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NUCLEAR WASTE PROGRAMS
SEMIANNUAL PROGRESS REPORT

April--September 1992

by

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ABSTRACT

This document reports on the work done by the Nuclear Waste Programs of the Chemical Technology Division (CMT), Argonne National Laboratory, in the period April-September 1992. In these programs, studies are underway on the performance of waste glass and spent fuel in projected nuclear repository conditions to provide input to the licensing of the nation's high-level waste repositories.

SUMMARY

The volcanic tuff beds at Yucca Mountain, Nevada, are being studied as a potential site for locating the U.S. high-level nuclear waste repository. The potential site at Yucca Mountain is unique among sites that have been considered previously in that it lies several hundred meters above the local water table in a hydrologically unsaturated zone. Because only water vapor or small volumes of liquid water in the repository horizon are expected to contact the waste forms, traditional test methods used to assess glass durability may not be appropriate for the Yucca Mountain environment. Therefore, we have designed alternative test methods which better represent the expected repository environment and are using them to study the interactions that may occur and to project the long-term behavior of emplaced waste. Several tasks are in progress to assist DOE's Environmental Restoration and Waste Management Program in demonstrating that the Defense Waste Processing Facility and the West Valley Demonstration Project will produce a waste glass product that will perform well in an unsaturated environment typical of what may be expected at Yucca Mountain.

Long-term tests at 90°C are underway with EJ-13 well water and radioactive sludge-based and simulated nuclear waste glasses having three different compositions, designated 131/11, 165/42, and 200. In tests up to 720 days at an initial ratio for the glass surface area to solution volume (SA/V) of 340 or 2000 m⁻¹, little difference was found between the radioactive and simulated waste glasses. However, in tests with the 200-type glass at SA/V = 20,000 m⁻¹, the simulated glass leached faster than the radioactive counterpart by a factor of 40 within one year. This accelerated glass reaction is associated with the formation of crystalline phases, such as clinoptilolite (and/or potassium feldspar), and a pH excursion in the leachate. The radiation field generated by the radioactive glass reduces the solution pH, which, in turn, may retard the onset of the increased reaction rate.

Long-term tests are also underway to evaluate the effects of radiation on glass reactions under high SA/V conditions. Gamma radiolysis blank tests (i.e., no glass, dose rate of 3500 rad/h, initial gas/liquid volume ratio of 100) at 25, 90, and 200°C indicate that NO₃⁻ and NO₂⁻ yields vary inversely with temperature, with the lowest yields occurring for the highest temperature. No differences in yields were noted when dose rates of 50,000 rad/h or gas/liquid ratios of 10 were used. In other tests, glass wafers (1-mm thick) were exposed to a gamma radiation field in humid air at temperatures of 150 and 200°C. After 35 days, these wafers had reaction layer thicknesses 15 times greater than their nonirradiated counterparts. The sequence of alteration phases that form on the glass appeared to be accelerated in the irradiated tests.

Static leach tests at SA/V ratios of 10 to 20,000 m⁻¹ are being conducted to assess how the SA/V ratio affects the rate and mechanism of the glass reaction. Test results through two years show the predominant effect of the SA/V ratio to be the extent of dilution of the reaction products. The higher pH and silicic acid concentrations that are attained in the leachate at high SA/V ratios influence the reaction rate: the higher pH accelerates 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.

Colloids formed during waste glass dissolution are being characterized by analyzing leachate from earlier glass waste tests. These studies are prompted by the possibility that radionuclide release may be controlled by colloid formation. The major colloid phase present in the leachate was found to be alkali-rich clay; other phases identified include calcite, kaolinite, chrysolite, mica, and heulandite. These colloidal particles form during waste glass dissolution by either precipitation in the leachate or spallation from the reacted glass surface. The high pH, which occurs at high SA/V ratios, increases colloid stability, in spite of a high salt concentration.

A methodology is described for relating glass-water reactions of naturally occurring glasses (e.g., obsidian) to experimental results with nuclear waste glasses. The results from an experimental study with tektite (a silica-rich natural glass) indicate that water diffusion will not be the rate-controlling reaction process for the reaction mechanism of nuclear waste glass.

In addition to glass studies, experiments are in progress to determine radionuclide release rates by exposing simulated spent fuel to repository-relevant conditions. Results from drip tests with UO₂ pellets (nonirradiated) and EJ-13 well water for 5.5 to 6.8 years indicated an overall decrease in leachate pH relative to that of the starting EJ-13 (pH = 8.22). Analyses of filtered residues from the long-term samples indicated the presence of titanium oxides, calcium silicates, and uranium phases as colloidal materials. Similar tests have been started with irradiated spent fuel.

Studies have been initiated to demonstrate the efficacy of using analytical electron microscopy for identifying uranium-bearing phases present in contaminated soils.

I. UNSATURATED GLASS TESTING PROGRAM FOR OFFICE OF ENVIRONMENTAL RESTORATION AND WASTE MANAGEMENT

The Unsaturated Glass Testing Program is a technical support activity performed for DOE's Office of Environmental Restoration and Waste Management (EM). This program was initiated in 1989 to evaluate factors likely to affect glass reaction in an unsaturated environment. The EM Office recognizes that the following information is needed before hot start-up of the Defense Waste Processing Facility (DWPF) and West Valley Demonstration Project (WVDP): (1) the prediction of long-term glass performance in a repository environment and (2) the determination of the relationship between the release of radionuclides from a glass waste package and the performance assessment of the repository. However, these tasks will not be completed until a repository license is applied for, which will occur several years after the DWPF begins production of waste forms for storage and disposal. The Unsaturated Glass Testing Program will provide data so that the modeling and performance assessment programs will have a firm basis that (1) accounts for important physical parameters which will affect glass reaction in an unsaturated environment and (2) relates the mechanistic basis of glass reaction to conditions which will exist in an unsaturated environment.

The goals of the Unsaturated Glass Testing Program are to (1) review parameters that will be important to evaluating glass performance, (2) perform testing to further quantify the effects of variables deemed important to the glass performance, and (3) initiate a long-term testing program to characterize glass performance under a range of bounding repository conditions, which are identified in the "Yucca Mountain Project Scientific Investigation Plan."¹ Results from the testing program will also be used to validate models generated to predict long-term performance. The information developed in the Unsaturated Glass Testing Program, when combined with data generated by the glass waste producers and by the Yucca Mountain Project (YMP), will form the basis of a well-founded program that will ultimately qualify vitrified high-level waste for repository disposal.

A. Critical Review of Parameters Affecting Glass Reaction in an Unsaturated Environment (J. J. Mazer)

The repository environment at Yucca Mountain has been predicted by the YMP to be hydrologically unsaturated, with possible air exchange with the neighboring biosphere.² 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 what is known about these conditions has not been compiled for use within the waste glass research community. A critical review was found necessary and its preparation is currently underway.

During the projected lifetime of an unsaturated repository, large amounts of liquid water are not expected to come into contact with the waste; however, water vapor or small volumes of transient water may contact the waste 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 effects of temperature, radiation fields, glass composition, and alteration phases resulting from glass hydration. A detailed critical review will be made of how each of these parameters affects waste glasses as a part of this task.

The purpose of the Critical Review Task is to review the existing literature in order to evaluate the state of knowledge on how each identified critical parameter influences glass reaction. Each review will be issued as a stand-alone document; they will be integrated into a summary compendium document. The results from this task will be used in support startup of the DWPF and WVDP.

