leachate. It was also noted in the layers from the 2000 m^{-1} series that the uranium phases were most often found underneath the backbone, further evidence in support of spallation occurring, possibly during sampling. Finally, by 280 days no clay material was present in the leachate. In the $20,000 \text{ m}^{-1}$ tests, the maximum amount of colloidal material occurred at around 100 days, while at 340 m^{-1} the maximum occurred after around 300 days. This pattern of development is related to the increase in ionic strength which occurs more rapidly at the higher SA/V. (See Fig. 36.) The large ionic strength causes compression of the electric double layer and leads to flocculation and eventual sedimentation due to van der Waals attractive (V_A) forces between colloids overcoming interparticle repulsion potential (V_R) [85]. At the lower SA/V, there is more time available for colloidal growth and increase in crystallinity before the ionic strength induces sedimentation. This ionic strength effect is dominated by the pH, which serves to increase interparticle repulsion by increasing the negative surface charge of the colloids. As the pH of the leachate increases with increasing SA/V, the colloids are effectively stabilized at the high SA/V, in spite of being exposed to such a high solute concentration.

Fig. 35.
Colloids from a 202U Glass
Leachate Reacted at 340 m^{-1} .
Clay colloids forming in
(a) DIW were found to be less well
developed than those found in (b)
EJ-13 solutions. The arrows point
to examples of colloids. The
corresponding SAED patterns from
these tests are also shown (c and d).
These show the absence of the 33-,
06- line in the DIW test. It has been
shown that the 06-reflection in
X-ray diffraction reflects iron
content [84]. At the higher SA/V
(e) of $20,000 \text{ m}^{-1}$, edge on clay
crystallites are not observed. The
clay colloids are hardly visible.

Fig. 36.
Schematic Graph Showing Particle Potential Energy vs. Particle Separation for a Range of SA/V Ratios. At the higher SA/V particle flocculation is more probable.

EJ-13 had an interesting effect on leachate colloids. There was a large increase in the total amount of colloidal material in EJ-13 tests. EJ-13 is a solution of very low ionic strength, so this could not account for the differences in colloidal material; in fact, no large differences were observed in the leached glass layers [86]. The difference is probably due to small colloids within the groundwater acting as nucleation centers for colloidal growth. This allows the free energy barrier to crystal growth to be overcome sooner than in DIW tests. The free energy (ΔG) for the formation of a round planar crystallite in solution is:

$$\Delta G = (-2\pi r h \Delta G_v) + 2\pi r(h+r)\gamma \quad (5)$$

where ΔG_v is the bulk free energy involved in forming a nucleus of unit volume, r is the radius of the crystallite, h is the height, and γ is the surface energy. In solution, there is no strain term in the equation for growth, unlike in the leached layers. (For crystal growth, ΔG must be negative.) It is energetically more difficult to nucleate a planar crystallite than a spherical one because there is a positive r^2 in the surface energy term.

Uranium was only detected in tests run at $SA/V > 2000$. According to the calculated k factors for the uranium L-line, this clay had a concentration of uranium of ~30 wt%. The nominal concentration of uranium in a 202U glass is <2 wt%. This was probably due to the effect of leachate pH on uranium solubility. As the pH increases with increasing SA/V, uranium more readily undergoes hydrolysis and real colloid formation. Uranium is also more likely to undergo complex formation with species such as carbonate in solution [87]. The uranium colloids may then have been adsorbed onto pre-existing clay colloids. The most uranium was observed at 2000 m^{-1} due to the competition between uranium colloid formation (highest at high SA/V) and the availability of clay colloids (highest at low SA/V). If the relationship between uranium and the colloids was based purely on the larger total release at the higher SA/V, then we would have observed the greatest amount of uranium at $20,000 \text{ m}^{-1}$.

Table 26 displays the average compositions of clay colloids found in the leachate of SRL 202U glass tests. Trends are difficult to see in these results. Compositions varied widely due to interference from salt material and different types of colloidal phases.

Table 26 displays the average compositions of clay colloids found in the leachate of SRL 202U glass tests. Trends are difficult to see in these results. Compositions varied widely due to interference from salt material and different types of colloidal phases. There appears to be an increase in potassium at all SA/V ratios with time and a decrease in aluminum in 20,000 m⁻¹ and 2000 m⁻¹ tests. Silica content increases with time in tests at both 20,000 and 2000 m⁻¹ and possibly at 340 m⁻¹. The iron content does not undergo any change, but this may be due to some other phase formation which has not been accounted for in this table.

Calculation of size distributions using the AEM was not possible; light-scattering techniques are better suited to such a task. The shape of a colloid may also be disrupted once the colloid has dried on a perforated carbon grid. In spite of this, trends in colloidal particle morphology have been found with respect to test parameters. There are methods for preserving the structure, such as rapid freezing [88] or use of the hydrophilic resin nanoplast [89]. In the freezing technique, the sample is cooled quickly, a binding agent is then added, and a replica is produced (i.e., all compositional data are lost). The colloidal particle interactions may then be studied, thus providing information on the stability of colloids, as well as size distribution data. Nanoplast resin has been shown to preserve the structure of aquatic colloids to allow compositional data to be obtained. This latter technique is currently under investigation and has already been successful with other samples.

The AEM study has shown that most leachate colloids are either planar or elongated. This has serious implications for the methods commonly employed to determine size distributions of particles. The Stokes-Einstein theory assumes that the particles are spherical in order to calculate their diffusion constant (D) [90]:

$$D = k T / 3\pi \eta d \quad (6)$$

where η is the viscosity, k is the Boltzmann constant, d is the diameter of the particle, and T is the temperature.

Whether colloids will become major vectors for radionuclide transport depends on their stability, which in turn depends on the solution conditions of pH and ionic strength. Experiments conducted recently, using light-scattering techniques [91] and these AEM techniques, have suggested that nuclear waste glass colloids will undergo flocculation with time and perhaps eventually fall out of solution. Provided the colloidal system remains stable, particles could be transported through cracks and pores within the rock surrounding a repository. Colloids generally travel faster than water through capillaries, with larger particles traveling faster than smaller ones. Colloidal transport is difficult to understand owing to the large number of parameters that have to be included in any model. This study has revealed a number of other complications that will have to be included in any modeling of colloid migration. In the next section, the types of colloids found in this year's study of colloids are described.

b. Identification of Colloids by AEM

Phase identification is possibly the main function of the AEM. Its unique ability to obtain compositional, morphological, and diffraction data on submicron particles makes it ideal for investigating the leached layers of waste glass and colloidal material in the leachates of these tests.

Table 26. Composition of Colloids Found in SRL 202U Leachates^a

Element (wt%)	Si	Mg	Al	K	Fe
<i>20,000 m⁻¹</i>					
14 days	62.72	0.8	3.61	7.62	16.56
28 days	28.45	0.5	16.17	3.88	34.21
91 days	58.07	2.12	6.24	8.36	15.31
14 days (EJ)	56.33	0.12	10.7	0	14.76
28 days (EJ)	59.62	6.71	5.57	8.73	13.16
182 days (EJ)	45.42	0	5.78	12.05	25.18
<i>2000 m⁻¹</i>					
14 days	65.3	3.07	12.06	2.62	7.05
70 days	60.12	0	3.27	18.3	8
140 days	69.01	1.75	4.97	5.41	10.96
280 days	77.27	0	1.14	9.66	5.11
<i>340 m⁻¹</i>					
28 days	24.71	0.21	22.33	1.77	43.82
91 days	61.02	3.15	9.04	3.45	17.06
28 days (EJ)	67.53	3.22	3.73	1.97	16.29
180 days (EJ)	49.87	1.21	3.35	8.31	18.77
360 days (EJ)	67.54	2.39	14.32	6.92	6.56

^aAfter being normalized without sodium.

Table 27 summarizes the colloidal investigations from the Long-Term Testing Task. All of these tests had been in progress for upwards of 182 days before termination, and it is therefore difficult to make comparisons or find trends in the results. Smectite clays were observed in all tests, but little else can be drawn from the results.

Uranium silicate colloids were observed eventually in all tests. Figure 37 shows two examples of these. The phase was identified as the weeksite group mineral haiweeite, $[\text{Ca}(\text{UO}_2)_2\text{Si}_6\text{O}_{15} \cdot 5\text{H}_2\text{O}]$. These phases were found to be extremely beam-sensitive, probably due to the water content in them (i.e., a combination of radiolysis and displacement damage resulted in rapid amorphization). They show the characteristic uranium silicate morphology of elongated crystallites. The uranium silicates were often found associated with clay material, suggesting that they may have formed during spallation. For spallation to have occurred in a batch tests, it probably occurred during sampling. Uranium titanium colloids found in the "Effects of Radiation" leachate are an exception to this, as evidence indicates that these formed in solution.

The clay colloids from the Effects of Radiation Task were found to be more crystalline than any other leachate colloids. High-resolution images of smectite clay lattice fringes with c-axis spacings of 1.0 nm were obtainable. It was in these tests that tentative observation of an electron channeling effect was found first. (See Section 7d.) This situation is similar to the one with the layer analyses, as they are also much more crystalline than other layers from other experiments. Examination of an SRL 131A glass reacted for 180 days at 90°C in a gamma radiation field confirmed that rutile is a possible leachate phase. The colloids were

Table 27. Identification of Phases Present in "Long-Term Testing" Leachates

Test	Time	Phases Observed
<i>200R glass</i>		
20,000 m ⁻¹	182 days (DP162)	smectite, zeolites?
	546 days (DP167)	uranium silicates, smectite
2000 m ⁻¹	280 days (DP126)	fibrous clay, trace uranium, Al rich silicates, kaolinite
340 m ⁻¹	182 days (DP92)	Ca-phosphate, uranium montmorillonite, kaolinite
	364 days (DP94)	smectite (montmorillonite)
<i>200S glass</i>		
20,000 m ⁻¹	182 days (DP181)	Al- silicate, Ca rich phases, phosphate, and uranium
	330 days (DP188)	Ca-phosphate, silicates and smectite
	364 days (DP182)	sodium silicates, Al oxide
340 m ⁻¹	182 days (DP108)	smectite, nontronite
	364 days (DP110)	smectite, Ti oxide

identified as magnesium silicate phases, titanium oxides, mica, and iron oxide phases. A titanium-uranium phase was also found, though it is unclear whether it was crystalline or not. (See Fig. 38.) This phase has been observed in the reacted layers of a leached 131 glass and was tentatively identified as brannerite [35]. The uranium-titanium phase colloids were not more than 100 nm long and have most likely precipitated in the leachate. They were scattered all over the perforated carbon film and were not, in general, associated with the clay fraction. Their regular shape suggested that they should have been crystalline, but it was not possible to demonstrate this.

The 131A glass reacted for 360 days in DIW was investigated for colloidal particles. A particle rich in calcium was found to contain strontium and barium (Fig. 39a). This phase was crystalline, and the aluminum-to-silicon ratio suggested that it might be a zeolite. Electron diffraction matched with heulandite, ideally ($M^{2+}Al_2Si_7O_{18} \cdot 6H_2O$). As well as this phase, magnesium silicates, calcite, and dolomite were observed. The d spacings for the zeolite phase were 3.257Å, 3.79Å, 4.37Å, 2.44Å, and 2.15Å. The composition is listed in Table 28. An EELS plot using the R-plot method for detecting low levels of elements, shows the presence of strontium in the colloid. (See Fig. 39b.) The method used is described in the next section.

The most common types of clay colloidal phases found appeared to be smectite; however, other types of clays have been observed, some of which remained unidentified. A number of phases have been identified including calcium carbonate, titanium oxide, manganese oxide, and iron oxide. A number of the phases listed in Tables 27 and 29 are suspected of being contaminants, but the results do show that the number and variety of phases increased with reaction time, at least with the Effects of SA/V Task glass. It also appears that the greater variety of phases occurred with the higher SA/V ratio experiments.

Comparison with the phases identified within the surface layers either by SEM, XRD, or TEM has shown that a few phases were unique to the leachate. This suggests that processes are occurring in the leachate to form these products. Because computer modeling of the waste glass depends upon knowledge of the types of phases likely to be present, such

Fig. 37. Uranium Silicate Colloids Found in (a) 131A Glass Leachate Reacted for 560 Days at 2000 m^{-1} (the SAED pattern showing the $B[00l]$ zone axis) and (c) in a 200R Glass Reacted at $20,000\text{ m}^{-1}$. A diffraction patterns of a uranium silicate colloid (wecksite) from a PMP test (d) is consistent with polysynthetic twinning of the monoclinic structure.

Fig. 38.

Uranium Titanium Phases Found in the Leachate of 202U and 131U Tests Reacted for 180 Days at 90°C and 340 m^{-1} in a Gamma Radiation Field: (a) micrograph shows the elongated structure, (b) SAED of the phase and (c) EELS second difference spectrum used to detect transuranics, though none except uranium are visible.

Fig. 39. (a) Micrograph of Zeolite Colloid and (b) an "R-plot" EELS Used in Detecting Low Levels of Sr in Colloidal Phase

Table 28. Composition of Zeolite Phase

Element	Atom%	wt%
Si	53.5	50.5
Al	31.2	29.0
Ca	13.1	17.6
Fe	1.5	2.8

Table 29. Phases Found in SRL 202U and SRL 131A Glass Leachates from the "Effects of SA/V" Task

Test	Time	Phases Observed
20,000 m ⁻¹	14 days	smectite
	28 days	titanium oxide, smectite
	91 days	kaolinite, smectite, mica, titanium oxide, uranium
	14 days (EJ-13)	kaolinite, smectite
	28 days (EJ-13)	mica, Ca phases, Mg oxide
	91 days (EJ-13)	Al rich colloids, Ti phase, Ca phase(calcite), phosphate phase, uranium
	182 days (EJ-13)	smectite, uranium
	364 days (EJ-13)	uranium silicates, smectites, Ti oxide and Al rich phases
2000 m ⁻¹	14 days	Calcite
	30 days	Ca oxide, Ti phase
	70 days	iron silicate, uranium, iron oxide, smectite
	140 days	dolomite, phosphate phase, smectite
	280 days	dolomite, iron rich phases
340 m ⁻¹	28 days	Al rich particles, smectite
	91 days	Al rich +Fe, Ti phase, calcite, kaolinite, smectite
	180 days	no FDS signal
	28 days (EJ-13)	smectite
	180 days (EJ-13)	smectite
<i>Fully Radioactive Glass</i>		
2000 m ⁻¹	131A glass, 560 days	smectite, wecksite
340 m ⁻¹	131A glass, 364 days	zeolite (heulandite), Ti phase, iron particles, dolomite, quartz

information is important. Figure 40 demonstrates two electron diffraction patterns (from a 131A glass test leachate) which show some interesting features that aid in the identification of the phases. In Fig. 40a the c^* -axis pattern of a magnesium silicate is shown. The pattern is a regular hexagonal pattern, but there is an obvious increase in intensity of a number of reflections. These result from the ordering of magnesium between the silicate layers due to a charge effect; a random arrangement of magnesium cannot be maintained. The phase is chrysotile. The second pattern is a convergent beam electron diffraction pattern which permits a view of the symmetry of the phase. The composition of the phase was silicon and oxygen and the pattern reflects six-fold symmetry, therefore the phase was hexagonal quartz (possibly a contaminant).

The concentrating of hazardous elements within colloids is an interesting effect that may be difficult to predict. Hence, these studies clearly show the need to carry out investigations with fully radioactive production glasses at different SA/V ratios, so that correct predictions for the release rate of radionuclides from waste glass can be made. These investigations will enable one to determine the more mobile elements and the mobile forms/phases. Actinides other than uranium are in such low concentrations in the glass that it is not possible to detect these with an EDS system, but the EELS system and autoradiography of the particles may accomplish this.

Fig. 40. (a) SAED Pattern of a Magnesium Silicate Colloid (Chrysotile) from a 131A Glass Reacted at 340 m^{-1} Which Displays Ordering and (b) a Silicon Oxide Particle (Quartz). CBED pattern of the $[0001]$ zone axis shows the higher order Kikuchi lines.

c. Colloidal Particle Analysis by Electron Energy Loss Spectroscopy

The use of Electron Energy Loss Spectroscopy (EELS) during the examination of colloidal particles has been explored during this reporting period. Various EELS edges have been examined. EELS does have the immediate advantage of having a better spatial resolution than EDS, so the technique was used to confirm the composition of small colloidal phases. EELS cannot be applied as routinely as EDS analysis, but it may yield new information on the colloids. At present, work has been performed in observing the oxygen K-edge at 532 eV in various colloids, both amorphous and crystalline. Deconvolution routines have not yet been tried, so little data can be extracted. However, the oxygen edge appears to have much more fine structure in the crystalline colloids.