The technical approach used to perform this task has been to assemble all known, up-to-date information in the scientific literature relating to how each critical parameter affects nuclear waste glass reaction. We have included reviews and discussions of studies of materials other than nuclear waste glasses when this ancillary information is applicable to effects of the parameter being reviewed on waste glass reaction. Existing data will be synthesized, where possible, to provide a framework for comparing the results obtained from different studies.

All of the references used in the critical reviews have been collected in a computerized data base. It lists the reference; along with keywords and the ANL reviewer's comments regarding the reference. The references included in the data base include published journal articles, symposia proceedings, unpublished manuscripts, letters, and literature searches. The data base has a word search capability that facilitates the review process and helps ensure that no known pertinent literature is overlooked by the critical review authors.

A preliminary critical review was written to provide a foundation for subsequent detailed reviews of each parameter.³ The first such report, detailing the effects of temperature on waste glass performance, has been completed.⁴ This report stated 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 reactions change as a function of time or temperature (i.e., 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 these reactions, which has not yet been achieved. Until glass reaction mechanisms are better understood, caution should be exercised in using temperature as an accelerating parameter.

The next parameter to undergo a detailed critical review is the effect of glass composition on glass durability. This review is currently in progress. Models of glass structure are presented to help explain the fundamentals of how water may interact with glass. Brief reviews of glass dissolution models are combined with this information to form a basis for critically reviewing theoretically and empirically based models relating glass composition to glass durability. All available studies in this area are being obtained and, where possible, the available data will be presented in a manner that will allow a comparison of the results obtained in different studies.

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. The preparation of each review requires several steps: (1) reviewing an outline of the expected content of each section; (2) preparing a draft of the manuscript and submitting it for internal review; (3) revising the drafted manuscript and submitting it for an external review by acknowledged experts in that field; and (4) revision into the final document, which is published and distributed.

B. Long-Term Static Testing of Fully Radioactive Glass
(J. K. Bates, X. Feng, T. J. Gerding, J. C. Hoh, and J. W. Emery)

Long-term static testing is performed on fully radioactive glasses under conditions that may exist in an unsaturated environment so that a comparison can be made between the reaction of simulated and fully radioactive glasses. Of the planned 212 long-term tests, 126 have been terminated. The longest tests have been in progress for more than 30 months.

The early results reported from this study^{5,6} show that the reactivity of simulated waste glasses is similar to that of fully radioactive glasses. However, the longer-term tests at higher SA/V ratios suggest that the reactivity of the two glass types may be significantly different. The normalized releases of B, Li, Na, and Si for all the three glass compositions (165/42, 131/11, and 200) tested at 340 and 2000 m⁻¹ are similar for both radioactive and simulated glass for periods up to 728 days. However, at 20,000 m⁻¹, the simulated glass 200S showed leach rates higher than those of 200R by factors of 35, 23, 9, and 10 for the normalized release of B, Na, Li, and Si, respectively. The leach behavior of 200S differed from 200R at 20,000 m⁻¹ after 330 days (i.e., the glass dissolution rate for 200S glass was greatly accelerated between 182 and 364 days while the release rate for 200R showed almost no increase during the same interval) and the slow reaction trend has extended through 560 days.

The acceleration of glass reaction for 200S at 20,000 m⁻¹ has been correlated with solution pH and crystalline phase formation.⁷ During acceleration, the solution pH of 200S increased from 11.82 to 12.29. Several types of phases have been identified in the surface layers of 200S after reaction acceleration; they include a clinoptilolite phase, a button-like Si- and Ca-rich phase, an Si- and Fe-rich clay phase, and an almost pure amorphous Si phase.

The data above demonstrate the need for long-term tests at high SA/V ratios for the comparison studies. Figure 1 shows that the data for 200S and 200R glasses at SA/V ratios of 340, 2000, and 20,000 m⁻¹ for various times can be represented by a single curve when plotted against the product of SA/V and $t^{0.5}$. This product has been used to simulate long-term glass corrosion over short periods.^{8,9} For example, we have observed rate acceleration of 200S glass at 20,000 m⁻¹ for 330 days, and we would expect a similar acceleration for this glass tested at 2000 m⁻¹ at up to 90 years if the $(SA/V) \cdot t^{0.5}$ scaling holds. Thus, we would not have seen the difference between 200R and 200S glasses during our working lives if we had tested these glasses only at 2000 m⁻¹. Our data cannot be represented by a steady function of product of SA/V and t^1 .

The successful scaling of waste glass dissolution data by the product of SA/V and $t^{0.5}$ has been recently suggested^{10,11} as evidence for a diffusion-controlled dissolution mechanism. This mechanism requires the support from the investigation of the integrity of the surface layers and the adherence of the layers to bulk glass. However, our preliminary results from the surface examinations indicate 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 before reaction acceleration, but are more than 6500 nm thick after acceleration. It will be 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 20 times thicker with similar porosity and adherent properties are associated with the highest observed glass reaction rate.

The data obtained in the long-term static testing program indicate that static tests at 340 and 2000 m⁻¹ for up to 720 days on three DWPF nuclear waste glass compositions have shown that radioactive and simulated nuclear waste glasses with similar chemical compositions have very similar reactivities and have the same leach trends. However, a large difference in reactivity (up to a factor of 40 in leach rates of boron) has been observed between 200R and 200S when tested at 20,000 m⁻¹ for less than one year. The accelerated glass reaction rate with the simulated 200S glass is associated with the formation of crystalline phases such as a clinoptilolite and with a pH excursion. The data presented here indicate that the reaction progress for both 200S and 200R glasses can be

Fig. 1. Leachate Concentrations of B, Li, Na, and Si vs. the Product of SA/V and $t^{0.5}$ for 200S and 200R Glasses: (a) B, (b) Li, (c) Na, and (d) Si for 200S, (e) B, (f) Li, (g) Na, and (h) Si for 200R. The lines are a guide for the eye.

represented as a steady function of the product of SA/V and $t^{0.5}$. The SA/V ratio appears to be a useful corrosion acceleration parameter. Meaningful comparison tests between radioactive and simulated nuclear waste glasses should include long-term and high SA/V tests.

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

C. Effect of Radiation
(D. J. Wronkiewicz)

1. Introduction and Background

Radiation effects on high-level waste glasses are an important consideration for radionuclide immobilization because of their potential to influence the glass stability. Radiation may affect the long-term performance of glass waste in an unsaturated repository environment by inducing radiation damage to solid materials and by interacting with air, water vapor, or liquid water to produce a variety of radiolytic products.

Ionizing radiation will excite electrons and ionize water molecules and dissolved gases to form reactive radicals and new molecules. The predominant water radiolysis species formed include hydrated electrons (e_{aq}^-), hydrogen ions (H^+), hydroxyl ($\bullet OH$), hydroperoxyl ($HO_2\bullet$), hydrogen atoms ($H\bullet$), molecular oxygen anions (O_2^-), and the molecular species hydrogen (H_2) and hydrogen peroxide (H_2O_2). Dissolved molecular nitrogen and carbon dioxide in the water may also undergo radiolytic decomposition with a several-step recombination of the dissociation products with oxygen, water, and other associated radiolytic products to form nitrogen and carboxylic acids, respectively.¹²⁻¹⁴ A notable decrease occurs in the pH of deionized water exposed to gamma and alpha radiation due to the formation of nitric acid in the irradiated air above the test solution and its subsequent dissolution in water.^{12,15-17}

Under the geologically unsaturated conditions expected at the proposed Yucca Mountain repository, the most likely scenario for water contact with the waste glass if the container ruptured is the following: Thin films of water would condense on the glass surface. Radiolytic products might then rapidly concentrate in the small amount of water present on the glass. In such a high glass surface area/liquid water volume (SA/V) environment, the bicarbonate present in the small volume of leachate would be quickly overwhelmed by nitric acid produced in radiolysis reactions.¹⁷ Any excess nitric acid that subsequently condensed on the glass surface would probably react with the glass and might significantly affect the degradation of the waste form.

The limited quantity of solution expected to condense on the glass surface would also preclude any volumetric dilution of the radiolytic and glass dissolution products. Rapid increases in the concentrations of glass dissolution products would also result in the leachate becoming saturated by certain secondary alteration minerals, accelerating the eventual precipitation of secondary phases. This process might promote continued rapid dissolution of the glass as secondary phases sequester elements from the leachate and lower the activity of certain ions in solution, thereby promoting additional dissolution of the glass.¹⁸

2. 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. Comparisons of alteration profiles from glasses reacted in irradiated versus unirradiated conditions will be used to characterize the influence of irradiation on alteration rates. These comparisons will also allow an evaluation of the influence of radiation and the radiolysis environment on the stability and formation of secondary mineral phases. Detailed scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), analytical electron microscopy (AEM), and X-ray diffraction (XRD) comparisons between alteration assemblages developed on glass in irradiated versus unirradiated conditions will be used to characterize the influence of irradiation on phase development.

3. Technical Approach

Experiments with glass monoliths were housed in 22-mL stainless steel test vessels. The glass samples for these tests were cut into ~1- x 10-mm wafers, with several different glass compositions being tested, including uranium-doped SRL 131 and 202 compositions, and SRL 131, 165, and 202 glasses doped with actinides and technetium-99. The 202 glass is similar to that projected for waste disposal, while the 131 glass is less and the 165 glass is more durable than the 202 glass.

Two types of SA/V tests were conducted with glass monoliths present, all with two to four replicates. In the first test type, four glass monoliths are immersed in 2 mL of EJ-13 water at an SA/V ratio of 340 m^{-1} and at 90°C . This batch monolith test design allows the highest SA/V ratio to be attained, the glass monoliths to be completely immersed in water, and enough solution aliquots to be collected for all desired analyses. These experiments were exposed to an external gamma radiation flux of $\sim 3 \times 10^3 \text{ rad/h}$. Solution aliquots were taken from these tests to analyze for pH, carbon, cation, anion, and filtered size distributions of actinides. Results from these irradiated tests will be directly comparable to 340 m^{-1} unirradiated tests from the SA/V task.

The second test type involves exposing glass disks to an irradiated vapor-rich environment while they are suspended inside the test chamber via Teflon (unirradiated) or Pt-Rh (irradiated) support wires. These tests were conducted at much higher SA/V ratios ($\sim 4000 \text{ m}^{-1}$), although the exact ratio of these vapor hydration tests 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. Deionized water was added to each vessel, enough to saturate the air inside the heated vessel without causing solution runoff from the suspended sample. The experimental temperatures ranged from 150 to 200°C . The elevated temperatures of these experiments are used to accelerate the glass reactions into reasonably short experimental time frames. Previous testing¹⁹ 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 technetium-doped samples were exposed to an external gamma dose rate of $\sim 3 \times 10^3 \text{ rad/h}$, thereby subjecting them to an internal alpha-beta and external gamma source. This dose rate was chosen as an upper bounding condition to evaluate whether radiation could potentially affect glass reactions. The cumulative gamma exposure for the 56-day tests was $\sim 5 \times 10^6$ rads. Because insufficient solution was present in these tests to take aliquots for analysis, extensive solid phase characterizations were made of altered surface material by utilizing optical microscopy SEM/EDS, XRD, and AEM techniques.

4. Results and Discussion

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. A thin film of water sorbs onto the glass surface. Hydration forms an *in situ* hydrated layer penetrating into the glass and secondary mineral phases precipitate on the reacted surface. The goal of the initial vapor hydration studies is to determine if ionizing radiation will influence the hydration aging of glass. Both the irradiated and unirradiated samples rapidly developed both an *in situ* alteration layer and a ubiquitous precipitate layer that formed as the solution contacting the glass became saturated with leached components.

(1) Layer Formation

The irradiated 202A monoliths had reacted completely 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 $\mu\text{m}/\text{day}$. However, the reaction progressed unevenly on these samples, with rapidly developed alteration fronts occurring along preferential zones (possibly 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. The cause of the fracturing is not known, but it may be a result of the release of thermal stresses incorporated during sample casting, the stresses induced by water diffusion into the glass, or a result of radiation damage to the glass.

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. 2). Up to three additional layers, some also banded, enveloped this Si-Fe core. The layer immediately overlying the Si-Fe core consisted of a brownish gel that was lighter in color at the base and pitted at the surface. Its composition was consistent with the presence of nontronite and saponite clays. Overlying this brown layer was a thin sheet of white, fine-grained, ameboid Ca-Si crystals. This thin Ca-Si layer was, in turn, overlaid by a heterogeneous mixture of crystalline material interwoven into a cohesive layer. Several 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.

The 202U samples that were reacted without external radiation developed an alteration layer ~130- μm thick only after 56 days of reaction. Comparing the rate of alteration layer development between the two tests indicates that layer development may be accelerated by a factor of ~15 times due to radiation exposure at high glass SA/V ratio conditions. Two individual layers were identified on 202U glasses. A layer of smectite was detected on the surfaces of all 202U samples tested less than 21 days. 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 layer was blanketed with a layer of 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.

Fig. 2. 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 due to electron distortion. (a) Secondary electron image (SE) of auto-fractured section of 202A glass shows banded Si-Fe core material (200X). (b) Backscattered electron image (BSE) of a 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 wecksite, large trapezohedron, and dimpled analcime (deposits on Pt-Rh wire run from upper left to lower right). The bright BSE images of the fine-grained Na-U-Si phase result from the silver mounting medium, which impregnated the 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 (100X).

(2) Surface Precipitates

Alteration patterns for both the irradiated and unirradiated 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. 2c and 2d). 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 unirradiated tests (Fig. 3). For example, analcime, weeksite, phillipsite, and adularia were detected on earlier tests of the 202A glasses. The transient phase herschelite, which formed early in the 202U tests, was not detected at all on the 202A samples, although it is possible that herschelite first precipitated and then dissolved before the seventh day, when the first samples were collected. A number of secondary precipitates also were only detected on the 202A samples, the most notable being Na-weeksite, boltwoodite, and haiweeite.

Fig. 3. Alteration Mineral Paragenetic Sequence Identified for SRL 202 Glasses. Solid lines represent 202U samples while dotted lines represent 202A glass reactions.

Electrons accelerated to 30 kV were utilized during SEM/EDS analysis to excite the L-shell electrons of any transuranic elements present. These elements were not identified in any of the secondary phases examined, suggesting that concentrations were maintained below

detectability within the alteration layers. More sensitive autoradiography techniques will be employed in future studies to better characterize the distribution of transuranics within altered glass profiles.

Preliminary 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.

b. Batch Leach Tests

Anion and cation solution analyses have been received for batch leach tests conducted on actinide- and technetium-doped 202A glass at 340 m^{-1} and 90°C under an external gamma irradiation field for time periods between 540 and 720 days.