Uranium M_{4,5} edges have been investigated at 3728 and 3552 eV, respectively. It was found that the intensity required to yield information at this energy loss was such that the phase structure became amorphous. However, such a technique may be used to detect low levels of elements, particularly other actinides. An EELS difference technique has been applied to these particular colloids to detect transuranics, so far without success. This method, termed the "second difference technique" requires that three spectra are acquired at slightly increasing energy offset [92]. The technique removes the channel-to-channel gain variation and enhances true peaks. Three spectra are acquired at ~5-8 eV difference between them. The routine -A+2B-C, where A, B and C are acquired spectra at increasing energy offset. (See Fig. 38c.) An alternative technique, known as the R-plot, can also be used to detect low levels of elements. The advantage of the technique is that only two spectra are required to completely remove the channel to channel gain variation.

$$R = 2(I(n)_1 - I(n)_2)E / (I(n)_1 + I(n)_2)\partial E \quad (7)$$

where $I(n)_1$ is the intensity of edge 1 at energy loss E and ∂E is the energy difference. The R-plot was also used to look at Sr during one of the colloidal particle investigations in the 131A glass test leachate (Fig. 39b). The EELS analysis took around 6 seconds to yield a clear result.

Energy resolution is an important issue with EELS. One way to improve it is to reduce the voltage on the instrument. It has been found that when the voltage is dropped to 100 kV, it is fairly easy to obtain energy resolutions of the order of 1.4-1.6 eV. Work is continuing in this area.

d. Electron Channeling in Clay Colloids

Clay colloids could be found which displayed (00 l) lattice spacings during high resolution observation. It was observed that the composition determined by EDS for the same clay was different depending on the orientation. For example, it was found that the iron content was lower when the clay colloids were lying flat to the surface of the carbon film. In addition, elements such as aluminum and magnesium were found to be at a higher concentration when the clay colloids were flat. Considering that when the clay colloids are textured, all orientations are random except for one, the [00 l] direction, it is possible that an electron channeling effect is occurring. Electron channeling is a complex process when considering more than two reflected beams. An enhanced signal in the interlayer cations occurs when the electron beam is channeled down the $hk0$ directions, and a reduced interlayer cation signal may be generated when the beam travels down the [00 l] direction. (See Table 30.)

Table 30. Composition of Clay Colloids

El wt%	flat	edge
Si	42.9	37.2
Na	2.83	2.03
Mg	11.2	3.1
Al	8.4	3.9
K	2.4	2.8
Mn	1.5	9.1
Fe	28.9	35.3
Ni	0.7	5.5

Absorption effects would tend to reduce the signal of light elements in edge on crystals. Absorption will have to be included in the equation in order to dismiss this explanation. Channeling can be explained from the solution of the two-beam dynamical equation [93]. There are two possible independent solutions for the diffracted wave each with a corresponding transmitted wave solution. These are termed "Bloch waves," and both have the same amplitude but differ by a reciprocal lattice vector. The related diffracted and transmitted waves have the same absorption coefficient. On tilting to 35° with a textured clay sample the $hk0$ lines are at the Bragg position, enhancing the atoms on these planes.

This has moderate implications for analysis of clays in general. Only by analyzing material that displays a number of random directions can accurate analysis be performed. Unfortunately, what is often thought to be random orientation may not be due to texturing. These results show that an analysis of textured clay colloids may be unrepresentative because the sample will always be at the Bragg position. In layer analysis studies, one is often faced with clays with apparently one predominant orientation. The beam in these cases is often perpendicular to the c -direction, but this is unlikely to lead to inaccurate results due to channeling effects because the clays are bent and are not at the Bragg position.

e. Summary of Colloidal Study

Glass alteration results in a new source term for colloids for the engineered barrier system to deal with. These colloids may act as regions for actinide adsorption to occur. The uranium silicate colloids found in the longer reacted tests are most likely the result of spallation during sampling.

This work has demonstrated that colloids are produced during waste glass dissolution and that these will probably contain actinide elements. The AEM has been shown to be a useful tool for completely characterizing colloidal material; in addition, data on the effect of waste glass tests parameters on colloid stability has enabled a picture of colloid formation in the leachate to be constructed. More studies are in progress, including work on the physical properties of leachate colloids (e.g., zeta potential measurement). Comparison with AEM work will provide an improved understanding of colloid formation and waste glass reaction in general.

X. TECHNICAL REVIEW OF ANALYTICAL ELECTRON MICROSCOPY OF GLASS REACTION

A. Introduction, Background, and Objective

Analytical Electron Microscopy (AEM) analysis of the reacted glass samples is an important component of the High-Level Nuclear Waste Technical Support Program at Argonne. As part of this project, the University of New Mexico (UNM) is providing peer review input by performing Analytical Electron Microscopy and Scanning Electron Microscopy (SEM) analyses of reacted glass samples to confirm conclusions reached at ANL. This work is being done under the ANL-UNM Contract No. 10362402.

This report covers the extensive AEM and SEM analyses performed at UNM on three reacted 131U samples.

B. Technical Approach

1. Sample Preparation

The three samples received from ANL for analysis in this reporting period are 131U-56-1a, 131U-91-1a, and 131U180-1a. These samples were composed of SRL 131, uranium-doped glass that was reacted in a water saturated vapor environment at 150°C for 56, 91, and 180 days, respectively.

Analytical transmission electron microscopy of cross-sectional samples allows the examination of microchemical and microstructural changes from the top of the reacted surface to the unreacted glass underneath. These samples are very thin sections several hundred angstroms thick that are cut perpendicular to the original sample surface. An ultramicrotomy slicing technique [1] was used to obtain these thin sections. In this process, small chunks containing the reacted surface layer and usually a thin layer of glass were broken off from the sample surface. Each chunk was then embedded in resin to form a block. Finally, thin sections, approximately 90 nm thick, were microtomed from these blocks and were transferred to copper mesh grids covered by perforated carbon films. The samples are so fragile and delicate that most of the thin sections were found to be shattered and separated from both glass substrate and the embedding resin under TEM observation. More than 30 grids, each containing 15 to 20 microtomed sections, were prepared and carefully studied in order to achieve the data gathered in this report.

2. Scanning Electron Microscopy

SEM with energy dispersive X-ray spectroscopy (EDS) analysis has been performed on the sample surfaces to obtain morphological overview of the reacted glass surface as well as to observe the composition-morphology relationship of the secondary phases on the surface. SEM analyses were conducted before the sample surfaces were damaged during the TEM sample preparation process. A Hitachi s-800 scanning electron microscope with a field emission electron source and a windowless PGT EDS system was used for the analyses. During the analyses, the electron energy was set at 20 kV. The PGT EDS system does have the light element detectability. However, the analyses only provided qualitative information on chemical composition of the reacted surfaces.

3. Analytical Electron Microscopy

AEM was performed using a JEOL JEM-2000FX microscope with a Noran TN-5500 EDXS system. The microscope was operated at 200 keV during analyses. Extensive TEM imaging including high resolution electron microscopy (HREM), selected area electron diffraction (SAD), and EDS studies were conducted.

The magnification of the microscope at its higher end was calibrated using the 0.34-nm (002) lattice fringes from a graphitized carbon specimen at a set objective lens condition. However, due to small variations in specimen height and lens conditions, an error of $\pm 5\%$ could be incurred in the magnification of the HREM images. The camera length used for the electron diffraction was calibrated using a Si [111] zone axis pattern; the error in measurement is within $\pm 3\%$.

Many factors contribute to the errors induced in the quantitative EDS analysis. First of all, since the Noran EDS system used has a relatively thick ($7.5\ \mu\text{m}$) Be window, most low energy characteristic x-rays excited from light elements were absorbed. So, elements with atomic number smaller than that of Na(11), which include O, B, and Li, cannot be detected. Secondly, the quantitative software used, SQMTF, can only handle eight elements, but there are many more elements present in the glass samples. Also, no absorption corrections were made for the results of analyses, mainly because local sample thickness can not be determined accurately. Nevertheless, valuable information on glass leaching process can be obtained by comparing the EDS analyses obtained from various areas of the sample.

The eight "major" elements included in the quantitative analysis of this study are Si, Fe, Mg, Ca, Al, Ni, Mn, and O. (Although O was undetectable with the EDS system, it was calculated according to the oxide formula of the other seven elements.) The K-factors used for these elements have been well calibrated in the laboratory from simple minerals and 202U glass in the past, and a detailed error analysis was reported [2].

C. Results and Discussion

1. SEM Analyses

In the SEM analyses, well-developed analcite ($\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$) crystals were identified on top of the honeycomb-like smectite layers on all of the three samples. (This was confirmed by both EDS data and their morphology which implies cubic crystal structure.) The analcite crystals on the sample surface increased greatly in abundance with the increasing reaction time. Flower-like structures that do not show compositional difference with the underlying honeycomb-like smectite have also been observed on the surfaces of 131U-91-1a and 131U-180-1a samples. They are believed to be smectite as well, but with a different morphology. The density of these flower-like structures increased significantly with the reaction time.

Figures 41a and 41b are SEM micrographs of 131U-56-1a samples and shows a honeycomb-like smectite layer covering the sample surface. Figures 42a and 42b are SEM micrographs of 131U-91-1a that show a large spherical aggregate of analcite crystals and flower-like smectite on top of honeycomb-like smectite. Figures 43a and 43b are SEM micrographs of 131U-180-1a and show a high density of the flower-like smectite, with a single analcite crystal on top of the sample surface.

Fig. 41. SEM Micrographs of the Surface of a ^{131}U -56-1a Sample Showing the Honeycomb-Like Smectite. (a) Lower magnification (3X); (b) higher magnification (10X).

Fig. 42. SEM Micrographs of the Surface of a ^{131}U -91-1a Sample. (a) Low magnification (3X) showing a large spherical aggregate of analcite crystals; (b) higher magnification (10X) showing the flower-like smectite on top of the honeycomb-like smectite.

Fig. 43. SEM Micrographs of the Surface of a 131U-180-1a Sample. (a) High density of the flower-like smectite on top of the honeycomb-like smectite; (b) single analcite crystal on top of the smectite.

2. AEM Analyses

a. Sample 131U-56-1a

Figure 44 is a cross-sectional TEM micrograph covering the entire surface layer of a 131U-56-1a sample. Figure 45 emphasizes the top and the middle section of the layer, respectively. As can be seen clearly in this micrograph, the primary smectite layer consists of two major parts, a top layer $\sim 1 \mu\text{m}$ thick in which the basal planes are perpendicular to the surface and a bulk alteration layer 2-3 μm thick that is composed of many different sublayers and features. These sublayers and features include regions with different crystal sizes and regions that are still amorphous (remaining glass but less dense), as well as many cavities in between the smectite crystals. Note the cracks, which are perpendicular to the sample surface and might have been generated during the course of TEM sample preparation.

EDS analyses have shown that the top surface layer is enriched in Mg, Al, Mn, and contains a small amount of Cl compared to the glass composition, while the remaining amorphous regions in the bulk alteration layer are apparently depleted with Mn. The small crystallites adjacent to the amorphous regions contain a little more Mn and less Ca than the amorphous region, and the sublayers with large smectite grains have a composition similar to the top surface layer, except the former contains less Mg and no Cl contamination.

Figure 46 is a high-resolution TEM micrograph showing the amorphous region, a smectite sublayer with larger crystals, and small smectite crystallites in between. The lattice fringe spacing in the micrograph varies from 1.2 to 1.5 nm, similar to that of the smectite basal spacing. The physical relationship of the three unique regions in the bulk alteration layer is consistent with the trend of change in chemical composition and indicates that the small crystallites adjacent to the remaining amorphous regions are newly nucleated compared to the larger crystals even though some larger crystals were found at greater depth. In other words, nucleation of smectite in this reacted sample is not homogeneous and may start underneath uncrystallized regions.

Fig. 44. Cross-Sectional TEM Micrograph Showing the Entire Surface Alteration Layer of a 131U-56-1a Sample

Fig. 45. Cross-Sectional TEM Micrograph Emphasizing the Top and Middle Parts of the Smectite Layer Formed on a 131U-56-1a Sample

Fig. 46. High-Resolution TEM Micrograph Taken from the Bulk Alteration Layer of a ^{131}U -56-1a Sample. It shows an amorphous region (on the left), a smectite sublayer with larger crystals (on the right), and small smectite crystallites in between.

The formation of cavities was observed with the formation of smectite crystals in the reacted glass. This is easy to understand because the smectite crystal has higher density than the glass matrix. Figure 47 is a high-resolution TEM micrograph taken from the bulk alteration layer of ^{131}U -56-1a that shows the formation of smectite crystals with cavities. It is interesting to notice in the micrograph that the smectite crystals are bent around the cavities or terminated at the cavity.

Figure 48 is a high-resolution TEM micrograph showing the mixture of large smectite sublayer, small smectite crystallites, and cavities. Figures 49a and 49b are selected area electron diffraction patterns from the region with larger smectite crystals and the region with only small smectite crystallites, respectively. The major d-spacings measured from both patterns are virtually the same (0.47, 0.27, and 0.16 nm). However, the diffraction rings in Fig. 49a are less continuous than in that of Fig. 49b, indicating that there are fewer crystals and a preferred orientation in the region of larger crystals.

Fig. 47. High-Resolution TEM Micrograph Taken from the Bulk Alteration Layer of 131U-56-1a Showing the Formation of Smectite Crystals and Cavities. (Note that the smectite crystals bend around the cavities.)

Fig. 48 High Resolution TEM Micrograph Showing the Mixture of Large Smectite Sublayer, Small Smectite Crystallites, and a Cavity in the Bulk Alteration Layer of a 131U-56 Ta Sample

Fig. 49 Selected Area Electron Diffraction Patterns from (a) the Region with Larger Smectite Crystals and (b) the Region with Only Small Smectite Crystallites. The major d spacings measured from the both patterns are virtually the same (0.47, 0.27, and 0.16 nm)

High-resolution TEM micrographs of the large smectite crystals taken from the top surface and the bulk layers of the 131U-56-1a sample, respectively (Fig. 45), show that the smectite crystals at the top surface are mostly straight, with the basal plane perpendicular to the sample surface, while many crystals underneath are significantly bent. That difference in crystal morphology must be related to the differences in the local strain fields.

b. Sample 131U-91-1a

Most thin sections from the 131U-91-1a sample were shattered during microtoming, probably due to the thickness of the fragile alteration layer. Figure 50 is a low-magnification TEM micrograph taken from a relatively intact section from this sample. It is estimated that the alteration layer thickness on this sample is ~20 μm or even larger. Figure 51 is a higher-magnification TEM micrograph that shows the top surface of this section. As indicated in Fig. 51, at the very top surface of the layer (left in the micrograph) there is a region which contains relatively larger smectite crystals and underneath that is an uniform layer of small smectite crystallites. Part of the interface between the two regions was broken (lower part of Fig. 51), indicating a very weak bonding at the boundary between the two different parts of the alteration layer, and filled with resin which was used during sample preparation.

The smectite grain size in the top surface layer of the 131U-91-1a sample is 200 nm or larger. The basal spacings measured from a high-resolution micrograph of this region are between 1.2 and 1.5 nm. The basal plane of the smectite crystals of this layer did not exhibit specific preferred orientation like that observed in the top surface layer of the 131U-56-1a sample. Comparing to the underlying bulk alteration layer, the top layer are enriched with Fe and Mn, but has less Ca.

Underneath the top surface layer are randomly oriented small smectite crystallites with very uniform grain sizes (20 to 40 nm long and less than 10 nm wide, as shown in Fig. 52), suggesting a homogeneous nucleation process. There are no remaining amorphous regions or large crystals found in the entire bulk alteration layer. If the experimental conditions (except for the reaction time) are truly identical for 131U-56-1a and 131U-91-1a, the larger crystals seen in the bulk layer of the 131U-56-1a must have undergone recrystallization during the prolonged reaction at 150°C.

c. Sample 131U-180-1a

The alteration layer on the 131U-180-1a sample is much thicker than that in the other two samples. Although more than 200 sections have been microtomed, none of them appeared intact. Figure 53 shows a relatively good section that is believed to be only a portion of the alteration layer on the sample. The thickness of the section is more than 20 μm . The microstructure of the entire section seems to be very uniform, but EDS spectra show some variation in chemistry from area to area. Figure 54 is a TEM micrograph taken from the section at moderate magnification. The d-spacings measured from the selected area electron diffraction patterns of the layer match that of the smectite in the other two samples. The smectite crystals in this section are about 20-40 nm long and 10 nm or less in width, with basal spacing of 1.2-1.5 nm, the same as that of the bulk smectite layer in 131U-91-1a. The microstructure of the section suggests homogenous nucleation of the smectite within the entire layer.

Fig. 50. Cross-Sectional TEM Micrograph of a Relatively Intact Section of the Alteration Layer on Top of a 131U-91-1a Sample

Fig. 51. Cross-Sectional TEM Micrograph of the Top Surface of the Alteration Layer on a 131U-91-1a Sample

Fig. 52. High-Resolution TEM Micrograph and Corresponding Selected Area Electron Diffraction Pattern from the Bulk Smectite Layer underneath the Top Surface Layer in a 131U-91-1a Sample

Fig. 53. Cross-Sectional TEM Micrograph of a Relatively Intact Section of the Alteration Layer on Top of a ^{131}U -180-1a Sample

Fig. 54. TEM Micrograph at Higher Magnification and Selected Area Electron Diffraction Pattern Showing the Microstructure of the Alteration Layer on a ^{131}U -180-1a Sample

D. Summary

Detailed SEM and cross-sectional AEM have been performed on the surface alteration layer of three ^{131}U glasses reacted at 150°C for different lengths of time.

The surfaces of all the samples are covered with a honeycomb-like smectite alteration layer. The thickness of the layer increased with the reaction time. Large analcite, $\text{Na}(\text{AlSi}_2\text{O}_6)\cdot\text{H}_2\text{O}$ crystals and flower-like smectite, with increasing density of both with the reaction time, have been found on top of the honeycomb-like smectite layers.

The primary smectite layer in 131U-56-1a consists of two major parts, a $\sim 1\text{-}\mu\text{m}$ -thick top layer in which the basal planes are perpendicular to the surface and a bulk alteration layer that is composed of regions with several different features, suggesting an inhomogeneous smectite nucleation process.

The microstructure of the bulk smectite layer on 131-U56-1a and 131U-180-1a are found to be quite uniform with high density of small crystallites, suggesting a homogeneous recrystallization process.

XI. WATER DIFFUSION OF NUCLEAR WASTE GLASSES

A. Introduction, Background, and Objective

Chemical durability of glasses is strongly influenced by water content [94,95]. Water can enter into glasses by diffusion. However, the data on water diffusion into glass from the vapor phase are scarce, especially at low temperatures, in contrast to data on glass dissolution or leaching in solvents. The objective of the present research is to obtain water diffusion data for the simulated nuclear waste glasses in order to evaluate chemical durability of the glasses. This report reviews the water diffusion study of the simulated nuclear waste glasses at the Rensselaer Polytechnic Institute (RPI) during the past year.

B. Technical Approach

Three simulated nuclear waste glasses, SRL 131U, SRL 165U, and SRL 202U, were studied. These glasses were prepared at Argonne National Laboratory (ANL) and supplied to RPI as blocks with approximate dimensions of 15 mm x 15 mm x 50 mm. Chemical compositions of the three glasses determined by ANL are summarized in Table 1.

Glasses were cut into platelets with dimensions of 12 mm x 10 mm x about 40 μm and then polished by using 400 and 600 grit SiC papers, 15- μm diamond powder, and CeO_2 powder in sequence. After polishing, all the specimens were washed twice with acetone in an ultrasonic cleaning bath for two minutes each and finally washed with ethanol in the ultrasonic cleaning bath for three minutes. For as-polished thin samples, inhomogeneities consisting of streaks and bubbles could be seen visually.

The water diffusion coefficients were experimentally determined at various temperatures using two different method, hydration and dehydration. Infrared spectroscopy (IR) was the main experimental characterization tool for water diffusion into or out of glass. According to Beer's law, the amount of water uptake or loss is proportional to the change in absorbance, ΔA_t , after treatment time, t as follows:

$$\Delta A_t = \log(I_0/I_{3540})_t = t - \log(I_0/I_{3540})_{t=0} \quad (8)$$

where I_0 is the transmission at the wave number of $\sim 4000 \text{ cm}^{-1}$ and I_{3540} is transmission at $\sim 3450 \text{ cm}^{-1}$, corresponding to "free" OH stretching vibration. The value of ΔA_t is positive for hydration and negative for dehydration.

The dehydration method was used to measure diffusion coefficients at temperatures from 300°C to 500°C in a dry atmosphere. The specimens were treated in either dry air (at 450°C and 500°C) or dry nitrogen (at 300°C to 400°C). To reduce the moisture content in the gases, they were pumped through a cold trap (liquid nitrogen), drierite, and a molecule sieve first and then into the tube furnace which contained the glass specimens. During the dehydration process, it is assumed that the surface concentration is zero. Then the amount of water diffused out through the specimen surface ($x = 0$) over a given period of time t , M_t , is equal to the integration of flux at the surface, J_0 [96]. Thus,

$$M_t = \int_0^t J_0 dt = \int_0^t \{ D (\delta C / \delta X)_x = 0 \} dt$$

$$= 2 (D/t)^{1/2} (\delta C / \delta \xi)_{\xi=0} \quad (9)$$

where D is the diffusion coefficient, C is the water concentration, $C(x,t)$ and $\xi = x/(Dt)^{1/2}$. For a specimen with thickness d , Eq. 9 can be expressed by

$$(M_t - M_i)/(M_\infty - M_i) = 1 - \sum_{n=0}^{\infty} \{ [8/(2n+1)^2 \pi^2] \exp [-D(2n+1)^2 \pi^2 t/d^2] \} \quad (10)$$

where M_i is an initial water content. M_t and M_∞ are the amount of water diffused out at time t and time of diffusion process reaching saturated level, respectively. When the diffusion time is short or equivalent when the thickness of the specimen is large, Eq. 10 yields [96]

$$(M_t - M_i)/(M_\infty - M_i) = 4/\pi^{1/2} (D t / d^2)^{1/2} \quad (11)$$

or

$$(M_t - M_i) = \{ 4/\pi^{1/2} D^{1/2} (M_\infty - M_i)/d \} t^{1/2} \quad (11a)$$

which makes the diffusion coefficient

$$D = (\pi / 16) \{ [(M_t - M_i) / t^{1/2}] / [(M_\infty - M_i)/d] \}^2 \quad (12)$$

Equation 11a shows that for the initial stage of water dehydration, water content decreases linearly with the square root of time. Since $(M_t - M_i)$ and $(M_\infty - M_i)$ are equal to $\Delta A_t/\epsilon$ and $(A_\infty - A_i)/\epsilon$, where A and ϵ are the water absorbance at $\sim 3540 \text{ cm}^{-1}$ and the extinction coefficient, respectively, the diffusion coefficient can be directly determined from the initial stage of the loss of water by

$$D = (\pi / 16) \{ [(\Delta A_t / t^{1/2}) / [(A_\infty - A_i)/d]] \}^2 \quad (13)$$

According to Eq. 13, diffusion coefficient can be determined from the slope of $-\Delta A_t$ vs. $t^{1/2}$, assuming A_∞ is equal to zero for complete removal of water in glass.

For the hydration studies, specimens were hydrothermally treated at 150°C in water vapor with relatively high water vapor pressures 2,619 and 3,571 mm Hg to accelerate the diffusion process. Specifically, the glasses were treated in a 45-mL Teflon-lined digestion bomb (No. 4744 bomb, Parr Instrument Corp., IL) was used. Each specimen was placed separately on the Teflon stage above 5 mL of deionized water in the bomb. The effect of water vapor pressure on water uptake at constant temperature, 150°C was investigated using pure water and NaCl-saturated water, respectively. The former generates 3,571 mm Hg water vapor pressure and the latter generates 2,619 mm Hg vapor pressure [97]. For thin specimen, it was possible to saturate specimens for relatively short time. Assuming a constant surface water concentration during hydration, when specimen is saturated, the water uptake can be described by Eq. 10.

In addition to water diffusion study, optical microscope, X-ray diffraction, and microhardness indentation were used to characterize glasses during the hydrothermal treatment.

C. Results

1. Dehydration

Figure 55 shows a typical infrared spectra of a specimen dehydrated for various experimental durations, revealing that the absorption peak of "free" OH stretching decreases with increasing time. Figures 56a through 56f illustrate the water loss as a function of the square root of dehydration time for the three glass specimens at various temperatures. The dependence on $t^{1/2}$ for the water removal was observed, suggesting that diffusion controlled the process. The linear regression coefficients, R^2 , range from 0.951 to 0.999. By substituting the slope value, $-\Delta A_t / t^{1/2}$, initial water absorbance, A_i , and the specimen thickness, d , into Eq. 13, the water diffusion coefficients were determined. (See Table 31.)

Figures 57a through 57c illustrate water diffusion coefficient obtained as a function of the reciprocal of absolute temperature for the simulated nuclear waste glasses. It appears that there are two temperature ranges with different activation energies, the lower activation energy being observed at lower temperature, although the presence of the low temperature range for SRL 131U is not clear with the data presently available. A similar phenomenon was previously reported for silica glass [100]. For high temperatures, linear regression analyses yield these activation energies: 28.4 kcal/mol for SRL 131U, 33.9 kcal/mol for SRL 165U, and 35.2 kcal/mol for SRL 202U. At low temperatures, the apparent activation energies are 18.3 kcal/mol for SRL 165U and 8.2 kcal/mol for SRL 202U. It should be noted that the surface concentration of dehydrated specimen is assumed to be zero to determine the diffusion coefficient. The error caused by this assumption is greater at lower temperatures since the solubility of water in a glass is higher at lower temperature [101]. Thus, the present data should be regarded preliminary until improved by repeated experiment. The presence of two activation energies observed here, however, suggests that the phenomenon may be universal in view of the similar, previous observation on silica glass [100].

Fig. 55. FTIR Spectra of SRL 131U Dehydrated in Dry Air at 400°C

Fig. 56. Water Loss for the Simulated Nuclear Waste Glasses Dehydrated at Various Temperatures

Fig. 56 Contd.

Fig. 57. Water Diffusion Coefficient vs. Temperature for the Simulated Nuclear Waste Glasses Dehydrated at Temperatures from 300°C to 500°C

Table 31. Water Diffusion Coefficient D^a from Dehydration for the Simulated Nuclear Waste Glasses

Temperature	D (cm ² /s)		
	SRL 131U	SRL 165U	SRL 202U
300°C	3.5×10^{-12} ($\pm 0.3 \times 10^{-12}$)	2.0×10^{-12} ($\pm 0.1 \times 10^{-12}$)	3.5×10^{-12} ($\pm 1.0 \times 10^{-12}$)
350°C	4.5×10^{-12} ($\pm 0.4 \times 10^{-12}$)	7.0×10^{-12} ($\pm 0.7 \times 10^{-12}$)	5.3×10^{-12} ($\pm 0.3 \times 10^{-12}$)
375°C	2.5×10^{-11} ($\pm 0.1 \times 10^{-11}$)	1.3×10^{-11} ($\pm 0.5 \times 10^{-11}$)	8.5×10^{-12} ($\pm 0.9 \times 10^{-12}$)
400°C	8.0×10^{-11} ($\pm 0.4 \times 10^{-11}$)	2.0×10^{-11} ($\pm 0.3 \times 10^{-11}$)	2.5×10^{-11} ($\pm 0.1 \times 10^{-11}$)
450°C	1.5×10^{-10} ($\pm 0.1 \times 10^{-10}$)	8.3×10^{-11} ($\pm 0.9 \times 10^{-11}$)	4.5×10^{-11} ($\pm 0.2 \times 10^{-11}$)
500°C	6.0×10^{-10} ($\pm 0.1 \times 10^{-10}$)	4.8×10^{-10} ($\pm 0.5 \times 10^{-10}$)	3.3×10^{-10} ($\pm 0.1 \times 10^{-10}$)

^aValues in parentheses are the standard deviations.

2. Hydration

Figure 58 shows a typical IF spectrum of SRL 131U hydrothermally treated at 150°C in 3,571 mm Hg water vapor for several selected experimental durations. Two absorption peaks exist in Fig. 57, one due to "free" OH stretching at about 3540 cm⁻¹ and the other due to hydrogen-bonded hydroxyl at ~2700 cm⁻¹ [102,103]. Figure 59 shows the corresponding absorbance increase of SRL 131U after the background spectrum of untreated specimen is subtracted. The 2700 cm⁻¹ peak was found to remain unchanged, while the 3540 cm⁻¹ peak increased with time. Thus, water uptake of each specimen was monitored by the change of absorbance of the peak at about 3540 cm⁻¹ during the hydrothermal treatment.

Figure 60 illustrates water uptake of the three simulated nuclear waste glasses treated in the conditions described above. Two features are evident: water uptake approaches a saturation and an abrupt upturn of water uptake takes place after the apparent saturation, followed by the second saturation. At the point of the first saturation, water concentration profile in specimen of SRL 131U was investigated by successively polishing the specimen using diamond paste in oil. Figure 61 illustrates the profiles of water contents in both untreated and treated specimens of SRL 131U. According to Beer's law, water absorption is linearly proportional to the specimen thickness if water content is uniform throughout specimen. The comparison made in Fig. 61 indicates that water is uniformly distributed for both untreated and treated specimens. It is assumed that other two glasses also have uniform water distribution after the same hydration treatment.

Fig. 58. FTIR Spectra of SRL 131U Hydrothermally Treated at 150°C in 3,571 mm Hg Water Vapor for Several Experimental Time Periods

Fig. 59. FTIR Spectra after Subtracting Background Spectrum from Fig. 60 ($t = 0$ hr)

Fig. 60. Water Uptake of Simulated Nuclear Waste Glasses Hydrothermally Treated at 150°C in 3,571 mm Hg Water Vapor

Fig. 61. Total Remaining Absorbance as a Function of the Specimen Thickness for SRL 131U Untreated and Treated at 150°C in 3,571 mm Hg Water Vapor

Using the water saturation level of each specimen treated for 350 hr, diffusion coefficients of the three glasses were determined by applying Eq. 14 as $2.9 \times 10^{-10} \text{ cm}^2/\text{s}$ for SRL 131U, $2.5 \times 10^{-10} \text{ cm}^2/\text{s}$ for SRL 165U, and $2.4 \times 10^{-10} \text{ cm}^2/\text{s}$ for SRL 202U. Figures 62a through 62c compare the experimental data with the theoretical profile generated from the determined diffusion coefficient.

Although the specimens appear to be saturated with water after 350 hr in 3,571 mm Hg water vapor at 150°C , continued hydration produced an abrupt upturn of water uptake for SRL 165U and SRL 202U. A similar phenomenon has been reported for water adsorption of a glassy polymer and was considered to be associated with polymer swelling and crazing [104]. If a similar process is assumed to operate for the glasses treated here, the observed increase in uptake after the initial apparent saturation at ~ 350 hr can be attributed to glass structure swelling. The apparent diffusion coefficients of SRL 165U and SRL 202U during the extended treatment were determined using this method, in which the saturation level was redefined by the water uptake after 805 hr. The resulting water diffusion coefficients are $7.4 \times 10^{-11} \text{ cm}^2/\text{s}$ for SRL 165U and $7.3 \times 10^{-11} \text{ cm}^2/\text{s}$ for SRL 202U, respectively. Figures 63a and 63b illustrate the normalized water uptake in these two water diffusion regimes, before and after the first apparent water saturation, for SRL 165U and SRL 202U. The apparent diffusion coefficients decrease with increasing treatment time. The similar time dependent (decreasing) diffusion coefficient of water was observed for silica glass at low temperature [105].

In order to further investigate the cause of the observed abrupt upturn, the glass specimens for SRL 202U, both untreated and treated at 150°C in 3,571 mm Hg water vapor for 505 hr, were observed under an optical microscope. In the treated specimen, two types of surface cracks were observed, some surrounding bubbles and others away from bubbles. The former are apparently caused during the specimen polishing process since they are observed in the untreated specimen. The latter appears only after water entry into glass.

Water entry into glass causes osmotic pressure increase and the subsequent volume expansion in the glass network. The increase of osmotic pressure due to water entry into glass would limit the water solubility in the glass [106]. The initial apparent water saturation that was observed for these glasses corresponds to this situation. With time, the osmotic pressure should be reduced by the glass volume expanding by relaxation or swelling. Under this condition, the water solubility of glass is expected to increase further, causing further water uptake. This may be the cause for the uptake time dependence shown in Fig. 60.

Many factors influence the water uptake, including temperature and water vapor pressure. Water vapor pressure effect on water diffusion for SRL 131U was investigated by treating the glass at 150°C in 2,619 mm Hg water vapor. Figure 64 shows the water uptake versus time for SRL 131U treated under this condition compared to that under higher vapor pressure. It is evident that the initial rate of water uptake is higher for the specimen treated under higher vapor pressure. The initial water solubility under two water vapor pressures was evaluated from the initial saturation of water uptake. It was observed that the ratio of the solubilities is 1.4, which is nearly equal to the ratio of the water vapor pressure, 1.36. It is known that the water solubility for glass increases with increasing water vapor pressure, proportionately to the square root of water vapor pressure at high temperature [107], but linearly to the pressure at low temperature [105].

Fig. 62. Comparison of the Experimentally Measured Water Uptake and the Theoretically Calculated Profile for the Simulated Nuclear Waste Glasses Hydrothermally Treated at 150°C in 3,571 mm Hg Water Vapor

Fig. 63. Comparison of the Experimentally Measured Water Uptake and Theoretically Calculated Profile for SRL 165U and SRL 202U Treated at 150°C in 3,571 mm Hg Water Vapor during the Two Stages of Water Uptake. (Note that the data in the first stage of water diffusion, before an abrupt upturn, are readjusted according to the apparent saturation level of water uptake for the second diffusion stage.)