Analyses indicate that pHs level off at ~ 9 after an early increase between 56 and 180 days. During the initial alteration process, alkali and alkaline earths present in the glass are released in concentrations greater than that necessary to neutralize the H^+ ions dissociated from radiolytic acids. In the later tests, a buildup of radiolytic acids in the leachate results from a decrease in the rate of ionic exchange with the glass as the increase in reaction layer thickness and the glass reaction rate slows down. An examination of cation solution trends indicates a decrease in the rate of Na, Li, K, and B release to solution after 180 days.²⁰ 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 occurrence at the same time as the pH change provides supporting evidence for a change in the rate of the ionic exchange process.

D. Relationship between High SA/V Experiments and MCC-1 (W. L. Ebert)

1. Introduction and Background

Static leach tests are being used to measure the durabilities of borosilicate glasses that may be used to vitrify high-level waste and will be used to measure the product consistency of glass produced by the Defense Waste Processing Facility (DWPF). Static leach tests performed in the laboratory will also be used to predict the long-term durabilities of waste glasses under possible environmental conditions. These tests are used to determine the reaction mechanism of glass dissolution, which can then be used to simulate long-term reactivities under different conditions. The reaction rate of long-term glass corrosion is presently considered to be the low rate typically attained in static leach tests after the leachate becomes saturated. However, static leach tests performed in CMT have shown the reaction rate to initially decrease as the reaction progressed, but to increase after long reaction times coincident with the formation of secondary phases under some test conditions. This raises the question of whether tests performed under other conditions will show a similar increase in the corrosion rate after longer time periods.

Static leach tests are being performed in CMT at various glass surface area/leachant solution volume ratios (SA/V) to assess their effects on the glass reaction. These tests also provide valuable insight into long-term glass reaction behavior. The major effect of the SA/V ratio on the

glass reaction is through dilution of the reaction products: tests at low SA/V ratios have larger volumes of solution per unit area of glass than do tests at higher ones and dilute reaction products to a greater degree. Reaction in tests at high SA/V are expected to proceed under nearly saturated solution conditions after short reaction times at the long-term reaction rate.

2. Technical Approach

Static leaching experiments were performed at 10, 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 product consistency test (PCT) conditions at 2000 m^{-1} . Other tests were performed at 20,000 m^{-1} using the same powdered glass. Tests were performed in J-13 groundwater, which is a reference groundwater of the Yucca Mountain Project. Reaction times were selected to demonstrate the temporal reaction trends and to compare data obtained from tests run for equivalent (SA/V) $\cdot$ t products. 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 U, Np, Pu, and Am, and then cast into bars. These actinide-doped glasses are referred to as SRL 131A and SRL 202A. Tests were performed in 304L stainless steel vessels in a constant temperature oven. A nominal SA/V ratio 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. These quantities 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.

3. Elemental Release Results from Leachates and Filtrates

The leachate and filtrate solutions were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and fluorescence spectroscopy. Figures 4 and 5 show the normalized elemental mass losses of several glass components from SRL 131A and SRL 202A glass at 10, 2000, and 20,000 m^{-1} that were computed from the leachate and 0.45- μm -filtered solutions. The normalized mass loss of an elemental is simply the measured solution concentration of that element, less the amount present in the initial leachant, divided by the product of the SA/V ratio of the test 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 4 and 5 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. The reaction rate also varies with the reaction time and the SA/V ratio of the test. These results demonstrate that the glass reaction rate, and/or the mechanism, is affected by the different solution chemistries attained in tests at different SA/V ratios. For each glass composition, the normalized elemental mass losses measured in tests at different SA/V ratios can be compared directly.

Fig. 4. Normalized Elemental Mass Loss from SRL 202A Glass. Tests were performed at (a) 10, (b) 2000, and (c) 20,000 m⁻¹ for (■) Li, (Δ) Na, (•) B, (◆) K, (○) Si, and (□) U.

Instead of plotting the normalized elemental mass loss against time, the measured concentrations can be plotted against the product of the reaction time and the SA/V ratio of the test. The product (SA/V)•t has been used as a single parameter to measure the extent of glass reaction, meaning that tests at different SA/V but equivalent (SA/V)•t ratios should yield the same extent of glass reaction. The boron data from replicate tests with SRL 131A and SRL 202A glass are plotted against (SA/V)•t in a log-log plot in Fig. 6. Tests at 2000 and 20,000 m⁻¹ performed for equivalent (SA/V)•t values clearly do not generate equivalent solution compositions for either glass. Tests reacted at higher SA/V ratios consistently have greater boron releases. 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 at equivalent (SA/V)•t values.

The data plotted in Fig. 6 can be further interpreted based on the current model of the glass reaction rate, which can be written as

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

or

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

where k is the forward reaction rate coefficient, $(1 - Q/K)$ is the reaction affinity, and R_f is the "final rate." Generally, Q in the affinity term is the silicic acid concentration in solution and K is the

Fig. 5. Normalized Elemental Mass Loss from SRL 131A Glass. Tests were performed at (a) 10, (b) 2000, and (c) 20,000 m⁻¹ for (■) Li, (Δ) Na, (●) B, (◆) K, (○) Si, and (□) U.

Fig. 6. Log([B]) vs. Log((SA/V)•t) for Tests with (a) SRL 202A Glass and (b) SRL 131A Glass at (●) 10, (■) 2000, and (◆) 20,000 m⁻¹. Lines drawn with a slope of 1 through data point at 20,000 m⁻¹.

"saturation concentration" of silicic acid. The final rate, R_f , is the rate when the solution is saturated (i.e., when Q equals K). According to the above equation, the short-term data in a plot of $\log([B])$ versus $\log((SA/V) \cdot t)$ will yield a slope of 1 and a y-intercept equal to the log of the rate coefficient times the reaction affinity term. The short-term data represent the forward rate of glass reaction under dilute conditions where the affinity term is near one (i.e., Q equals 0). Longer-term data is expected to deviate negatively from the line fit to the short-term data, that is, as the silicic acid concentration increases and the affinity term and the reaction rate decrease, 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 drawn through the long-term data points, which has a slope of 1, represents the "final dissolution rate" under "saturated conditions." The analysis above is based on the assumption 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 (in k , K , and R_f) are implicitly included in the analysis, because it is the experimental data at short and long times that 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. 6a for the data from tests run at 20,000 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 (where $\log((SA/V) \cdot t)$ equals 0) of about -3 (i.e., $\log[B] = -3$). Dividing this value by the atomic fraction of boron in SRL 202A glass (0.0248), the initial rate (based on the boron release) is about 0.040 $g/m^2/day$. This value represents a minimum approximation of the forward rate for tests with SRL 202A at 20,000 m^{-1} . Another line is drawn through the intermediate-term data points and has a y-intercept of about -4. This value corresponds to a rate of about 0.0025 $g/m^2/day$, which is the minimum rate achieved in tests with SRL 202A glass at 20,000 m^{-1} at intermediate reaction times. The longer-term data points in Fig. 6a 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. 6a 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 m^{-1} . From Table 1, the final dissolution rate at 2000 m^{-1} is expected to be less than 0.0002 $g/m^2/day$. 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 m^{-1} , although some duplicate tests showed much less reactivity.

Similar analyses were performed on data from tests with SRL 131A glass. (See Fig. 6.) At 20,000 m^{-1} , approximate forward and final dissolution rates are 0.8 and 0.05 $g/m^2/day$, respectively. Long-term data show that the glass at 20,000 m^{-1} continues to react at the final

Table 1. Measured Reaction Rates^a of SRL 131A and 202A Glasses at Different SA/V Ratios, $g/m^2/day$

	SA/V		
	10 m^{-1}	2000 m^{-1}	20,000 m^{-1}
SRL 131A ^b	0.14/0.050	0.27/0.021	0.84/0.053
SRL 202A ^b	0.099/0.013	0.025/0.0016	0.04/0.0025

^aRate is based on boron release.