Fig. 64. Water Uptake as a Function of Time for SRL 131U Treated at 150°C in 3,571 and 2,619 mm Hg Water Vapors

Although three apparent stages of water uptake exist, under 2,619 mm Hg water vapor, the process appears slower than that under the higher water vapor pressure, the sudden break taking place after longer treatment time. This further supports the view that during water entry into glass, the increase of osmotic pressure and the subsequent volume increase by the network relaxation or swelling are responsible for the uptake. Applying Eq. 14 to each of the diffusion stages and treating the plateau before the upturn as the apparent saturation, the apparent diffusion coefficients for the three stages were determined to be $12.0 \times 10^{-11} \text{ cm}^2/\text{s}$, $7.2 \times 10^{-11} \text{ cm}^2/\text{s}$, and $3.3 \times 10^{-11} \text{ cm}^2/\text{s}$, respectively. The apparent diffusion coefficient again decreases with increase of the treatment time, which is similar to that for specimens treated at 150°C in 3,571 mm Hg water vapor. Data are compared with theoretical predictions using the estimated diffusion coefficients in Fig. 65.

When the diffusion coefficients evaluated from the initial plateau in the uptake curve are compared for glasses treated under different water vapor pressures, it was found that the diffusion coefficient increases with increasing the vapor pressure. The ratio of diffusion coefficients corresponding to high to low vapor pressure is 2.4 for SRL 131U. It is shown that the diffusion coefficient increases with water content, especially at high water content [101,107].

Fig. 65. Comparison of the Experimentally Measured Water Uptake and the Theoretically Calculated Uptake Profile for SRL 131U Hydrothermally Treated at 150°C in 2,619 mm Hg Water Vapor. (Note that the data in the first and the second stages of water diffusion, before an abrupt upturn, are readjusted according to the apparent saturation level of water uptake for the third diffusion stage.)

3. Hydration Effect on Microhardness of Simulated Nuclear Waste Glasses

It has been reported for silica glass that water interaction with glass reduces its microhardness [108]. The effects of water content on Knoop microhardness of the simulated nuclear waste glasses were investigated by measuring the hardness values of specimens, both untreated and treated at 150°C in 3,571 mm Hg water vapor for 805 hr.

Table 32 summarizes average Knoop microhardness numbers for both specimens untreated and treated at 150°C in 3,571 mm Hg water vapor for 805 hr. The relative water contents for both conditions of each glass are also summarized in Table 32. For all the untreated glasses, their Knoop microhardness numbers are similar, approximately 385 kg/mm². For the treated glasses, their hardness values are reduced by approximately 30% to 258 kg/mm² and 286 kg/mm² for SRL 165U and SRL 202U, respectively.

Table 32. Knoop Microhardness Numbers and Relative Water Contents of the Simulated Nuclear Waste Glasses

	SRL 131U		SRL 165U		SRL 202U	
	Untreated	Treated ^a	Untreated	Treated ^a	Untreated	Treated ^a
Knoop Hardness (kg/mm ²) ^b	383.7 ± 18.8	--	393.6 ± 15.9	257.6 ± 15.1	384.6 ± 9.0	286.0 ± 18.5
Hardness Reduction (H _{un} - H _{tr})/H _{un} x 100%		--		35.0		26.0
Relative Water Content, A/d (cm ⁻¹)	4.5	--	3.8	9.3	4.0	10.9
Relative Water Content Increase [(A/d) _{tr} - (A/d) _{un}] / (A/d) _{un} x 100%		--		145.0		173.0

^aTreated at 150°C in 3,571 mm Hg water vapor for 805 hr.

^bAverage of ten indentation measurements with standard deviation.

^cAbsorbance at the wavenumber ~3,540 cm⁻¹.

D. Discussion

1. Effect of Initial Water Content on Water Diffusion

The present study revealed that water diffusion coefficients for the simulated nuclear waste glasses are SRL 131U > SRL 165U > SRL 202U, although the difference in diffusion coefficient is not substantial. This trend can be attributed to the water content difference. Figure 66 illustrates water absorption A versus specimen thickness d for untreated glasses. According to Beer's law, the slope of A versus d is the water concentration C times the extinction coefficient ϵ . If the extinction coefficient is assumed to be the same for the three glasses, it can be seen that initial water content for SRL 131U is about the same as that for SRL 165U, while that for SRL 202U is somewhat lower. It is well known that the water diffusion coefficient is higher for glass containing higher water content [101,107].

Although the extinction coefficient is unknown for these glasses, the values for various borosilicate glasses containing Li, Na, and K have been reported [109]. According to this report [109], the extinction coefficients for the "free" OH stretching absorption for glasses with ~45 wt% SiO₂ are ~ 75 to 85 l/mol-cm. Since the glasses used in these studies contains from 44.6 wt% to 52.9 wt% SiO₂, using an average extinction coefficient, 80 l/mol-cm, the initial water concentration was estimated to be ~0.064 mol/l (~0.04 wt%) for SRL 131U and SRL 165U and ~0.049 mol/l (~0.03 wt%) for SRL 202U. The observed high-to-low diffusion coefficients for these glasses seem to associate with that factor, although other factors

Fig. 66. Water Absorbance as a Function of Specimen Thickness for the Simulated Nuclear Waste Glasses, Showing the Difference in Their Initial Water Content

influencing the diffusion coefficient of the glasses are also possible, such as different chemical compositions. (See Table 1.) However, various effects of chemical compositions on water diffusion are too complicate to draw a conclusion at the present stage.

2. Surface Crystallization

The major problem encountered in hydration study of the simulated nuclear waste glasses was the surface crystallization of specimens. This is expected when the glasses are heat treated at high temperature. The water vapor atmosphere tends to promote the rate of crystallization, thus causing the crystallization even at lower temperatures.

After 15 hours, the surfaces of the SRL 131U specimen treated at 250°C in 29,834 mm Hg water vapor were severely attacked by the water. X-ray diffraction analyses were conducted on the surface of the treated specimen before and after polishing off the first surface layer. Figure 67 shows the X-ray diffraction patterns for both cases, which clearly reveal the presence of crystalline phases. For the phase identification, published information for the similar nuclear waste glasses [94,110] was used. Matching the X-ray diffraction patterns of this study with the reported phases revealed analcime $[\text{Na}(\text{Si}_2\text{Al})\text{O}_6 \cdot \text{H}_2\text{O}]$, tobermorite $[\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}]$ and stevensite $[(\text{CaNa})_x\text{MgSi}_4\text{O}_{10}(\text{OH})_2 \cdot z\text{H}_2\text{O}]$ as the water vapor hydration products for SRL 131U. In addition, the X-ray diffraction analysis also suggests the existence of $\text{Na}_5(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$. The similar phase of $(\text{NaKCs})_2(\text{UO}_2)_2(\text{Si}_6\text{O}_{15})_3 \cdot 4\text{H}_2\text{O}$ has been reported elsewhere [110].

Fig. 67. X-Ray Diffraction Patterns of SRL 131U Corresponding to the Surfaces Shown in Figs. 66a and 66b

This surface crystallization makes it difficult to obtain reliable water uptake data for determining water diffusion coefficient. In addition, water vapor condensation on specimen surfaces also causes the formation of a highly hydrated layer which would subsequently flake off when the specimen was removed from hydrothermal unit.

3. Diffusion Coefficient, Temperature, and Vapor Pressure Dependence

To summarize the dependence of water diffusion coefficient on temperature and water vapor pressure, Figs. 68a through 68c show the diffusion data for all three glasses measured at various conditions. Difference in diffusion coefficients are known to exist. For silica glass measured at high temperatures, those obtained from dehydration are less than ones from hydration by a factor of ~ 4 [111]. To estimate the diffusion coefficient at room temperature under low vapor pressure, the SRL 202U data were used. The dashed line in Fig. 68 represents the linear regression result for SRL 202U with a correlation coefficient of 0.91. The estimated diffusion coefficient at room temperature (25°C) and under low vapor pressure is $\sim 3.9 \times 10^{-15} \text{ cm}^2/\text{s}$.

E. Summary

Water diffusion studies of simulated nuclear waste glasses were conducted using both dehydration and hydration methods. Two temperature ranges for diffusion coefficient with different activation energies were observed. In general, the diffusion coefficient decreases in the order SRL 131U, SRL 165U, and SRL 202U, but the difference is rather small. The diffusion coefficient of water into glasses at room temperature is estimated to be $\sim 3.9 \times 10^{-15} \text{ cm}^2/\text{s}$. The difference in the water diffusion coefficient of these glasses appears to be associated with initial water concentration of these glasses. The results of these studies, done at high temperatures to accelerate the reaction process, will have to be correlated with other evaluations of the reacted glass surfaces (see Sections VI and X), to fully understand the role water diffusion plays in the reaction of nuclear waste glasses. For this purpose, the glass samples reacted in this study have been returned to ANL for AEM analysis.

Fig. 68. Temperature and Vapor Pressure Dependence of Diffusion Coefficient for the Simulated Nuclear Waste Glasses

XII. MODELING TASKS AT LAWRENCE LIVERMORE NATIONAL LABORATORY

A. 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 perform simulations of a wide range of tests types including MCC and PCT tests, site-specific tests, to model natural analogues, and to make performance assessment calculations of glass durability under repository conditions. Present long-term models for glass dissolution are limited because they rely on fitting parameters obtained through regression of short-term laboratory experiments. Our approach is to perform experiments that supply the necessary modeling parameters based on a mechanistic understanding of glass dissolution (using factors such as temperature and the pH dependence of glass rate constant) and validate the resulting model using site-specific test results and natural analogue observations. The validated model can then be used with confidence for performance assessment calculations of glass behavior in a repository.

In FY 1992 we performed several series of flow-through tests on SRL 165U, SRL 202, SRL 131, their simple analogues, and a series of SRL 202 analogue glasses having a range of silica concentrations. (See Table 33. Compositions of SRL glasses provided by ANL; CSG and S-202 glasses are nominal compositions). From the results of these tests, we determined the rate constants for SRL 202 and SRL 131 glasses as a function of pH at 70°C. We also investigated the dissolution rates of SRL 165 analogue glass in our pH buffers that were doped with varying concentrations of Al, B, and Si in order to determine the effects of these dissolved species on glass dissolution rates. (In FY 1991 we measured the effects of Ca and Mg.) Finally, we determined the effect on durability of adding incremental amounts of SiO₂ to SRL 202 analogue glass.

We also analyzed CSG, S-202, and a series of Na-B-Si glasses using nuclear magnetic resonance (NMR) spectroscopy in order to identify the molecular structure of these glasses. The NMR results tell us how various ions in the glasses are bonded, what their coordination numbers are, and to what extent clustering occurs in the glasses. Clustering refers to segregation of glass components into compositionally enriched zones (i.e., boron into boron-rich zones). This information is important in determining how we interpret dissolution tests of glass. Elements concentrated in preferred zones may be easier or harder to leach from the glass than the same elements in the homogeneous matrix. Clustering may also give rise to interconnected pathways for water diffusion for certain glass compositions, once the more soluble elements are removed. These pathways could increase the rate of water diffusion into the glass and therefore greatly increase the dissolution rate of the glass.

Coordination numbers are important because the ability of water to hydrolyze metal-oxygen bonds is related to the metal coordination number. For example, three-fold coordinated boron, which is denoted by B3, is easier to hydrolyze and remove from the glass than four-fold coordinated boron (B4). All of these factors are important in understanding the effects of glass composition on glass durability. However, only glasses that contain low concentrations of paramagnetic elements such as iron can be analyzed by NRM. For this reason, our NMR work has been limited to our simple analogue glasses and not actual complex production glasses.

Table 33. Compositions of Glasses Used in Flow-Through Dissolution Tests, mol %

Oxide	CSG	SRL 165	SRL 202	SRL 131	S-202
SiO ₂	59.33	58.60	55.44	51.41	56.27
Al ₂ O ₃	7.33	2.67	2.56	2.26	7.91
B ₂ O ₃	7.75	6.47	7.79	9.78	7.79
Mn ₂ O ₃	-	0.53	0.43	0.49	-
Fe ₂ O ₃	-	4.72	4.86	5.60	-
ZnO	-	0.03	0.01	0.01	-
Na ₂ O	18.79	11.62	9.79	13.8	22.19
K ₂ O	-	-	2.68	2.89	-
Li ₂ O	-	9.33	9.63	7.09	-
Cs ₂ O	-	0.02	-	-	-
FeO	-	0.32	-	-	-
CaO	6.81	1.93	1.46	1.17	5.59
MgO	-	1.16	2.23	2.29	-
SrO	-	0.07	0.02	0.01	-
BaO	-	0.03	0.10	0.07	-
MnO	-	1.07	0.86	0.99	-
NiO	-	0.76	0.75	1.17	-
U ₃ O ₈	-	0.08	0.16	0.23	-
TiO ₂	-	0.12	0.78	0.57	-
ZrO ₂	-	0.36	0.06	0.13	-
P ₂ O ₅	-	0.14	-	-	-
TOTALS	100.0	100.0	99.6	100.	99.8

B. Flow-Through Tests

Glass dissolution tests were performed in flow-through-type reactors described previously [2,22]. Powdered or monolithic glass samples weighing ~1 gram were reacted with pH-buffered fluids, some of which were doped with additional elements. The fluids were pumped through the system at a rate slow enough so that dissolved species from the glass were above detection limits, but fast enough so that they did not exceed saturation with respect to alteration phases. 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.

Buffers were chosen to minimize possible interferences of buffer species with the glass dissolution process as much as possible (Tables 34, 35, and 36). Thus, we selected buffers which did not contain ligands known to form strong complexes with glass species. Phthalic, hydrochloric, and boric acids and potassium hydroxide have been used previously in dissolution tests of silicate minerals [112], as well as simple waste glasses [22]. We used in addition, bis-tris[bis-(2-hydroxyethyl)amino]-tris[(hydroxymethyl)methane], tris[tris(hydroxymethyl)-aminomethane], and potassium phosphate. We also used potassium carbonate buffers, both the mixture KHCO₃-KOH and a simple KHCO₃ solution open to the atmosphere. Although carbonate and bicarbonate ligands are known to complex metals such as uranium and iron, carbonate ligands are present in Yucca Mountain groundwaters at about the same concentrations

used in our tests. In addition, our results show that carbonate-glass interactions apparently do not significantly affect dissolution rates because rates in both carbonate and boric acid solutions at the same pH are nearly equal.

High-temperature pHs of the buffer solutions were calculated using the program EQ3NR [113]. The calculations were constrained to have appreciable amounts of both pH buffer species, the protonated and deprotonated species. In general, we did not allow either pH buffering species to be less than 20% of the total at the temperature of interest. Given the desired pH and total concentration as inputs, EQ3NR program computed the amount of chemical reagents needed for the buffer. It also computed the pH of the buffer at 25°C to compare with measured values after the buffers were prepared.

During the experiment, glass dissolution modifies the pH of the leachate even though the leachate is a pH buffer. Although this is a minor effect in most cases, we have taken it into account in our data regression as follows. The 25°C pH of the reacted fluid and buffer composition are used as input to EQ3NR, along with the measured concentrations of dissolved glass species (e.g., silicon, aluminum, calcium etc. from the ICP analyses). One of the major components of the system (usually potassium) is allowed to vary in concentration in order to satisfy charge balance and to agree with the measured pH. The results from this 25°C calculation are then used to constrain the high-temperature (70°C) calculation. The revised total potassium is fixed, but the pH is allowed to change. This 70°C calculation gives the pH used in plots of dissolution rate versus pH at 70°C. The corrected pH is usually not substantially different from the pH of the pure buffer solution at 70°C, except at the highest and lowest pHs where reaction rates are fastest. The difference between the pHs of the input and reacted buffers can be obtained by comparing the pH of the buffer solutions in Tables 34, 35, and 36, with the corresponding pHs in the pH versus rate plots for each set of experimental results described below.

Initial flow rates were 50-60 mL/day. 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. In all tests so far, the steady-state dissolution rates were approximately the same at both flow rates, indicating there were 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.

Dissolution rates for each element were taken from the dissolution rate versus time plots at the point where the rates became steady with time. For example, the rate at about 10 days was used as the dissolution rate of the SRL 165 glass. Short reaction times are preferred because the surface area of the glass may change as dissolution proceeds (surface areas were measured using BET). Because we measure surface area at the beginning of the flow-through experiments, our rate calculation is best at low times. In many of our high pH experiments, where significant amount of glass dissolves, we see a lowering in glass dissolution rate with time, probably due to the diminishing amount of glass surface area as the glass particles dissolve away. For stoichiometric dissolution, any element can be used to compute overall glass dissolution rate. For regimes where dissolution was non-stoichiometric, we have reported glass dissolution rates in terms of silica-normalized data.

We performed the flow-through tests using both synthetic uranium-doped SRL 165U, SRL 202, and SRL 131 glasses prepared at ANL and simple analogues of these glasses. As described in previous work [2], analogue glass refers to a glass composed only of oxides of Na, Ca, B, Al, and Si that are in proportions similar to those of sets of structurally similar components in the complex glasses. For example, the formula for the simple analog SRL 202 glass was derived as follows. The mole fractions of all monovalent ions in the SRL 202 glass that are believed to exist in the glass in a similar structural role as sodium (e.g., sodium, lithium,

cesium) are added together and used to determine the amount of sodium in the analogue glass. Thus, we use sodium as a proxy for all monovalent ions in the complex glass that serve as charge compensators, either at sites where trivalent ions substitute for silicon or at non-bridging oxygen sites. A similar methodology and calculation is used for the other components using calcium, aluminum, boron, and silicon as the simplified component set. Based on experimental results presented last year for SRL 165 glasses, the analogue glass reacts at nearly the same rate and with the same pH dependency as the complex SRL 165 glass, indicating that our method for choosing an analog compositions in general is valid.

The simple analogue glasses have some clear advantages over the complex waste glass compositions in our experimental work. They have no redox dependence, so the redox state of the experiment does not have to be controlled. Because they do not contain extremely insoluble species (e.g., Ti, Zr, and Fe), the flow-through tests can be more readily interpreted without complications due to secondary-phase formation. Once the dissolution behavior of these glasses is understood, the effect of redox state and secondary-phase effects can be more reliably identified and quantified. The simple glasses can also be examined using NMR spectroscopy. Glasses that contain even small amounts of paramagnetic elements such as iron cannot be probed with NMR. Finally, we have shown that the durability of complex glasses is virtually identical to that of analogue glasses in work performed so far. In order to quantify the effects of glass composition on durability, our five-component analogs provide a tractable matrix of compositions that need to be examined in order to provide a statistically valid treatment of the data.

1. Test Series 1: SRL 131 and SRL 202 Glasses

Tests of SRL 131, SRL 202, SRL 165, and CSG glasses were performed at 70°C in the pH solutions described in Table 34. These tests had two purposes: (1) to gather flow-through-rate data for two previously untested glass compositions (SRL 131 and SRL 202), and (2) to check for any effects of buffer chemistry on dissolution rate for the tris, bis-tris, carbonate, and phosphate buffers. Earlier work has shown that some organic buffers decrease glass dissolution rates by up to a factor of three [114]. Our test results allow us to directly compare SRL 165 and CSG results with previous tests of these same glasses in phthalic and boric acid buffers in the same pH range.

The repository waters are expected to be neutral to weakly alkaline in pH, but few good pH buffers are available for the pH range of 7 to 9. Adding the phosphate, tris, and carbonate buffers allows better coverage over this pH range.

Table 34. Compositions of Buffers Used in Test Series 1

Buffer	Reagents		pH at 25°C	pH at 70°C
Bis-Tris	5 mM Bis-tris	2.6 mM HCl	6.48	5.83
Phosphate	5 mM KH ₂ PO ₄	2.3 mM KOH	7.0	6.99
Tris	5 mM Tris	2.4 mM KOH	8.06	7.03
Carbonate	5 mM KHCO ₃	3.1 mM KOH	10.3	9.8

Figure 69 shows the glass dissolution rate versus pH for the four glasses tested. The rate of silica release was used to determine the rate after being normalized to the different silica contents of the four glasses. Data regression for these flow-through tests was previously described in detail [2]. Additional data on the CSG glass is plotted to show the deviation between the present test results (labeled CSG-2) and previous results in phthalic and boric acid buffers. The agreement between the two data sets is satisfactory. However, most of the present data at near-neutral pHs show dissolution rates lower than previous measurements, possibly due to adsorption of the organic buffer species or phosphate on the glass surface. Only in the pH 10 carbonate buffer does the CSG glass dissolve faster than the rate in previous measurements in the borate buffer.

There was a consistent trend of dissolution rate at each pH for the four glasses. Glass durabilities were in the order $\text{CSG} > \text{SRL 165} > \text{SRL 202} > \text{SRL 131}$ over the entire pH range. This is the same trend that was observed in closed system tests of these same glasses.

This test series also showed a systematic anomalous behavior in which the sodium concentrations increased dramatically after about four days to a concentration about ten times higher than expected based on other elemental release rates. (See Fig. 70.) The sodium concentrations reached an apparent steady-state value after about ten days. The anomalous sodium increase affected all four glasses in all four buffer solutions at the same time. No other elements were affected. We were unable to explain these results, and the sodium data was not used in any further calculations of dissolution rates. The only possible source of sodium contamination was sodium hydroxide in the CO_2 trap for the argon that was kept in contact with the buffer solutions. This anomalous behavior has not been seen in any subsequent tests. There appeared to be no affect on pH of the buffer solutions either upstream or downstream from the sample cells.

We may perform more work with these buffers in conjunction with surface titrations to determine whether the buffers affect surface charge and therefore dissolution rate. For example, note how the SRL 131 glass dissolves much faster in phosphate buffer than in tris buffer at nearly the same pH. (See Fig. 69.) Surface titrations could tell us whether surface charge, which has been shown to correlate with dissolution rate, is significantly different in these two solutions due to the different buffer species present. Such information is necessary in order to predict dissolution rates under repository conditions, where a variety of anionic species such as phosphate may be present.

Fig. 69.
Dissolution Rates of CSG and SRL Glasses vs. pH. CSG-1 refers to data from previous tests of CSG glass. CSG-2 refers to results from test series 1 reported here. Buffer names mark the pH where each buffer was used.

Fig. 70.
Rate vs. Time Data for SRL 165
Glass in Bis-Tris Buffer Showing
Anomalous Sodium Behavior
after Four Days

The data from test series 1 have been combined with test results described below to regress an equation for the rate constant for SRL 131 and SRL 202 glasses. We have incorporated the regression equation into our glass dissolution model and use it to calculate SRL 131 and SRL 202 glass dissolution rates.

2. Test Series 2: CSG and SRL 202 Glasses in Doped Buffers

In this test series, we measured the effect on glass dissolution rate of adding small amounts of Si, B, and Al to the pH buffers. Both CSG and SRL 165 glasses, which had already been tested in the same buffer solutions without dopants, were used. Buffer compositions are given in Table 35. We used special buffers in some of the experiments that were unique to this test series. The aluminum-doped buffers were self buffered by aluminum-hydroxide species at pH 5 and 6.5. The silica-doped buffers were self buffered by potassium silicate at pH 9 at concentrations of 2 and 4 mM K_2SiO_3 . All tests were performed at 70°C. Glass powders were used over the entire matrix of conditions, glass disks were used in addition to the powders at pHs of 8 and 10 in the silica- and alumina-doped buffers. The alteration layers on the wafers were preserved and will be examined later.

Our glass dissolution model predicts that glass dissolution rates should slow down as dissolved glass species build up in solution. The affinity term in the rate equation presently used has the form $(1 - Q/K)$, where Q is the activity product of dissolved glass species and K is the solubility product for glass (or whatever dissolving phase is controlling the dissolution rate). Increasing the concentrations of dissolved glass species through doping increases the value of Q and consequently decreases the value of $(1 - Q/K)$. This effect will become even larger when the doped buffer solution reacts with the glass, thus becoming even more enriched in glass species. It was hoped that the results of these tests would enable a quantitative evaluation of the affinity term in our rate equation. However, for reasons described below, only limited qualitative information can be obtained from these test results.

One of the problems with using doped buffers in flow-through tests is that the buffer solutions may become supersaturated with respect to mineral phases, which may then precipitate. If precipitation has occurred, the measured solution concentrations downstream from the glass do not accurately reflect glass dissolution rate. They reflect both the glass dissolution and the mineral precipitation rates.

Table 35. Compositions of Buffers Used in Test Series 2

Buffer	Reagents		pH at 25°C	pH at 70°C
Al-Doped (2 mM Al(ClO ₄) ₃ in all buffers)				
Al(ClO ₄) ₃	2 mM Al(ClO ₄) ₃	2.2 mM KOH	5.1	4.0
Al(ClO ₄) ₃	2 mM Al(ClO ₄) ₃	7.2 mM KOH	6.5	6.0
Tris	5 mM Tris	6.6 mM KOH	8.5	7.5
Borate	5 mM B(OH) ₃	11.0 mM KOH	9.4	9.0
KOH	26.4 mM KOH	--	12.2	11.0
Si-Doped (2.5 mM K ₂ SiO ₃ unless otherwise indicated)				
Phthalate	5 mM KPhth	1.6 mM HCl	4.0	4.0
Phthalate	5 mM KPhth	1.1 mM KOH	5.2	5.5
Tris	5 mM Tris	4.0 mM HCl	8.0	7.0
Silicate	2 mM K ₂ SiO ₃	0.2 mM HCl	9.7	9.0
Silicate	4 mM K ₂ SiO ₃	0.6 mM HCl	9.7	9.0
B-Doped (2.5 mM B(OH) ₃ unless otherwise indicated)				
Phthalate	5 mM KPhth	0.34 mM HCl	4.0	4.0
Phthalate	5 mM KPhth	2.4 mM KOH	5.2	5.5
Tris	5 mM Tris	2.7 mM HCl	8.0	7.0
KOH	29.2 mM KOH	50 mM B(OH) ₃	9.3	9.0
KOH	71.6 mM KOH	50 mM B(OH) ₃	12.2	11.0

In addition, precipitation of mineral phases changes the pH of the leachate. For example, an iron rich clay such as nontronite would lower the pH as shown by the reaction:

EQ3NR was used to help determine whether the buffer compositions used in this test series were supersaturated with mineral phases. We anticipated that it might be impossible to dope the buffer solutions with appreciable amounts of relatively insoluble components such as alumina and silica without supersaturating with one or more aluminosilicate phases. EQ3NR results confirmed that most of our silica- and alumina-doped buffers were in fact supersaturated with mineral phases during glass dissolution. Although species concentrations are kept low in flow-through tests, even very small amounts of added Na, Ca, Si, and Al from the glass cause saturation levels for common aluminosilicate phases to be exceeded. For example, the silica-doped pH 5.2 phthalate buffer (experiment CSGP3, Fig. 71) after 19 days was calculated to be supersaturated with respect to muscovite, smectite, kaolinite, aluminum and silicon oxide polymorphs, and the zeolite stibite. Log saturation indices for these phases were between 0.3 and 6.

Typical normalized release rates for the silica doped tests are shown in Fig. 71. Steady-state dissolution is apparently reached after about ten days. Most of the doped tests eventually showed stoichiometric dissolution, although in many cases the curves did not flatten out until after a week or more of reaction. This contrasts with results from undoped tests, where steady state was usually observed after a few days.

Fig. 71.
Normalized Release Rates for
Elements in CSG Glass in Silica-
Doped pH 4.2 Phthalate-Buffered
Experiment. Release is nearly
stoichiometric after 20 days.

The precipitation of unwanted mineral phases may explain some anomalous results in this series of flow-through tests, where we did not always see steady-state conditions (i.e., the dissolution rate was not constant with time). Figure 72 shows an example of this for the pH 9.2 silica-doped buffer. The elemental dissolution rates apparently level off at about 5 days, then change dramatically and level off at a much different value after about 12 days. Comparison with Fig. 73 shows that the irregular behavior coincides with the time during which the pH drifted from its initial and desired value of around 9 to a final value of 3. Apparently, the buildup of dissolved glass species caused precipitation of secondary phases, which lowered the pH. Thus, these data provide little quantitative information on the pH dependence of CSG glass dissolution rate in silica-doped buffer solutions. Although there was no obvious indication from visual inspection that secondary phases formed in these tests, we have not yet characterized the run products with microscopic techniques

However, some experiments where there was a high degree of supersaturation with respect to mineral phases did result in good steady-state behavior. Figure 71 shows data from experiment CSGP3 mentioned above. The degree of supersaturation of secondary phases in experiment CSGP3 was comparable to that of experiment CSGP8. The results of CSGP3 showed a reasonable steady-state plateau and the pH drift for that buffer was not large. (See Fig. 73.) Supersaturation therefore did not always cause anomalous results, although it was probably a major problem in some of the experiments.

Fig. 72.
Normalized Release Rates for Elements
in CSG Glass in Silica-Doped pH 9.2
Potassium Silicate-Buffered Experiment

Fig. 73.
pH vs. Time for Silica-Doped Buffers. High pH buffers became acidic presumably due to precipitation of silica-bearing phases after reacted with glass.

Figures 74 and 75 show the pH versus time plots for the boron- and aluminum-doped buffer experiments. The pH values of the boron-doped buffers were fairly steady with time. This is reasonable because boron is a relatively soluble element and did not increase the saturation indices of mineral precipitates. The aluminum-doped buffers were more affected than the boron-doped buffers, especially at intermediate pHs. Neither showed the major pH changes shown in the silica-doped tests.

Results for the silica-, alumina-, and boron-doped flow-through tests of CSG are summarized in Fig. 76. The solid curve is a regression to the dissolution rate data for CSG glass in undoped buffers measured previously [22]. In general, silica decreases the rate substantially at neutral to alkaline pHs, but has little effect at low pHs. The opposite is true for aluminum, which has little effect at high pHs, but significantly decreases the rate at low pHs. Boron may decrease the rate slightly, but the data points are probably within experimental error of the previous tests in undoped buffers.

Fig. 74.
pH vs. Time for Boron-Doped Buffers. All but the lowest pH phthalate buffer remained nearly constant in pH during the experiments.

Fig. 75. pH vs. Time for Aluminum-Doped Buffers

Fig. 76. Dissolution Rate vs. pH for CSG Glasses Doped with Si, Al, and B. Solid curve is rate for CSG glass in undoped solutions.

It is interesting that these data agree with predictions of the pH dependence of dissolution rate for mixed oxides based on surface charge measurements [115]. The surface charge developed on aluminosilicate mixed oxides appears to be due mainly to silicon sites at high pHs and to aluminum sites at low pHs. Consequently, because dissolution rates are known to correlate directly with the amount of surface charge, it is expected that silicon will have the greatest influence on dissolution rates at high pHs and aluminum will have the greatest effect at low pHs. In our experiments, dissolved aluminum affects the dissolution rate at pHs below neutral and dissolved silica affects dissolution rates at pHs above neutral. This qualitative agreement may be an important clue as to what ultimately controls glass dissolution rates. More experiments aimed at understanding the surface chemistry of glass dissolution are needed.

3. Test Series 3: SRL 202 and SRL 131 Glasses in Standard Buffers

These tests were performed in order to measure the rate constant for SRL 202 and SRL 131 glasses as a function of pH. The tests are nearly identical to those performed previously on CSG and SRL 165 glasses. Buffer solutions of pH 2, 4, 6, 8, 9, and 10 were used. (See Table 36.) The conditions were chosen so that the differences in the performance of the four glasses can be compared directly. The only difference between the conditions of these tests and those of [22] is the addition of the tris buffer at pH 8 (Table 36), in addition to the use of phthalic and boric acid and potassium hydroxide buffers. Table 33 shows the SRL 202 and SRL 131 glass compositions.

a. SRL 202 Glass

Results of the SRL 202 glass dissolution test are shown in Figs. 77 and 78. Buffer pH values as a function of time are shown in Fig. 77. Note that the buffers were stable over time, unlike similar plots for the doped buffers. The normalized dissolution rate (R) values as a function of pH for eight of the elements (Al, B, Ca, Fe, Mg, Na, Si, and U) in the SRL 202 glass are given in Fig. 78. The rate is slowest at around pH 6 and increases as a function of pH in both directions. Each symbol corresponds to a normalized release rate for a different element in the glass. Release is stoichiometric when the symbols fall on top of each other. We believe that non-stoichiometric release in these tests is primarily due to the formation of an alkali-depleted surface layer on the glass.

At pHs from 2 to 9, elemental release for elements other than iron is nearly stoichiometric. Iron is present at lower concentrations in solution, presumably due to precipitation of an iron-bearing phase. EQ3NR calculations show that hematite, goethite, and nontronite are all supersaturated over the entire pH range of this experiment. The supersaturation is greatest at high pHs. Hematite is calculated to be 8 orders of magnitude supersaturated at pH 11.

Table 36. Compositions of Buffers Used in Test Series 3

Buffer	Reagents		pH at 25°C	pH at 70°C
Phthalate	5 mM KPhth	16 mM HCl	2.0	2.0
Phthalate	5 mM KPhth	0.26 mM HCl	4.0	4.1
Phthalate	5 mM KPhth	4.1 mM KOH	5.9	6.2
Tris	5 mM Tris	2.6 mM HCl	8.06	7.03
Borate	5 mM B(OH) ₃	1.4 mM KOH	10.1	9.5
KOH	5 mM KCl	11.7 mM KOH	12.0	10.8

Fig. 77. pH vs. Time for Buffers Used in Test Series 3

At pHs of 10 and above, the release rates for Ca and Mg become much slower than Al, Si, and B, while Fe continues to be released slowly. At pH 12, sodium also is released much more slowly than the other elements. EQ3NR calculations for these fluid compositions indicate that several calcium-, magnesium-, and iron-bearing phases, such as clays, zeolites, and magnesium silicates, are supersaturated by up to 10 log units in these reacted fluids. These phases include nontronite, analcime, hematite, albite, epidote, and chlorite. Sodium may be incorporated into ion-exchange sites of clay and zeolite phases if they are in fact precipitating, which would explain its behavior in the pH 12 test. Solid-run products have been preserved and will be examined using X-ray, SEM, and electron microprobe techniques to identify any phases which have formed.

b. SRL 131 Glass

SRL 131 glass was tested in the same buffer solutions as SRL-202. Trends in dissolution rate with pH and non-stoichiometry of dissolution are identical to those for SRL 202 glass and will not be shown here.