^bReacted in EJ-13 water.

dissolution rate throughout the times tested. At 2000 m⁻¹ SRL 131A glass reacts at a final dissolution rate near 0.02 g/m²/day at or beyond about 140 days of reaction, and at 10 m⁻¹ it reacts at a rate near the final dissolution rate of tests at 20,000 m⁻¹ at reaction times beyond about 14 days.

The analyses above show that the apparent final dissolution rate varies with the SA/V ratio for both glass compositions. Differences can be attributed in part to the leachate pH: at a high SA/V ratio, the higher pH values accelerate the hydrolysis reaction to release boron from the glass. Tests with SRL 131A glass at 2000 and 20,000 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 m⁻¹ lead to a higher final dissolution rate. Likewise, the minimum rate observed for tests with SRL 202A glass at 20,000 m⁻¹ is greater than that achieved in tests at 2000 m⁻¹, which are expected to 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, which increases the solubility limit of silicon in solution. 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 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.

4. 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.

E. Analytical Electron Microscopy

(J. K. Bates, C. R. Bradley, E. C. Buck, and N. L. Dietz)

Analytical electron microscopy (AEM) is a combination of transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), and electron diffraction (ED). Point-to-point resolution for images obtained with TEM approaches 3 Å; the smallest region that can be investigated using ED, EDS, and EELS is about 200 Å. The AEM is a very powerful tool for the investigation of heterogeneous samples; very small inclusions, small crystallites, colloidal-size particles, and thin reaction and diffusion layers.

During this reporting period, we analyzed the reaction layers, the underlying glass, and the generated colloidal particles of samples from other tasks (i.e., those testing long-term, SA/V ratio, natural analogue, and low-temperature vapor-phase effects).

1. Analysis of Glass from Long-Term Tests

The "Long-Term Testing" task seeks to evaluate the long-term performance of fully radioactive glass and to compare it with that of nonradioactive glasses with the same nominal composition. The test matrix is designed to allow the investigation of several variables which may effect glass reaction including the following: SA/V-t scaling, glass composition, and inclusion of radionuclides in the glass.^{21,22} Samples have been prepared of all nonradioactive tests terminated to

date in this matrix, and preparation of radioactive samples has begun. Detailed analyses have been performed on several samples from the test matrix.

The alteration layer in most samples examined to date is a poorly crystallized smectite. Samples from longer-term reactions have compositions and electron diffractions that are consistent with smectites. Samples reacted for shorter periods of time give much weaker diffractions, suggesting that the layer is largely amorphous, even though the compositions are similar. In some cases, additional secondary phases have been observed to form on the sample surface. Clays that developed on the outer surface of the glass have been identified, compositional variations in the underlying glass as a function of depth have been investigated,⁷ and non-clay secondary phases have been observed. Furthermore, in some of these samples there is a backbone structure 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.

2. Analyses of Natural Analogues

Four natural basalt glasses were reacted under controlled conditions in the laboratory; the reaction products were characterized with AEM. Samples were reacted for 100 days, at 150°C and for 14, 50, and 60 days at 200°C. In all cases, a smectite layer (saponite or montmorillonite) developed on the outer surface of the glass; in some cases, a leached amorphous layer was observed beneath the smectite. A large (>1 µm) analcime crystal was identified on the 50-day sample.

3. Formation and Characterization of Colloids

Colloids have the potential to increase the release of radionuclides from waste materials into the environment. Most studies on nuclear waste colloids have concentrated on the formation of actinide pseudocolloids from groundwater colloids or actinide real colloid formation.^{23,24} Both actinide pseudocolloid and real colloid formation will be controlled by an initial solubility rate-determining step.²⁵ However, colloidal particles produced as a direct result of the alteration of the waste glass itself (i.e., via spallation), will not be dependent on such a step. This process has been shown to occur during simulated weathering of nuclear waste glass, where the particles produced have been found to adsorb americium and plutonium.²⁶ Analytical electron microscopy of colloids in waste glass leachates has revealed a new source of colloids for pseudocolloid formation as well as spalled-off phases.²⁷

The major phase present in all tests was a smectite clay with a turbostratic structure that was evident when the oblique-textured ED pattern was revealed. Uranium silicate phases were observed in all glass tests after ~360 days of reaction. These colloids appeared suddenly, suggesting that they were formed via spallation processes. They were often found in association with clay particles and were identified as weberite and uranophane-type uranium silicates.

Colloids formed in glasses reacted in EJ-13 water at 340 m⁻¹ and exposed to a gamma radiation field were found to be more crystalline than any other leachate colloids. Examination of a 131A glass reacted for 180 days at 90°C revealed crystalline titanium oxide, kaolinite, and chrysotile (a component of asbestos) colloids. The regular shape of a titanium-uranium colloid suggested that it was crystalline, though very few electron diffraction spots were observed. The phase was not observed in longer-reacted tests. This colloid has been observed in the surface layers of leached 131 glasses and has been tentatively identified as brannerite.²⁸ The uranium titanium colloids were 0.1 µm long, and were isolated from all other colloidal material, which suggested that they had formed within the leachate.

The pattern of clay colloidal development and eventual removal from the leachate appears to be related to the waste glass test parameters and their influence on the solution conditions. The influence of the SA/V ratio on colloidal stability is a result of its effect on leachate ionic strength. For example, at high SA/V ratios or long reaction times, the resulting high ionic strength prevents colloidal growth because sedimentation occurs before fully crystalline colloids can develop. However, the opposing effect of pH can stabilize the colloids by increasing repulsive forces. Very little colloidal material was observed after long reaction times in the 200S tests even though 200S glass has been shown to react more rapidly at $20,000 \text{ m}^{-1}$ than fully active 200R glass.²⁹ Further investigations are underway to assess the role of ionic strength and pH in the development of reacted layers in these leached glasses.

4. Future Work

Detailed characterizations of phases found on the glass samples from these test matrices will continue. This detailed characterization will entail identification of the secondary phases produced on the surface of the glass and observation of compositional gradients within the glass caused by the reaction process. Several additional phases are beginning to develop on longer-term tests that have recently been terminated. In addition, analysis of radioactive samples has begun, enabling direct comparisons to be made between fully radioactive glasses and simulated glasses reacted under identical conditions for the same reaction period.

Studies by AEM on the formation and characterization of colloids in the leachate will continue, with greater emphasis on the impact of colloids on overall glass behavior.

F. Natural Analogues (J. J. Mazer)

A natural analogue approach for relating water diffusion observed in long-lived natural rhyolitic glasses to water diffusion in nuclear waste glasses was previously developed.³⁰ This approach is based on the postulate that the resistance to water diffusion of tektites is similar to that of nuclear waste glasses. The results of experiments with tektite glass in water vapor atmospheres between 150 and 225°C for up to 400 days has previously been presented.³⁰ These experimental results were extrapolated to repository-relevant conditions for nuclear waste glass, resulting in a diffusion rate of $0.01 \mu\text{m}/\text{days}^{1/2}$ at 90°C and 100% relative humidity. This value is significantly lower than the final or long-term rate found for nuclear waste glass reactions and would seem to indicate that the water diffusion reaction process may not be the rate-controlling process for waste glass alteration. At lower temperatures or under conditions in which processes such as ion exchange or dissolution are suppressed, the nuclear waste glass reaction mechanism may change and become dominated by water diffusion; however, these results indicate that this would not reduce the glass durability.³⁰ Furthermore, it seems likely that physical evidence for water diffusion in nuclear waste glasses can be obscured or altered by other competing reaction processes.

In another natural analogue approach, we began experiments on basalt glasses, which are closer in composition to nuclear waste glasses than obsidians or tektites and have been the focus of other natural analogue studies.³¹⁻³³ The relationship between the natural reaction of basalt glass and vapor hydration experimental results has been shown to be more realistic than that with hydrothermal test results.³⁴ Collaborations with investigators studying archaeological sites have not yet resulted in adequate characterization of alteration conditions, so our experimental results were compared with water-rock interactions on the Martian surface.

Models of weathering processes on the surface of Mars involve hydrothermal alteration as the primary mechanism responsible for clay formation. Previous experimental studies of basalt glass interactions with water under hydrothermal conditions (i.e., high dilution, where the SA/V ratio is small) demonstrate that phyllosilicates and zeolites are the primary alteration minerals.³⁴⁻³⁶ Gas-solid weathering is thought to be less thermodynamically favorable and relatively unimportant;^{37,38} however, the experimental alteration of basalt glass under vapor hydration conditions (large SA/V) can result in the formation of clay minerals, zeolites, and hydrated calcium silicates.³⁴

We began a study of the reacted layers formed on basalt glasses experimentally altered under vapor hydration conditions to resolve this issue. High SA/V ratios promote reaction product buildup in solution and alteration mineral formation. It has previously been shown that these reaction conditions promote weathering processes similar to those found in nature for tektite glasses,³⁰ rhyolitic glasses,^{39,40} and basalt glasses.³⁴ The hydration of basalt glass is described for experiments at 150, 175, and 200°C and 100% relative humidity for up to 400 days. A smaller set of samples was examined in detail: at 200°C for 14 days and for 50 days, at 150°C for 100 days, and at ambient temperature. Preliminary characterization of the alteration layers with analytical electron and scanning microscopy suggest that the reaction mechanism includes precipitation of a smectite clay on the outermost surface of the glass. Between the clay and the unreacted glass is an amorphous gel-like phase (palagonite).

Qualitative EDS analyses were performed to characterize the composition of the alteration layers. The compositions were normalized to eight silicon atoms to facilitate comparisons between different features in the layer. Table 2 summarizes the results of the EDS analyses for the 14- and 50-day 200°C basalt samples. The 14-day sample has the most complicated alteration layer, while the

Table 2. Results of AEM/EDS Analyses of the Alteration Layers on Basalt Glass Samples Vapor-Hydrated at 200°C. Analytical results were normalized to eight silicon atoms.

	14-Day Samples				50-Day Samples	
	Outer Clay	Mid Clay	Inner Clay	Mottled Layer	Outer Clay	Inner Clay
Si	8.00	8.00	8.00	8.00	8.00	8.00
Mg	3.89	2.03	0.66	1.55	3.05	1.92
Al	2.79	2.14	1.74	2.48	2.20	1.88
Fe	2.68	2.06	2.03	1.64	3.04	2.02
K	0.25	0.11	0.07	0.11	0.70	0.02
Cl	0.14	0.30	0.51	0.11	0.38	0.25
Ca	0.09	1.28	2.99	1.75	0.20	1.85
Ti	0.05	0.46	1.04	0.31	0.10	0.45

50-day sample contains only two sublayers. In general, the alteration layers on both are enriched in Mg, Al, and Fe and depleted of Ca and Ti as the distance from the unreacted glass increases. The 14-day sublayer designated "mottled layer" has a composition very similar to the bulk glass. (See Table 3.) Selected area electron diffraction analyses of the mottled layer indicate it is amorphous and thus probably water-rich glass that has not yet reacted. Table 4 compares the compositions of the

Table 3. Compositions of Unreacted Glass and the Mottled Layer Found on the 200°C 14-Day Sample

	Mottled Layer	Unreacted Glass Assay
Si	8.00	8.00
Al	1.55	2.52
Mg	2.48	1.43
Fe	1.64	.51
K	0.11	0.13
Cl	0.11	0.00
Ca	1.75	1.77
Ti	0.31	0.21

Table 4. Results of EDS Analyses of the Outermost Clay Layer Found on Each Vapor-Reacted Basalt Glass Sample and Unreacted Glass

	Outer Clay Samples			Unreacted Glass Assay
	150°C 100 days	200°C 14 days	200°C 50 days	
Si	8.00	8.00	8.00	8.00
Al	3.08	2.79	2.20	2.52
Mg	2.04	3.89	3.05	1.43
Fe	2.11	2.68	3.04	1.51
Ca	0.20	0.09	0.20	1.77
K	0.03	0.25	0.70	0.13
Cl	0.36	0.14	0.38	0.00
Ca	0.20	0.09	0.20	1.77
Ti	0.13	0.05	0.10	0.21

outermost clay on each of the samples analyzed and an approximate composition for Fe-rich saponite. It is clear that the compositions are changing with time and temperature. AEM analyses also suggest that these phases are becoming more crystalline with time. It appears that the clay composition is evolving towards that of an Fe-rich smectite. This phase is the only one found on each of the samples considered. Further work is needed to determine how temperature and time affect clay compositions and crystallinity.

Although more work is required in this area, there are striking similarities between our experimental results and remote observations of the Martian surface. Iron-rich saponites have been postulated to be an important component of the Martian surface,⁴¹ and our experimental results show that this feature is produced from basalt glass weathering. Our results provide experimental evidence that basalt glass interactions with vapor atmospheres can be an important source of clay minerals. Therefore, the process of weathering igneous rocks on the surface of Mars by contact with the atmosphere may be more important than was previously thought.

Extrapolating the results of experiments performed at high temperatures ($>100^{\circ}\text{C}$) to conditions relevant to the surface of Mars is only meaningful if the glass weathering processes are the same in both systems. Assuming that identical processes are occurring on the surface of Mars and in our experiments, direct extrapolation of the data to 0°C results in a alteration rate of approximately $0.05\text{ }\mu\text{m}$ per year. A significant effect of relative humidity on alteration rates in vapor hydration experiments has been demonstrated for rhyolitic glasses.⁴² Thus, the limited amount of water in the Martian atmosphere probably means that the actual weathering rate may be significantly lower.

II. GLASS STUDIES FOR YUCCA MOUNTAIN PROJECT

The Yucca Mountain Project (YMP) is investigating the tuff beds of Yucca Mountain, NV, as a potential location for a high-level radioactive waste repository. As part of the waste package development portion of this project, which is directed by Lawrence Livermore National Laboratory (LLNL), work is being performed at CMT to study the behavior of the waste form under anticipated repository conditions. Work includes the following: (1) developing and performing a test to measure waste form behavior in unsaturated conditions, (2) studying the behavior of waste package components in an irradiated environment, (3) developing test methods to study the reaction of glass in water vapor and, subsequently, in liquid water, (4) developing static leaching tests to provide long-term release data to the glass modeling effort, and (5) characterizing reacted glass surfaces in detail.

A. Tests with Unsaturated Test Method (J. K. Bates and T. J. Gerding)

The YMP Unsaturated Test Method⁴³ is being used in the N2 and N3 test series, which are being conducted with actinide-doped glasses. Because of the alpha decay of the predominant radionuclides, these tests can be conducted in a contained area without shielding. Since the N4 test series will be conducted with "fully" radioactive sludge-based glass, modifications to the test method will have to be made. These tests will be performed as part of the EM program.