Figure 79 summarizes the results of test series 3, along with some results of previous tests. Glass compositions follow a trend in durability in the order CSG > SRL 202 > SRL 131. Previous tests showed CSG and SRL-165 glasses to have comparable durability [2]. Note also that there is some asymmetry in the plot, particularly for SRL 131 glass. The rate minimum for SRL 131 falls at a higher pH than the other glasses. Also, the dissolution rate is much higher than the other glasses at low pHs, but there is not as much difference at pHs above neutral. Note that the most significant compositional difference between SRL 131 glass and the other glasses is its larger amount of alkalis and boron. (See Table 33.) These observations are critical for modeling the dissolution behavior of these various glasses. Glass durability in various repository environments is also critically dependent on quantifying these types of behavior, as is the design of the waste package for optimum glass performance.

Fig. 78. Elemental Release Rates vs. Time for SRL 202 Glass in Buffer Solutions

Fig. 78 Contd.

Fig. 79.
Comparison of Dissolution Rates for SRL and CSG Glasses in Test Series 3. SRL 165 data plots in same approximate position as CSG data. Also shown are data points for CSG and SRL 165 glasses in the tris buffer solution.

4. Test Series 4: SRL 202 Simple Analogue Glasses with Variable SiO₂ Concentration

This test series was designed to examine the effect of silica concentration on glass durability. Other workers have shown that small increases in silica content can result in large increases in glass durability over a narrow range of compositions [116,117]. We have therefore synthesized a series of glasses having sequentially greater silica concentrations that overlap the compositional range previously studied [116]. We selected the simple SRL 202 five-component analogue as the starting composition. We varied the silica content of this glass from 45.18 to 51.87 wt% (49 to 57 mol %), while keeping all the other components relatively constant. (See Table 37.) It was previously found that significant increases in glass durability occurred when silica concentrations were increased from 47 to 48.5 wt% SiO₂ (53.3 to 54.8 mol %) [116].

The experiments were performed at pHs of 4, 6, 8, 9, 10, and 12, in buffers with compositions shown in Table 38. Figure 80 summarizes the results of these tests, showing the measured dissolution rate versus pH. In general, the more silica-rich glasses were more durable (dissolved slower) than the silica-poor glasses. However, some of the results are suspect because of irregularity of the data at some pHs. The trend at alkaline pHs does not smoothly increase as it has in previous tests; instead it is sawtoothed and therefore inconsistent with most of our previous flow-through results.

The same test results summarized in Fig. 80 at each pH are shown in Fig. 81, where silica content versus dissolution rate is plotted for each pH buffer. Our data at pHs of 4 and 6 show a fairly smooth decrease in rate with increasing glass silica content. The durability of the glasses at these two pHs does appear to level off at 52-53 mol % silica. The data at pHs 8 and 9 are anomalous, probably due to experimental problems not yet identified. The data at pH 10 (boric acid-KOH buffer) show a trend similar to the pH 4 and 6 data, with the glass durability leveling off above 52-53 mol % silica. However, the data at pH 10 (potassium bicarbonate-KOH buffer) show behavior exactly opposite the borate data; the durability's constant with increasing silica concentration up to 54 mol %, then increases dramatically. The pH 12 data are consistent with the pH 4 and 6 data.

Table 37. Glass Compositions Used in Flow-Through Dissolution Tests
as wt % Oxide Components

Glass	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	B ₂ O ₃
S202-1	24.83	5.65	14.55	45.18	9.79
S202-2	24.26	5.53	14.22	46.42	9.57
S202-3	23.73	5.40	13.91	47.61	9.36
S202-4	23.21	5.29	13.60	48.74	9.15
S202-5	22.72	5.17	13.32	49.83	8.96
S202-6	22.25	5.07	13.04	50.87	8.77
S202-7	21.80	4.96	12.77	51.87	8.59

Table 38. Compositions of Buffers Used in Test Series 4

Buffer	Reagents		pH at 25°C	pH at 70°C
Phthalate	5 mM KPhth	0.26 mM HCl	4.00	4.06
Phthalate	5 mM KPhth	4.1 mM KOH	5.89	6.16
Tris	5 mM Tris	2.6 mM HCl	8.06	7.03
KHCO ₃ ^a	5 mM B(OH) ₃	1.45 mM KOH	8.83	8.50
B(OH) ₃	5 mM B(OH) ₃	4.53 mM KOH	10.08	9.50
KHCO ₃	5 mM B(OH) ₃	3.13 mM KOH	10.0	9.79
KCl-KOH	5 mM KCl	11.65 mM KOH	12.0	10.81

^apH = 8.83 KHCO₃ buffer was allowed to equilibrate with atmospheric CO₂.

Fig. 80.
Dissolution Rates vs. pH for
S202 Glasses at 70°C. All rates
are silica-normalized.

The large number of anomalous data points with this data set make it difficult to draw reliable conclusions. In general, higher silica glasses are more durable, which we expected. We do not believe these data alone can be used to determine whether there is a sharp discontinuity in durability versus silica content that would be an important factor in optimizing melter production glass compositions. We intend to repeat some of these experiments and perform additional experiments in the coming year.

5. Comparison of SRL 165 and CSG Glasses

We have plotted all data that we obtained in our flow-through dissolution tests for the dissolution rates of SRL 165 and its simple analogues (CSG) versus pH (Fig. 82). The glasses behave almost identically in the tests, again indicating the simple analog composition chosen based on our understanding of coordination chemistry and chemical bonding in these glasses is fairly accurate.

A unique and previously unrecognized feature of this plot (Fig. 82) is the sharpness of the bottom of the V of the dissolution rate curve. Most rate models formulated to explain the V-shaped nature of rate-versus-pH plots for solid dissolution kinetics assume that there are at least two rate mechanisms operating, one at low pH and the other at high pH. Commonly, it is also assumed that H_3O^+ is involved in the rate-limiting step under acid conditions and OH^- is similarly involved under alkaline conditions. If this were true, the two rates should sum and, at pH 6 in Fig. 82, there should be a relatively flat bottom to the curve. Instead, the measured rate is significantly smaller than the sum of the two rates given by the regression curve in the figure. We cannot yet explain this behavior, but we suspect it may involve surface charge on the glass at the zero point of charge (around pH 6). We intend to collect surface titration data for these glasses and examine in more detail the relationship between surface charge, adsorbed metal species, and reaction rate in order to identify why the rate decreases so dramatically at this point.

These flow-through test results provide the rate constant as a function of pH for SRL 165, SRL 202, and SRL 131 glasses. Previous work has established the temperature dependence of the rate constant at around 20 kcal/mol. Together these data provide us with one of the critical input parameters for our glass dissolution model and allow us to compute the value of the rate constant in a model calculation where temperature and pH are changing. Using these data, we no longer need to regress the rate constant from our closed system reaction tests but instead it can be input as an independent parameter. This provides a major step towards validation of our modeling approach. Future tests in support of model development will be directed toward providing the additional parameters in the rate equation.

6. Future Work

We have measured the rate constant as a function of pH for the glasses of interest (SRL 165, SRL 202, and SRL 131) and their simple analogues. We now will focus our experimental work in two areas: (1) measuring glass dissolution rates under near saturation conditions, the conditions that will control glass dissolution rates under most anticipated repository environments; and (2) continuing our systematic investigations of glass compositional effects on glass durability. We will continue our flow-through tests in simple and doped buffers with both SRL and simple glass compositions. We will also obtain data from surface charge measurements from surface titrations both in simple solutions and in solutions doped with glass species. These later experiments may be used to estimate long-term glass dissolution rates where the glass is under near-saturation conditions.

Fig. 81.
Dissolution Rates vs. mol % SiO₂
for S202 Glass at Several pHs.
Glass compositions are in Table 37.

Fig. 82.
Comparison of Dissolution Rates
for SRL 165 and CSG Analogue
Glass. Regression line is based on
CSG data only.

C. Preliminary NMR Investigation of Sodium Borosilicate and Analogue SRL Waste Glasses

1. Introduction

This report describes the preliminary results of our nuclear magnetic resonance (NMR) spectroscopic study of the structure of borosilicate glasses. The goal of this task is to correlate the dissolution behavior of the glass and its change with conditions and glass composition with changes in short-range structure. This information will then be incorporated into models of glass dissolution.

Results for two different series of glass compositions are discussed below. One is a series of ternary sodium-borosilicate glasses (NaBS-1 to NaBS-4) that have approximately constant sodium content and varying ratios of B_2O_3/SiO_2 that span the compositional range over which a step was found in the durability coincident with a change from congruent to incongruent dissolution behavior in pH 2-buffered solution [117]. Such a discontinuity in the dissolution behavior must result from either a change of dissolution mechanism or a phase change in the glass (e.g., from homogeneous to phase-separated) and cannot be modeled unless a structural basis for the changing behavior can be described and incorporated into the model.

The second series of glasses (S202-1 to S202-7) is based on a five-component analogue of the SRL 202 composition (see Table 33) with changing silica content. No NMR data have been reported for glasses of similar composition, and the present study is an investigation of the applicability of NMR spectroscopy to these more complex glasses.

2. Samples

The NaBS glasses were prepared at ANL by fusing appropriate mixtures of $NaCO_3$, B_2O_3 , and SiO_2 at $1400^\circ C$ for 4 h then quenching into DIW. A portion of each sample was annealed at approximately $550^\circ C$ for 2 h. NMR data were collected for both the quenched and annealed NaBS samples. The S202 glasses were prepared by adding appropriate amounts of SiO_2 to the base-glass composition (S202-1), melting for 15 min at $1400^\circ C$, and then annealing for 4 h at $500^\circ C$. Table 39 contains the nominal compositions for all samples studied.

Table 39. Compositions of Sodium Borosilicate and Analogue SRL Glasses in NMR Study

Sample	Nominal Composition, mole fraction				
	Na ₂ O	CaO	Al ₂ O ₃	B ₂ O ₃	SiO ₂
NaBS-1	0.20	0	0	0.20	0.60
NaBS-2	0.20	0	0	0.30	0.50
NaBS-3	0.20	0	0	0.35	0.45
NaBS-4	0.16	0	0	0.54	0.30
S202-1	0.261	0.066	0.093	0.092	0.489
S202-2	0.254	0.064	0.091	0.089	0.502
S202-3	0.248	0.062	0.088	0.087	0.514
S202-4	0.242	0.061	0.086	0.085	0.525
S202-5	0.237	0.060	0.084	0.083	0.536
S202-6	0.232	0.058	0.083	0.081	0.546
S202-7	0.227	0.057	0.081	0.079	0.556
CSG	0.188	0.068	0.073	0.078	0.593

Nuclear Magnetic Resonance Spectroscopy

The B-11, Na-23, and Al-27 magic-angle spinning (MAS) NMR data were collected on a home-built instrument at the University of Illinois. The spectrometer is based on an 11.7 T magnet, corresponding to resonance frequencies 160.36, 132.22, and 130.25 MHz, respectively, for B-11, Na-23, and Al-27. The MAS rate was about 9 kHz for all spectra.

For B-11, the experimental conditions were selected to ensure that the relative intensities of the peaks for 3- and 4-coordinated B (B3 and B4) are quantitatively correct. The nonselective 90° pulse length was 11 μ s, and 1 μ s pulses were used to collect the data. A 2 s recycle delay between acquisitions was used, but varying the recycle delay from 50 s to 0.5 s produced no significant change in the relative intensity of the B3 and B4 peaks.

Relative populations of the local B structural groups N3s (symmetrical three-coordinated B, B3s), N3a (asymmetrical B3, B3a), and N4 (4-coordinated B, B4; N3s + N3a + N4 = 1) were obtained from least-squares fits to the center bands of the spectra. A computer program fit each spectrum to a sum of MAS NMR lineshapes (e.g., [118]), varying the free parameters using a direction set algorithm (Powell's method). Initial spectral parameters were obtained from the wide-line NMR data reported previously for glasses of similar composition [119]. Small changes in the values of the lineshape parameters change the relative intensities by less than about ± 0.03 absolute (integrals normalized to 1.0). Generally, the values of the quadrupole coupling constant (C_q) and asymmetry parameter (η) for the poorly resolved B3a component were fixed to the values reported previously and not varied during the fitting procedure. All intensities reported here were corrected for spinning-sideband and satellite transition spinning-sideband intensity.

The Na-23 and Al-27 spectra were obtained with 1 μ s pulses and 0.5 s recycle delay. The nonselective 90° pulse length was 7.5 μ s for Na-23 and 12 μ s for Al-27. Chemical shifts are reported relative to 1 M solutions of NaCl and AlCl₃.

Static (nonspinning) H-1 NMR spectra were collected for some of the NaBS glasses on a Bruker spectrometer at LLNL operating at 300 MHz. Hydrogen content of the glass sample was determined by comparing spectral integrals to those of a standard sample of benzoic acid. Water contents of glasses were estimated from these data.

3. Results and Discussion for NaBS Series

a. Na-23 Results

The Na-23 NMR spectra (Fig. 83) contain a broad asymmetric peak near $-16.5 (\pm 5)$ ppm with associated spinning sidebands (an artifact of the MAS technique, spaced at the spinning frequency). The spectral profile consists of a relatively sharp high-frequency edge and a tail extending to low frequencies; it is characteristic of a distribution of quadrupole coupling constants, reflecting a broad range of local Na structural environments.

The Na-23 NMR spectra change slightly, but systematically, with annealing and sample composition. For each composition, annealing the sample decreases the width of the peak by approximately 1 ppm, full width at half height (FWHH), but does not change the peak position. With decreasing silica content, from samples NaBS-1 to NaBS-4, the peak maximum shifts monotonically from $-16.2 (\pm 2)$ to $-17.7 (\pm 2)$ ppm and the peaks narrow from 26.9 to 22.9 ppm for the quenched samples (FWHH), and from 25.8 to 21.7 ppm for the annealed samples. These peak positions agree well with those of Bunker [120] for a similar series of sodium borosilicate glasses.

Fig. 83. Representative Na-23 MAS NMR Spectra of S202 and Na-Borosilicate Glasses

The trend of more negative Na-23 peak positions with decreasing silica content for the NaBS can be interpreted as a concomitant increase of the average Na coordination number, based on the well-known trend for cations of decreasing NMR chemical shift with increasing coordination number. The average Na coordination number can be expected to increase as the concentration of non-bridging oxygens (NBOs) decreases due to the lower local charge associated with the bridging oxygen bonded to a B4 compared to that of a non-bridging oxygen. The B-11 data presented below, which indicate that the concentration of NBOs decreases with decreasing silica content across the NaBS series agrees, with this interpretation of the Na-23 data. Previous studies of framework aluminosilicate glasses [121] and binary sodium silicate glasses [122] reported the opposite trend: more negative peak positions with increasing silica content.

b. B-11 Results

The B-11 MAS NMR spectra (Fig. 84) consist of a pair of strong central signals [(1/2,-1/2) transition], their associated spinning sidebands, and a set of satellite spinning sidebands, which are due to the satellite $\pm(1/2,3/2)$ transitions for B4, that extend past the ends of the displayed spectral region.

The central envelopes (Fig. 85) are very similar to those reported previously for sodium borosilicate glasses [120] and contain signals from at least two types of boron. The doublet in the +18 to +6 ppm region is due to 3-coordinated boron (B3) in a symmetrical configuration (e.g., 3 bridging oxygens) and the narrow peak near 0 ppm is due to the four-coordinated boron (B4).

For all the samples, the more negative B3 singularity (at about 8 ppm) is more intense than that at +14 ppm. This lineshape cannot be produced from a single B-environment, and indicates the presence of either a distribution of B-environments or a signal from an additional, poorly resolved component. We prefer the latter interpretation because (1) the B3 lineshape contains well-defined singularities, whereas a distribution of B-environments capable of changing the relative intensities of the two singularities would probably also smear the fine-structure, and (2) earlier wide-line B-11 NMR work (e.g., [119]) detected two types of B3 which are labeled symmetric and asymmetric based on the symmetry of the electric field gradient at the nucleus (EFG), as determined from the NMR lineshapes. (The asymmetry parameter is a measure of the departure of the EFG from axial symmetry and is defined to vary from 0 to 1.) The symmetric B3 has a low asymmetry parameter, around 0.1, whereas the asymmetric B3 (B3a) has an asymmetry parameter near 0.6 [119]. The asymmetric B has previously been attributed to B3 with one or two NBOs.

With decreasing silica content across the NaBS series, the relative intensity of B4 (i.e., N4) decreases, the shape of the B4 peak changes systematically, but the shape of the B3 peak changes very little. For the 20:20:60 sample, the B4 peak is symmetrical, but as the silica content decreases, this peak becomes asymmetric and shifts toward more positive chemical shift values. For the 20:30:50 and 20:35:45 compositions, the B4 peak appears to contain two components separated by about 2 ppm ($-0.3 \pm .2$ and $-1.9 \pm .2$), the fraction of the more negative component decreasing with decreasing silica content. The resolution of the B4 peaks is not sufficient to provide precise populations of the two components, but the ratio B4b:B4s is approximately 1:1 in 20:20:60, 1.5:1 in 20:30:50, and 2:1 in 20:35:45. Turner et al. [123] also reported two B4 peaks, at -0.2 and -1.8 ppm, for a commercial borosilicate glass (Pyrex).