1. N2 Unsaturated Tests

The N2 continuing tests (SRL 165 glass) have been completed through the 342-week sampling period. All of the batch tests have been completed, and three continuous tests and one blank test are ongoing, with samplings at yearly intervals.

2. N3 Unsaturated Tests

The N3 Unsaturated Test uses ATM-10 glass (simulated West Valley glass doped with actinides and ⁹⁹Tc) that was received from the Materials Characterization Center (MCC) and remelted to shape into the required glass form. This ongoing test was started July 6, 1987, performed according to the Unsaturated Test Method, and has been completed through the 272-week sampling period.

III. TESTS WITH UO_2

A. Tests with Unirradiated UO_2

(D. J. Wronkiewicz, E. C. Buck, and P. A. Finn)

Leachate samples have been collected from the 1.75- to 3.0-year PMP8U unsaturated drip tests, where the samples are supported by stainless steel stands. These tests examine the feasibility of utilizing the unsaturated test method with unirradiated UO_2 and also act as pilot studies for unsaturated tests with spent fuel. After the tests, fine-grained green and white precipitates were observed on the tops of the UO_2 pellets. Based on results from previous tests, these alteration phases are likely to be represented by the mineral phase dehydrated schoepite ($\text{UO}_3 \cdot n\text{H}_2\text{O}$, where $n < 2.0$). Detailed surface examinations of the alteration phase(s) will be made after the tests have been terminated.

Solution aliquots were collected for pH, carbon, anions, cations (including uranium), carbon grid-filtered, nonacidified uranium, and laser light scattering measurements. The sample with the greatest amount of surface alteration (PMP8U-10) also displays the lowest solution pH values, although the presently recorded value of 7.9 represents a slight increase from previous results (Fig. 7). The remaining three samples had pH values ranging from 8.4 to 9.2, with all samples exhibiting a pH slightly lower than in previous tests. The pH of the starting EJ-13 injectant was 8.2. Carbon analyses indicate that trends developed during earlier test intervals are continuing. Both total carbon and total organic carbon concentrations have remained relatively constant. Anion concentrations of F^- , Cl^- , SO_4^{2-} , and NO_3^- have increased less than twice those in the starting EJ-13 solution, while remaining solution results for cations and uranium have yet to be reported.

Fig. 7. Solution pHs for UO_2 Drip Tests as a Function of Time

Analytical electron microscopy investigations of carbon grid-filtered samples did not reveal the presence of any solid uranium phases. The results from laser light scattering measurements for ten different samples reveal the presence of particulate matter with average particle sizes ranging from 0.14 to 0.96 μm , which is the colloidal range. Reanalyzing a solution from Teflon-supported tests showed an increase in average particle size from 0.10 to 1.57 μm . This increase may reflect particle agglomeration during storage of the test solution.

B. Colloidal Examination of UO_2 Solutions

(P. A. Finn, D. J. Wronkiewicz, C. Mertz, and E. C. Buck)

Colloids that occurred in solutions leached from UO_2 were characterized. The first set of leachate samples examined were from the 5.0- to 6.8-year interval unsaturated leach test of unirradiated UO_2 samples. The leachate was water from the Yucca Mountain well J-13 that had been equilibrated with Topopah tuff at 90°C . The characteristics of the UO_2 stacks, which were placed on a Teflon stand, are found in Table 5. The relative position of the leachate solution when the tests were sampled is also given. The second set of leachate solutions came from a 1-year cycle of a 0.075 mL/3.5 d-leach test of three unirradiated 10-mm-thick UO_2 pellets that were placed on a stainless steel support stand. The leachate water was at the base of the UO_2 pellets when it was sampled. Some of the leachate solutions were passed through a 2-nm CF25 noncellulose filter to eliminate large colloidal particles.

Table 5. Characteristics of UO_2 Stacks in Leachate Tests

Sample No.	Description of UO_2 Samples	UO_2 Height (mm)	UO_2 Density (%TD)	Liquid Position in Test Vessel when Sampled ^a
PMP8U-2-1	11 discs, each 1.75 mm thick	19.25	95.04	Even with Teflon stand
PMP8U-2-2	11 discs, each 1.75 mm thick	19.25	95.04	
PMP8U-3-1	2 discs w/crushed UO_2 between them	22.50	81.98	Touching UO_2
PMP8U-3-2	2 discs w/crushed UO_2 between them	22.50	81.98	
PMP8U-6-1	3 pellets, each 10 mm thick	30	96.34	UO_2 immersed
PMP8U-6-2	3 pellets, each 10 mm thick	30	96.34	
PMP8U-7-1	3 pellets, each 10 mm thick	30	96.34	Below Teflon stand

^a UO_2 sits on a Teflon stand.

Two techniques were used to characterize the colloids, laser light scattering and transmission electron microscopy (TEM) examinations. For laser light scattering measurements under dynamic conditions, the diffusion coefficient (D) of particles undergoing Brownian motion is calculated from the autocorrelation function of the expression

$$I/D = t_c [(4\pi n/\lambda) \sin(\theta/2)]^2 \quad (1)$$

where t_c is the characteristic decay time derived from the autocorrelation function, n is the refractive index of the continuous phase, λ is the wavelength of light, and θ is the scattering angle. The hydrodynamic radius (R_h) is then obtained from the Stokes-Einstein relationship:

$$R_h = k_B T / (6\pi\eta D) \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature in degrees Kelvin, and η is the viscosity of the solvent. The viscosity and refractive index values were assumed to be those of the samples.

The autocorrelation function of the fluctuating scattered light intensity was analyzed by an iterative version of the exponential sampling method, which is part of the Malvern software. This method yields an intensity-weighted particle size distribution. A good fit is obtained if the difference between the decay shapes of the fitted curve and of the sample is less than 0.008 and if the two curves can be superimposed.

Laser light scattering measurements were done on a Malvern photon correlation spectrometer, using 1-mL cylindrical glass cells. Before analysis, the cells were shaken to suspend any settled material. The results are found in Table 6.

Table 6. Results of Laser Scattering Measurements

Sample No.	Date Run	Channel Width (ms)	Total Time (s)	PMT Count (kc/s)	Mean Size (nm)	Size Range (nm)	Fit Calc. vs. Data ^b
EJ-13-1	3/6	94	80	17.3	229	74 to 2612	1.57(-3)
EJ-13-1	4/3	500	200	11.3	300	98 to 2748	2.29(-3)
EJ-13-2	3/6	130	140	24.9	254	82 to 2552	1.12(-3)
PMP8U-2-1	3/6	200	120	3.2	101	33 to 1007	4.40(-3)
PMP8U-2-1	7/17	200	120	6.7	1570	----	1.75(-3)
PMP8U-2-2	3/9	200	200	1.6	110	37 to 994	7.29(-3)
PMP8U-3-1	3/24	150	600	0.5	100	33 to 858	7.22(-3)
PMP8U-3-1	3/24	200	1000	0.8	119	38 to 1359	4.85(-3)
PMP8U-3-2	3/25	350	1000	2.7	180	58 to 2188	5.06(-3)
PMP8U-6-1	3/26	1000	1000	0.7	576	194 to 2860	4.43(-3)
PMP8U-7	3/25	1000	1000	7.0	646	218 to 3410	4.52(-3)
PMP8U-9-1	7/7	100	600	7.0	560	----	2.84(-3)
PMP8U-9-1	7/15	50	1200	2.4	141	----	4.74(-3)
PMP8U-9-2	7/16	a					
PMP8U-10-1	7/15	75	600	2.2	165	----	5.95(-3)
PMP8U-10-1	7/17	150	600	12.5	9.62	----	4.10(-3)
PMP8U-10-2	7/16	a					

^aCounts too low, no fit. Solution had been filtered.

^bThese data indicate a good fit between calculated and experimental values.

The laser scattering measurements indicate that colloids are present in the first set of leach samples and in the injected fluid. The results appear the same for duplicate aliquots. The colloids in the injected fluid, EJ-13 water, have a different mean size and size range distribution than those found in the leach solutions.

The stability of the colloids was assessed by examining solution PMP8U-2 over a four-month period. The average particle diameter remained constant for the first three days, but increased after four months (from 101 nm to 1570 nm). This increase may be due to particle agglomeration. The mean size of the colloids in solution PMP8U-3 was similar to that initially in PMP8U-2, although the former solution was not measured until 18 days after the sample was taken.

The mean sizes of the colloids in both the PMP8U-6 and the PMP8U-7 samples were appreciably different than those in samples PMP8U-2 and PMP8U-3. The only similarity between the former two samples was the arrangement of the UO_2 pellets, which was identical, while the water injection rates were an order of magnitude different. The liquid level was below the UO_2 pellets for sample PMP8U-7 and above the pellets, that is, they were immersed, for PMP8U-6; therefore, the liquid level does not appear to be the contributing parameter to the difference in colloidal size.

For the second set of samples, the particle counts for the filtered samples, PMP8U-9-2 and PMP8U-10-2, were too low to obtain a meaningful result. For the unfiltered samples, PMP8U-9-1 and PMP8U-10-1, a consistent average particle diameter was not obtained (e.g., for PMP8U-9-1, the range was 141 to 560 μm). This result could be due to a sparsity of colloid particles and/or the presence of a dust particle. Therefore, no definitive conclusion could be drawn for these samples.

Samples for TEM analysis were made for PMP8U-6 and PMP8U-2 by wicking a drop of solution on a carbon grid. Because the solutions were not shaken, the TEM samples may not be representative of the average colloidal composition. The particles were 2000 nm in diameter and irregularly shaped. This size is at the upper end of the calculated distribution for the laser scattering measurements. For the PMP8U-2 sample, no uranium was detected in the one 2000-nm particle found. Uranium was detected in both particles from the PMP8U-6 TEM sample examined. Other elements detected in both particles were Si, O, Ca, Fe, Mg, and Ti; however, the relative abundance of each element was different in each particle except for silicon, which was the major element present. In one particle, calcium and iron were more abundant than uranium and magnesium; in the other particle, the reverse was found. In both particles, titanium was located at the same location as the uranium. Although titanium was detected with the uranium, and the mineral brannerite formed in geological oxidizing environments contains both U and Ti, the titanium in the TEM samples may be a spurious impurity.

C. Tests with Irradiated UO_2 - Spent Fuel

(J. C. Hoh, J. W. Emery, L. D. Hafenrichter, and P. A. Finn)

Unsaturated leach tests were designed, fabricated, and initiated to simulate the effect of unsaturated conditions expected in the Yucca Mountain radioactive waste repository on the leach/dissolution behavior of irradiated UO_2 . Specifically, these tests evaluate the performance of irradiated UO_2 at 90°C. The test matrix includes two types of irradiated fuel, ATM-103 and ATM-106, that represent the majority of the spent fuel expected in the repository. The average burnups of ATM-103 and -106 are 30 and 43 MWd/kgU, respectively. Three types of unsaturated tests are included in the test matrix to examine the effect of three different unsaturated environments: one has a saturated water vapor atmosphere, one uses a slow drip rate on the fuel to represent expected repository water velocity conditions of 0.5 mm/yr, and one uses a drip rate ten times faster to simulate the effect of unexpected conditions.

The Test Plan for the Unsaturated Testing of Spent Fuel was reviewed by technical and quality assurance staff at ANL and LLNL. The Safety Review document and formal safety review for initiation of the tests were completed. The Safety Review document to remove samples from the hot

cell was submitted. Experimental procedures (the Cycle Start Procedure, the Injection Procedure, and the Sampling Procedure) were drafted and reviewed by the quality assurance staff.

Before the tests could be initiated, the following required activities were performed. (1) An autoclave was set up to produce water that was saturated at 90°C with the mineral constituents from Yucca Mountain tuff. The water came from the J-13 well, a reference well for Yucca Mountain; the tuff is Topopah Spring tuff. They were in contact for 90 days to ensure that steady-state conditions were attained. Thereafter, samples were taken to determine the ion composition and concentration and the solution pH. (2) A filter was designed and fabricated for the fuel holder to minimize spent-fuel fines in the leach solutions. Like the fuel holder and the fuel cladding, it was made of Zircaloy-4. It was 1.333 cm (0.525 inch) in diameter and 20 mm thick and had 200 regularly positioned holes, each 7 nm in diameter, that were fabricated with an excimer laser. (3) Test vessels (schematic in Fig. 8) were fabricated from certified stainless steel. To ensure that the test vessels would be leaktight at 90°C, a torque wrench was used to seal different vessels at 60, 75, and 100 ft lb. The vessels were then held at 90°C for two to four months. All vessels sealed at 100 ft lb remained leak-tight. (4) The test vessels and the Zircaloy-4 sample holders were cleaned and conditioned with J-13 water. (5) An oven was modified to hold the test equipment and to allow remote control of its temperature. The oven's temperature profile was determined and the temperature control was calibrated. A water injection system to introduce μL quantities of water into the test vessels was designed, built, tested, conditioned with EJ-13 water, and installed on the shielded door of the test oven.

To initiate the tests, the hot cells known as the Senior Cave had to be renovated, which included the following improvements. The cells were decontaminated to where the background level was 5 mrem/hr. The main connecting shaft of the Parr manipulator, the steel door between cells C and B, and the servo-manipulators were repaired. The breathing air system was modified. Penetrations for pressure, electrical lines, and fiber optic lines were brought into the Senior Cave with shielding provided by lead shot housed in a step design. A camera coupled to a microscope was set up in the hot cell and linked to a video camera unit outside the cell to obtain visual records of the spent-fuel test samples. Tools were fabricated for use with the manipulators. An oven was set up in cell A and its thermal performance was verified. An acoustic device was installed to provide an audio signal when 100 ft lb of torque was reached in sealing each test vessel.

Spent fuel samples, designated ATM-103 and ATM-106, were transferred from the vaults to the hot cells. The fuel samples consisted of chunks, each 0.3 g (average chunk weight for ATM-106) and 0.3 to 1 g (range of weights for ATM-103). Three 8- to 8.5-g samples of ATM-103 and ATM-106 were prepared and placed in individual fuel holders. Magnified pictures (10X) were taken of the arrangement of the spent fuel in the holders, which were then installed in the appropriate test vessel with 5-10 mL of EJ-13 water; each vessel was sealed at 100 ft lb torque. Two of the vessels were for static vapor tests, and five were for injection tests. One of the latter is a control test and contains no spent fuel. The test vessels were placed in the preheated 90°C oven in cell A. The measured dose rate at the surface of each vessel was in the range 3-5 R/h. After two hours in the oven, the injection sequences, three at 0.075 mL/3.5 d and two at 0.75 mL/3.5 d, were initiated.

The leachate in the test vessels will be sampled at staggered intervals of two to six months. The tests will continue until steady-state conditions are achieved for element concentrations in the leachate.

Fig. 8. Test Vessel

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