We tentatively assign the component at -0.3 ppm to B in B-rich regions of the glass and the component at -1.9 ppm to isolated B in silicate-rich regions, based on the similarity of their chemical shifts to those of model borosilicate compounds. The mineral

Fig. 84. B-11 MAS NMR Spectra of NaBS and S202 Glasses. Nominal compositions of NaBS glasses given as mole percent Na₂O:B₂O₃:SiO₂.

Fig. 85. Sample Least-Squares Fit of the B-11 MAS NMR Center Band. Components are tentatively assigned as symmetric trigonal B (B3s), asymmetrical trigonal B (B3a), denburite-like tetrahedral B (B4b), and reedmergnerite-like tetrahedral B (B4s).

reedmergnerite (NaBSi_3O_8) contains B-tetrahedra corner-linked to four Si-tetrahedra (B4 (4Si) units) and has a B-11 chemical shift of -1.9 ppm [123], identical to one component found in the NaBS glasses. The B4 in reedmergnerite-composition glass also has a B-11 chemical shift of -1.9 ppm [126]. The chemical shift of the component at -0.3 ppm is very similar to that of the mineral danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$), -0.6 ppm [123], which contains B-tetrahedra linked to two Si-tetrahedra and two other B-tetrahedra (B4 (2Si) units). The presence of danburite-like units in Na-borosilicate glasses has also been inferred from Raman spectroscopic data [120].

Computer simulations of the B-11 spectra using three components (for symmetrical B3, asymmetrical B3, and B4) fit the experimental spectra reasonably well (Fig. 85) and provide the relative populations of the local B structural units (Table 40). The value of N_4 is not sensitive to whether the B4 peak is fit to one or two components. The relative intensities listed in Table 34 have been corrected for contributions from the central transition spinning sidebands and the satellite $\pm (1/2, 3/2)$ transition spinning sidebands, resulting in a net change of +0.010 to +0.014 for the B3 intensities over the raw integrals of the fitted center bands and a corresponding decrease of the B4 intensities.

Table 40. Summary of Structural Results for NaBS Series Glasses

Sample	Composition ^a	N3a (± 0.03)	N4 (± 0.03)	B4/Na	NBO/Na	NBO/Si
NaBS-1	20:20:60	0.096	0.664	0.66	0.34	0.22
NaBS-2	20:30:50	0.097	0.570	0.86	0.14	0.12
NaBS-3	20:35:45	0.101	0.484	0.85	0.15	0.14
NaBS-4	16:54:30	0.154	0.257	0.87	0.13	0.14

^a(Na₂O:B₂O₃:SiO₂).

The value of N4 obtained from these B-11 spectra of NaBS-1 and NaBS-2 agrees well with previous work, but there are some differences in the silica-poor compositions. For the NaBS-1 composition, Dell [124] and Bunker [120] obtained N4 values of 0.65 and 0.69, respectively, which are within experimental uncertainty of our value (0.66), although Bunker did not correct the populations for SSB intensity (this will decrease their value by about 0.02). For NaBS-2, our value for N4 and that obtained by Dell (obtained from their data by linear interpolation between nearby compositions) are the same (0.57 and 0.58). For the more silica-poor samples, we found significantly lower N4 (0.48 and 0.26 for NaBS-3 and NaBS-4) than reported by Dell (0.58 and 0.43, respectively for equivalent compositions) [124].

For the NaBS-1 composition, our value for N3a (0.096) agrees within experimental uncertainty with that obtained by wide-line B-11 NMR methods (0.075, [119]). However, our fits require significantly non-zero values of N3a for the remaining compositions, from 0.10 for NaBS-2 to 0.15 for NaBS-4, whereas the wide-line B-11 NMR data and the structural model of Dell [124] indicate no asymmetric B3 for equivalent compositions. The previous NMR work attributed the asymmetric B3 to boron with one or two NBOs, which should not be present when the Na/B ratio ($R = \text{Na}_2\text{O}/\text{B}_2\text{O}_3$) is lower than one. For all compositions having $R < 1$, previous models assumed that the sodium atoms are associated with diborate groups (i.e., charge-compensated by B4).

Our observation of B3a units in the silica-poor compositions and the relative chemical shifts for B3a and B3s suggest a structural assignment of the B3a resonance different from that of Dell [124]. The chemical shift of the asymmetric B3 units (+12 ppm) relative to that of the symmetric B3 units (+18 ppm) is the opposite of what one would expect if the asymmetric B3 were bonded to NBOs. By analogy with previous work for Al-27 and Si-29, the presence of NBOs on a B3 unit should make the chemical shift more positive relative to B3 with no NBO's. This trend has been observed in borosilicate gels, for which the asymmetric B3 (+19 ppm) is shifted to more positive values from the symmetric B3 (+12) ppm, consistent with the presence of NBOs on the asymmetric B3 [IRWIN].

An alternative interpretation of the relative shifts of B3a and B3s is that the presence of Si next-nearest-neighbor (NNN) cations linked to the B3a produces a negative shift relative to B3s, analogous to the effect of Si for Al NNN substitution on Si-29 chemical shifts in aluminosilicates. The chemical shift of B3s in the NaBS glasses is similar to that of sodium-diborate glass, in which most of the B3 have three B4 NNN [126]. The substitution of a B3-O-Si linkage for B3-O-B4 should shift the B3 to more negative chemical shifts relative to the diborate-like (B3-3(O-B4)) units, as observed for B3a.

If this assignment of the B3a is correct, then the model of Dell et al. [124] for the distribution of local structural units must be revised. The principal effect would be to decrease the number of NBOs found on the B3 and increase the number of NBOs on Si. Further

work on additional compositions and NMR spectra at different magnetic fields are needed to confirm this tentative assignment and is currently underway.

c. H-1 NMR Results

H-1 NMR spectra of the NaBS-1 and NaBS-4 samples show significant levels of hydrogen, presumably present in OH or H₂O units. For NaBS-1, both the quenched and annealed samples contain the equivalent of $0.6(\pm .1)$ wt % water, and the NaBS-4 sample 3.1 wt %. That the quenched and annealed samples contain approximately the same hydration levels suggests that the glass samples hydrate through incorporation of atmospheric water.

d. Summary

These NMR studies of Na-B-Si glasses were performed in order to understand why the relative durability of these glasses changes abruptly over a narrow compositional range, as reported by [117]. We also needed to begin our NMR investigations with a fairly simple borosilicate glass to establish the positions of shifts associated with particular types of molecular structures. The results show that boron exists in both three-fold and four-fold coordination in these glasses, and that boron is clustered into boron-rich zones with molecular structures similar to those in sodium-diborate glasses. We use information obtained from these simple glasses to interpret NMR data for SRL 202 analog glasses described below.

4. Results and Discussion for S202 Series

a. Na-23 and Al-27 NMR Results

Na-23 and Al-27 MAS NMR data were collected for the S202-3, S202-5, and S202-7 samples only. The Na-23 NMR spectra (Fig. 83) resemble those of the NaBS series glasses. The peak positions of the S202 glasses are at higher frequency (-11 to -13 ppm) relative to the NaBS glasses (-16 to -18 ppm) and shift monotonically with increasing silica content from -11.1 ppm for S202-3 to -12.5 ppm for S202-7. This trend of more negative Na-23 NMR peak position with increasing silica content is that opposite of that observed for the NaBS-series glasses but similar to those reported previously for sodium silicate [122] and framework aluminosilicate glasses [121]. The peak widths are 26.6 ppm (FWHH) and do not vary with sample composition.

The more positive Na-23 NMR peak positions of the S202-series relative to the NaBS glasses indicate a lower average coordination number for Na in the S202 glasses than for the NaBS glasses. This difference in average Na coordination number is consistent with the much lower concentration of charge-balancing framework cations (Al and B⁴) and consequent higher concentration of NBOs in the S202 glasses (cf. Tables 40 and 41). Unfortunately, there is currently no method available to quantify this change in average Na coordination number.

The Al-27 NMR spectra (Fig. 86) are similar in profile to the Na-23 NMR spectra, with a more pronounced high-frequency edge and low-frequency tail characteristic of a distribution of quadrupole coupling constants. The Al-27 peak positions are $57 \pm .5$ ppm and appear to shift slightly to lower frequency with increasing silica content, but by less than 1 ppm over this composition range. The peak widths increase monotonically with increasing silica content from 14.9 ppm (FWHH) for S202-3 to 16.0 ppm for the CSG glass. There is no significant intensity in the region for octahedral Al (near 0 ppm), indicating that all the Al in these glasses is tetrahedrally coordinated.

Table 41. Summary of NMR Results for S202 Series Glasses

Sample	mol % SiO ₂ (nominal)	N3a (± 0.03)	N4 (± 0.03)	NBO/alk	NBO/Si
S202-1	48.9	0.15	0.39	0.606	0.81
S202-2	50.2	0.13	0.45	0.589	0.75
S202-3	51.4	0.16	0.39	0.605	0.73
S202-4	52.5	0.17	0.42	0.598	0.69
S202-5	53.6	0.15	0.42	0.597	0.66
S202-6	54.6	0.15	0.47	0.585	0.62
S202-7	55.6	0.17	0.44	0.591	0.60
CSG	59.3	0.22	0.52	0.555	0.48

Fig. 86. Al-27 MAS NMR Spectra of the Five-Component Analogue Waste Glasses S202 and CSG. Chemical shifts are relative to external 1 M AlCl₃ solution.

b. B-11 NMR Results

The B-11 NMR spectra of the S202 glasses contain well-resolved peaks for B3 and B4, similar to those of the NaBS glasses (Fig. 84), but with poorly defined singularities on the B3 peak. The less-well-defined B3 lineshape indicates a broader distribution of local B3 environments in the S202 glass than in the NaBS glasses. As described above for the NaBS glasses, the low-frequency B3 singularity is more intense than the high-frequency singularity, requiring an asymmetric B3 component for acceptable simulation of the MAS NMR lineshape. The values of N3a and N4 (Table 41), obtained from three-component fits (B3s, B3a, and B4), show no systematic variation with silica content within the experimental uncertainty. From these values of N4 and the nominal concentrations of B, Al and network-modifying cations, the total concentration of NBOs can be calculated for each sample. The results show that the number of NBO's per network modifier charge ($2 \cdot f(\text{Na}_2\text{O}) + 2 \cdot f(\text{CaO})$) is approximately constant at 0.595 ± 0.010 across the series, whereas NBO/Si decreases from 0.81 for S202-1 to 0.48 for CSG.

The only systematic trend observed across the S202 series is a decrease of the B4 chemical shift from -0.2 for S202-1 to -0.7 ppm for S202-7 (Fig. 87). These B4 chemical shifts are similar to those we assign to the B4 in borate-rich regions (B4b) in the NaBS glasses (ca. -0.5 ppm) and significantly more positive than the B4 chemical shift for reedmergnerite (NaBSi_3O_8) glass (-2.0 ppm, [126]) and the shoulder assigned above to B4 in silicate-rich regions of the NaBS glasses (-1.9 ± 0.2 ppm). The danburite-like B4 chemical shifts and the values of N4 (slightly less than 0.5) for the S202 glasses suggest that most of the B4 occurs in borate-like environments rather than dispersed in the silicate network. Isolated B4 in the silicate network is most likely to have four Si NNNs, due to the high Si-content of these

Fig. 87. Variation of the Tetrahedral Boron Chemical Shift with Silica Content for the S202 Series Glasses

glasses. Because the chemical shift is sensitive to only short-range structural effects, the B-11 chemical shift of B4(4Si) units in the S202 glasses should be similar to that of reedmergnerite crystals and glass [126]. The NMR data are not sensitive to the structure at distances greater than about 10 Å, thus the size of these inferred borate-like clusters must be obtained from other experimental techniques, such as electron microscopy.

5. Summary of NMR Work

a. B-11

The B-11 MAS NMR data give specific and quantitative information on the local structure and speciation of both the NaBS and S202 glasses. For example, the concentration of NBOs in each sample could be determined from the relative concentrations of B3 and B4 obtained from the NMR data. The good resolution of the B-11 MAS NMR spectra of the bulk glasses indicates that this will be a good technique for monitoring structural changes during glass dissolution and this work will be pursued for FY 1993.

For the NaBS glasses, we can partially resolve two B4 resonances, which we assign to B4 in borate and silicate-rich regions based on the chemical shifts. Resolution of two B4 components in the NaBS glasses indicates that the ratios B3/B4 and B4b/B4s can be used to help correlate dissolution behavior to glass structure. For example, selective removal of a diborate-like component during incongruent dissolution would produce a 1:1 decrease in B3 and B4b. Even if separate B4b and B4s resonances cannot be resolved, such structurally selective dissolution behavior can be detected by a progressive negative shift of the B4 peak. High-resolution NMR experiments for NaBS glasses after various periods of leaching are planned for FY 1993. The chemical shift of the B3a component of the NaBS glass is not consistent with previous assignments of this resonance to B3 bound to one or two NBOs, but may instead be due to B3 with Si (rather than B) NNN. This result, although preliminary, indicates that some refinement of existing structural models of borosilicate glass may be necessary. Currently, we are preparing additional glass compositions for high-resolution B-11 NMR experiments to help clarify the nature of the B3a resonance.

For the S202-series glasses, we observed B4 chemical shifts characteristic of borate-like environments. This result is surprising because of the relatively low B- and high Si-content of these glasses. Dissolution of clustered borate-rich regions can provide a mechanism for the release of Na and B from the glass with little disruption of the silicate framework. B-11 NMR spectra obtained at several stages of dissolution should indicate whether this clustering has any affect on the leaching rates. We expect that selective dissolution of diborate-like regions will shift the B4 peak to more negative values, whereas congruent dissolution of all B structural units will lead to a uniform decrease of intensity with no change in the spectral profile.

b. Na-23

Information obtained from the Na-23 NMR data is only qualitative, but the NMR spectra were sensitive to whether the sodium atoms occur mostly in silicate or borate-like environments. The NaBS and S202 series gave non-overlapping ranges of Na-23 NMR peak position and opposing trends of peak position with varying silica content. These results can be interpreted in terms of the Na coordination number, consistent with current models of silicate glass structure. For the NaBS glasses, 70 to 85% of the sodium atoms are charge-balanced by B4, giving an average coordination number higher than in the S202 glasses, where that figure is less than 15% and most of the sodium atoms are charge-balanced by NBOs.

Unfortunately, there is currently not enough Na-23 NMR data of model compounds available from which to construct a quantitative relationship between coordination number and NMR chemical shift.

NMR results are fundamental to our understanding of the glass dissolution mechanism. We have shown that SRL 202 analog glasses are inhomogeneous on a length scale of a few tens Angstroms. More soluble Na-B rich zones are present that very likely etch away faster than the silica-rich zones (experimental work in FY 1993 will address this). Once etched out, these zones could provide permeable channelways where water can more readily diffuse through and react with the glass. Glass dissolution rates will reflect these enhanced water diffusion rates when they are present. In addition, boron and alkali release rates do not accurately reflect bulk glass dissolution rates, and must be corrected for the effect of the reduced durability of Na-B rich zones. For these reasons we believe an understanding of the fundamental glass structure is essential for proper interpretation of leach data, and NMR is the best technique for obtaining this information.

D. Model Development

1. Introduction

The objective of this task is to develop and apply a computer model for 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 1992 concentrated in two areas: (1) the effect of ion exchange on glass dissolution and implications for accelerating tests using high surface-area-to-volume ratios; and (2) analysis of the affinity term in the rate equation. The modeling work related to SA/V effects was presented at the annual Materials Research Society Meeting and published as part of the proceedings [127]. The work related to the affinity term was presented at the Goldschmidt Conference on Geochemistry and the 7th International Symposium on Water-Rock Interactions [128,129].

We also received a new version of the Geochemists Workbench Code Package (formerly called Gt), and made the necessary code and database modifications to incorporate our glass dissolution model into this new set of computer codes.

2. Work Summary

a. Ion Exchange and SA/V Effects

The use of high surface-area-to-volume ratios (SA/V) has been proposed as a method to accelerate glass durability tests [130]. The reason is that the glass dissolution rate is proportional to the amount of reactive surface area; thus, species build up in solution faster in high SA tests and reach conditions that would only be achieved at greater times in lower SA tests. It follows that if the elemental concentrations measured in glass dissolution experiments are plotted versus (SA/V)*time rather than versus time, the data points would all plot along a single curve. It follows that high SA/V tests may, therefore, speed up the glass dissolution process, and advanced reaction stages can be investigated in relatively short time periods.

Some kinetic data for glass dissolution do scale along a single curve when plotted versus $(SA/V) \cdot \text{time}$ [28]. However, much of the experimental data do not (e.g., [86]). The reason for a lack of systematic behavior is unclear. In some cases, data scale well with $(SA/V) \cdot \text{time}$, particularly for tests at low SA/V ratios (less than 1000 m^{-1}). Tests performed at high SA/V ratios show a trend similar to that in Fig. 88, with higher SA/V tests being accelerated more than low SA/V tests at the same value of $(SA/V) \cdot \text{time}$. Measured pH values are also higher in high SA/V tests at the same value of $(SA/V) \cdot \text{time}$.

The purpose of our modeling work was to determine those conditions where $(SA/V) \cdot \text{time}$ scaling is applicable to glass dissolution tests. We were most interested in the effect of ion exchange on the scaling of glass dissolution rates.

(1) Model Calculations

Our modeling calculations* include provisions for the following processes: kinetically controlled glass dissolution, precipitation of secondary phases as they become saturated (no nucleation or precipitation kinetics), aqueous phase speciation, and ion exchange. The SA/V ratio was varied by changing the glass surface area while maintaining a constant leachate volume. Quartz, tridymite, and talc were suppressed from the modeling calculations because they do not form in glass dissolution experiments in the time frame of our

Fig. 88. Boron Concentrations in Closed System Dissolution Tests of SRL 131 Glass at 90°C in Equilibrated J-13 Water [86]

*Calculations were performed using the React code of the Geochemists Workbench software package [131].

simulations (1000 days) but would be predicted to form in the simulations, based on their thermodynamic properties. We used a rate constant of 4.5×10^{-11} g/cm²/sec for SRL 131 glass at 90°C, extrapolated from the results of 70°C flow-through tests of SRL 131 glass at comparable pHs (using an activation energy of 20 kcal/mole). For the simulations shown here, we did not allow the rate constant to change with pH.

Ion exchange was accounted for by including two reactants in the simulations: SRL 131 glass and a second reactant composed of Na, K, Li, and B oxides with the cations in the same proportions as in SRL 131 glass. Boron is included because it is known to be released at about the same rate as the alkalis even though it is not involved in an ion exchange process. Boron hydrolysis affects the solution pH and, therefore, it must be included in the reactant. The ion exchanger is set to react nearly to completion in the first two days of the reaction, simulating the early rapid ion-exchange process that causes the initial pH rise in solution. The mass of the ion exchanger was fixed to maintain an alkali-depleted surface layer of about 0.06 microns (see below). The combination of SRL 131 glass and ion-exchanger reactants simulates the observed early nonstoichiometric glass dissolution during which the gel and diffusion alteration layers form, followed by steady-state dissolution where the alteration layers (not including secondary phases) maintain a nearly constant thickness as the glass dissolves. This model does not imply that ion exchange ceases but that, once formed, the ion exchange zone maintains a constant thickness throughout the reaction period.

(2) Modeling Results

We first examined the effect of ion exchange alone on the leachate pH, ignoring glass dissolution. The simulation consisted of ion exchanging some mass of glass in either distilled water or J-13 water. For a fixed glass surface area, the given mass corresponds to some finite depth of ion exchange in the glass. Figure 89 shows that for distilled water, ion exchange causes pH increases of up to 3.5 at the highest SA/V ratio of 20,000 m⁻¹ for an ion exchange depth in the glass surface of only 100 Å. The effect is smaller, but still appreciable, for simulations in J-13 water because of the much higher pH buffer capacity of dissolved carbonate in the J-13 water versus distilled water. These calculations show that significant changes in leachate pH will occur even with water penetration depths and subsequent ion exchange of the glass to a depth of only a few hundred Å. This process is expected to occur rapidly, within a few hours or days of glass reaction.

We next performed simulations of the experimental conditions of Fig. 88: SRL 131 glass reacting for 1000 days with equilibrated J-13 water at 90°C. SA/V ratios were the same as for the experiments (10, 2000, and 20,000 m⁻¹), with an additional simulation at 1 m⁻¹. The first set of simulations predict glass dissolution at several SA/V ratios without accounting for ion exchange. The purpose of these simulations is to determine whether (SA/V)•time scaling should apply to the case where glass dissolution is kinetically controlled by a rate equation that includes an affinity term, such as the model of Grambow [132]. Simulation results (not shown) show perfect (SA/V)•time scaling as expected. (SA/V)•time scaling may therefore be valid for glasses which dissolve primarily through the mechanisms included in these simulations (i.e., excluding ion exchange and other processes).

A final set of simulations included provisions for an ion-exchanged layer approximately 60 nm thick. The thickness chosen is an averaged value based on SIMS profiles through reacted glasses [133]. Figure 90 shows the predicted rate of boron release (an indicator of total amount of reacted glass) versus (SA/V)•time for an SRL 131 glass at 90°C in EJ-13 water. (Water composition is given in Table 2.) Experimental data from

Fig. 89. Calculated pHs for Distilled (DI) and J-13 Waters vs. Depths through Which Ion Exchange Occurs. Numbers denote SA/V ratios of the simulations.

Ebert [86] is shown for comparison. At low SA/V ratios of 1 and 10 m^{-1} , the scaled calculated boron release rates are essentially identical. However, at higher SA/V ratios the scaled data deviate, with boron releases from high SA/V tests being higher than those from lower SA/V tests. Tests performed at different SA/V ratios therefore do not scale according to $(\text{SA/V}) \cdot \text{time}$. Adding a simple ion exchange model to the simulations prevents $(\text{SA/V}) \cdot \text{time}$ scaling.

Figure 90 shows that for high $(\text{SA/V}) \cdot \text{time}$ values, the predicted glass dissolution rates eventually converge to a single curve. This occurs because for large amounts of glass dissolution, the amount of ion-exchanged glass becomes small relative to the total amount of glass dissolved. The simulations predict that given enough time the pH of the low SA/V test will catch up with the value for the high SA/V test and follow nearly the same reaction path. (See Fig. 90.)

Our model predicts the same trends as the experimental data [134] but clearly underestimates the release rates at high SA/V ratios. (See Fig. 90.) Better agreement will result when we incorporate the pH dependence of the rate constant.

Good agreement between predicted and measured release rates in high SA/V tests depends on our ability to predict the "long-term" glass dissolution rate [132], where the glass approaches saturation and the dissolution rate is much smaller than the initial rate. In our simulations, the long term rate is calculated using the equation

$$\text{rate} = Ak_f (1 - Q/K) \quad (17)$$

Fig. 90. Calculated (lines) and Measured (symbols) Boron Concentrations Released from SRL 131 Glass vs. $\log (SA/V) \cdot \text{Time}$. Four lines (alternate dashed and solid) are for SA/V ratios of 1, 10, 2000, and 20,000 m^{-1} bottom to top. The glass has the same conditions as Fig. 69.

where A is surface area, k_f is the rate constant, Q is the activity product for dissolved species from the gel layer, and K the solubility product for the gel layer [26]. The affinity term $(1 - Q/K)$ is controlled by the concentrations of dissolved species in equilibrium with the surface gel layer. Solution concentrations are controlled in turn by the secondary phases in equilibrium with the system. The long term glass dissolution rate, therefore, is determined by the secondary phases that precipitate and control dissolved element concentrations. Accurate predictions of long-term rates by our model, therefore, are dependent on our ability to predict the amounts and types of secondary phases that precipitate. This is the primary reason for the lack of agreement between model and experimental results in Fig. 91.

(3) Discussion

Ion exchange is the primary reason glass dissolution data do not scale when plotted versus $(SA/V) \cdot \text{time}$. When glass first begins to react with water, an ion-exchange zone develops on the surface and alkalis and boron are released into solution. Alkali exchange reactions, such as $\text{Na}_{\text{glass}} + \text{H}^+ = \text{Na}^+ + \text{H}_{\text{glass}}$, raise the solution pH. The higher the SA/V of the system, the more the pH is raised. Because this effect takes place in the first few hours or days of reaction, depending on temperature, and is rapid relative to the duration of the test, the effect causes tests having different SA/V ratios to start at different pHs and follow

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Fig. 91. Calculated (lines) and Measured (symbols) pHs for Solutions Reacted with SRL 131 Glass vs. $\log (SA/V) \cdot \text{Time}$. Four lines are for SA/V of 1, 10, 2000, and 20,000 m^{-1} bottom to top. 1 and 10 m^{-1} lines superimpose. Conditions are same as for Fig. 88.

different reaction paths. The different paths are characterized by different sets of secondary phases and, therefore, different long-term dissolution rates (see above). Such experiments are, therefore, not expected to scale according to $(SA/V) \cdot \text{time}$.

It is also known from flow-through glass tests that glass dissolution rates increase at higher pHs in alkaline solutions [22]. Experimentally observed faster dissolution rates observed at higher SA/V ratios (Fig. 88) are probably a consequence of this trend [134].

Figure 92 shows calculated values for the affinity term $(1 - Q/K)$ of the SRL 131 glass as a function of reaction progress. The affinity term is actually calculated for the reacted glass surface layer with its thermodynamic properties approximated as a solid solution of hydrous and amorphous endmembers [26]. Note on Fig. 92 that the initial value of the affinity term is about 0.7, not 1. This is because the glass is being reacted in equilibrated J-13 water, which has significant concentrations of dissolved glass species such as silica and aluminum already present. The glass is therefore partially saturated at the start of the experiment. At low SA/V ratios (1 and 10 m^{-1}), the affinity term gets smaller (the rate slows down) as the glass dissolves, and species build up in solution, as expected. Note, however, that for high SA/V ratios (2000 and 20,000 m^{-1}), the affinity term actually increases at first, in spite of the fact that the solution is becoming more concentrated in dissolved glass species, which should act to decrease the affinity term. The reason for this behavior is that ion exchange causes the pH to rise. The glass/gel becomes more soluble with increasing pH, which tends therefore to

Fig. 92. Calculated Affinity Term ($1 - Q/K$) for SRL 131 as a Function of Reaction Time for SA/V Ratios Shown

increase the value of the affinity term. The effect of the increasing pH is greater than the effect of increasing the concentrations of dissolved glass species during dissolution. The net effect is that the affinity term increases initially as the glass dissolves. The model thus predicts that the glass dissolution rate should actually increase at first, and then slow down with time. Eventually the pH stops rising and the affinity term decreases, as seen in Fig. 92.

The effects of glass dissolution on solution chemistry can be explained in terms of masses of reservoirs of two reactants, the ion exchanger (diffusion layer in the altered glass) and bulk glass. The dominant solution effect of the ion exchanger is to raise the pH through ion exchange. The effect on the unaltered glass is complex; it is a result of the relative amounts of bulk glass dissolution, which raises pH, and the precipitation of secondary phases, which lowers pH [135]. The net effect of bulk glass dissolution is commonly little change in pH, as evidenced by the nearly flat pH versus time curves for most glass dissolution experiments at long times. Initially, the amount of ion-exchanged glass is large relative to the total amount of glass dissolved. After the glass alteration layers develop and reach an approximately constant thickness (excluding secondary phases), the relative importance of the ion-exchanged mass decreases as more glass dissolution takes place. After long time periods, the solution chemistry is dominated by bulk glass dissolution and the precipitation of secondary phases. This is why the curves in Fig. 90 converge at high values of $(SA/V) \cdot \text{time}$.

Several factors contribute to whether (SA/V)•time scaling is achieved. The amount of exchangeable alkali is important. High alkali glasses that undergo relatively large amounts of exchange will tend to not scale, and the SA/V limit above which they deviate from (SA/V)•time scaling will be low. Durable alkali-poor glasses should scale to relatively higher SA/V ratios. Also, time-dependent processes, such as nucleation and growth kinetics and colloid formation, may also invalidate (SA/V)•time scaling. We have also ignored changes in effective surface area that may arise due to precipitation of secondary phases.

(4) Conclusions

We used modeling to investigate the effect of variable SA/V ratios on glass dissolution behavior. The model provides for kinetic control of glass dissolution rate, precipitation of secondary phases, and ion exchange. Our results show that (SA/V)•time scaling may apply to experiments having low SA/V ratios. At higher SA/V ratios, rapid early ion-exchange causes the solution pH to rise. The pH values do not scale according to (SA/V)•time. Higher SA/V tests reach higher pHs at the same value of (SA/V)•time and, therefore, follow different reaction paths. At the same value of (SA/V)•time, glasses in high SA/V tests react faster than those in low SA/V tests, mainly because the glass dissolution rate is known to increase with pH under alkaline conditions [33]. The cutoff in SA/V ratio above which the test results are not expected to scale will vary with glass composition and durability. Glasses with a high alkali content will reach relatively higher pHs than glasses with low alkali contents and thus will deviate from good scaling behavior at lower SA/V ratios. Most waste glasses may begin to scale poorly at SA/V ratios above 100 to 1000 m⁻¹. Therefore, high SA/V tests cannot be used to accelerate glass dissolution reactions unless the nonscaling pH effect is accounted for. Two possible ways to further investigate the SA/V effect are: (1) external control of solution pH during the test using a flow-through reactor or pH-stat and (2) performing tests on pre-reacted glasses which have already formed steady-state surface alteration layers

b. 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. This conclusion is based on analysis of numerous glass dissolution experiments performed over several decades. Because silica is the major component of glass, dissolved silica concentration correlates well with the decrease in reaction rate and has been used to predict glass dissolution rates empirically [132].

The saturation effect is incorporated in our current rate expression 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 written in the same way as the expression for Q. As species build up in solution, the value of Q increases and the term approaches a value of zero at saturation.

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 really should be written in a more general form as

$$\left(1 - \left(\frac{Q}{K}\right)^m\right)^n \quad (18)$$

where m and n are exponents which must be determined experimentally. Transition state theory predicts a form where $n = 1$ and m is some real number. The case where $n \neq 1$ is also possible and is a nonlinear rate law.

In order to better constrain the affinity term in our rate equation for glass dissolution, we used the results of closed system dissolution tests of CSG glass at 100°C in a dilute (0.003 M) 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 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.

Closed system tests of CSG glass at 100°C show nearly stoichiometric release of Si, B, Al, and Ca until about 30 days (Fig. 93). After 30 days, Ca concentrations decrease, probably due to calcite precipitation. EQ3NR analysis of the solutions at 30 days show supersaturation with respect to both calcite and calcium zeolites. However, the glass is probably still dissolving stoichiometrically. Resolution of Na release rate (not plotted) was poor because it was present in the leachate.

Fig. 93. Normalized Elemental Concentrations vs. Time for CSG Glass Dissolving at 100°C in 0.005 M NaHCO_3 Solution

The rate of release of elements from the glass is given by the slope of the elemental release curves in Fig. 93. Therefore, we use data for the fastest-released element (silica in this case) and calculate the derivative at each of data points (Fig. 94). 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.

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 n and m . The value of K , the equilibrium constant for the dissolving solid, depends on two factors: (1) the solid assumed to be controlling dissolution rate; and (2) the thermodynamic model chosen for that solid. The two solids that could be rate controlling are the anhydrous glass itself and the hydrous alkali-depleted surface gel layer of the glass, depending on what specific reaction is rate controlling. Earlier modeling results [135] showed that the anhydrous glass is thermodynamically too 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, which contrasts with the experimental data.

If the surface gel layer is assumed to be the rate-controlling solid, there are several options for calculating its thermodynamic properties. The surface gel layer is silica- and alumina-rich, with most of the boron, sodium, and calcium having been removed during leaching. We have found that estimating the thermodynamic properties of the surface layer as a solid solution of cristobalite and gibbsite best fits our observed dissolution rate data. Several other phases were considered, including quartz and amorphous silica for Si, and corundum, diaspore, and boehmite for Al.

Fig. 94. Cumulative and Derivative Si Release from CSG Glass at 100°C

Once we have selected a thermodynamic model for the rate-controlling solid, we can investigate the form of the affinity expression. Three options are shown in Fig. 95, along with our measured rate of silica release. The first option, labeled "Crist+Gibbsite", is the simplest model where n and m in the affinity term are equal to 1. The curve does not predict as large a decrease in rate as is observed experimentally. The second model labeled "Crist+Gibbsite(mod)" refers to the same model as the first, but with the thermodynamic properties of the gel layer arbitrarily changed to best fit the observed dissolution rate after 60 days. As can be seen, the curvature of this model is not what is observed. The final model is similar to the first model except that $n = 2$. The affinity term is squared. Of the three attempts, this model best fits both the change in magnitude and the slope of the observed data.

We have, therefore, added an exponent of 2 to our affinity term in the glass rate equation based on these results. In future work we will model additional experimental results with different glasses using our modified affinity term function to determine how generally applicable this model is. The mathematical form of the affinity term is clearly of great importance in extrapolating our test results to long time periods. At this time we cannot attach a physical significance to the modification of the affinity expression. However, it may be clear when we better identify the rate-controlling reaction on a microscopic level.

Fig. 95. Computed Normalized Rate of Glass Dissolution Based on Four Thermodynamic Models for Glass Alteration Layer (see text)

c. Future Work

Modeling work in FY 1993 will concentrate on SRL 202 glass, which has the most diverse set of experimental test results of any waste glass. The experimental results will be obtained mainly from tests performed at ANL, although additional data are available from MCC and PCT tests from other laboratories. We will use our modified model to see if we can predict results from this variety of test types and conditions. Successful simulations of this wide variety of tests are essential for validation of the model and data base. The model results should allow us to make predictions of long-term glass durability from short-term test results, such as the PCT test. The more diverse the conditions under which the model makes accurate predictions, the more convincing it is that the mechanistic basis of the model is correct. Recent developments obtained from our surface chemical investigation and NMR investigations will be added to our modeling code as appropriate.

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