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Nuclear Waste Programs Semiannual Progress Report

October 1991–March 1992

by J. K. Bates, C. R. Bradley, E. C. Buck,
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Chemical Technology Division

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NUCLEAR WASTE PROGRAMS
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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 October 1991–March 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 560 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.

Irradiated leach tests were also conducted in stainless steel vessels for up to 360 days with actinide-bearing glass monoliths immersed in EJ-13 water at SA/V = 340 m⁻¹, temperature of 90°C, and dose rate of 3500 rad/h. Results showed invariant concentrations of most anions for solutions in contact with the glasses. An exception is nitrogenous species: nitrate was depleted relative to EJ-13,

whereas nitrite is significantly enriched. The solution pH trends leveled 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 vessel walls, while the remainder was concentrated in the undissolved (>50 Å particle size) fraction. Release of neptunium was dominated by the dissolved fraction (<50 Å particle size).

Static leach tests at SA/V ratios of 340 to 20,000 m⁻¹ are being conducted to assess how the SA/V ratio affects the rate and mechanism of the glass reaction. During this report period, tests were performed to assess the effect of leachant composition (deionized water or EJ-13 well water) and vessel interaction (vessel made of Teflon or stainless steel) on glass (SRL 202) reaction. Standard leach tests were performed at 90°C over 360 days. The results showed a small effect of the leachant composition on the glass reaction but no effects of the vessel. Long-term tests in the Teflon and steel vessels are still in progress.

Reaction products resulting from experimental activities in the Unsaturated Glass Testing Program are being analyzed by analytical electron microscopy (AEM). This technique employs a combination of transmission electron microscopy, X-ray energy dispersive spectroscopy, electron energy loss spectroscopy, and electron diffraction. The information obtained from the AEM studies provides important input to the modeling efforts for waste glass performance, as well as better understanding the effects of radiation, glass composition, SA/V ratio, and other factors on the glass reaction process.

Colloids formed during waste glass dissolution are being characterized by AEM analyses of 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 smectite; other phases identified include kaolinite and mica. These colloidal particles form during waste glass dissolution by either precipitation in the leachate or spallation from the reacted glass surface.

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) in water vapor atmosphere between 150 and 225°C for up to 400 days indicate that water diffusion may not be the rate-controlling reaction process for the reaction mechanism of nuclear waste glass.

Long-term tests to simulate glass performance are in progress with actinide-doped glasses. The test method involves dripping water onto a cylindrically shaped glass-metal assemblage that is suspended in an enclosed test vessel at 90°C. These tests have been ongoing for over 6 years.

In addition to glass studies, experiments are in progress to determine radionuclide release rates by exposing simulated spent fuel to repository-relevant conditions. Preparations are underway for unsaturated testing of well-characterized samples from a pressurized water reactor. During testing, EJ-13 well water will be periodically dripped on these samples at 90°C and water injection rates of 0.075 mL or 0.75 mL every 3.5 days. The reactivity of the spent fuel will be determined by measuring leachate composition and the type and extent of secondary phase formation on the fuel as a function of time (≥ 2 years).

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 the pH = 8.22 of the starting EJ-13. Analyses of filtered residues from the long-term samples indicated the presence of titanium oxides, calcium silicates, and uranium phases as colloidal materials.

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

The Unsaturated Glass Testing Program is a technology support activity performed for DOE's Office of Environmental Restoration and Waste Management (EM). This program was initiated in 1989 with the goal of evaluating factors that will likely affect glass reaction in an unsaturated environment; this evaluation is to be done before hot startup of the Defense Waste Processing Facility (DWPF) or the West Valley Demonstration Plant (WVDP). The EM Office recognizes that the following tasks must be addressed: (1) prediction of the long-term glass performance in a repository environment and (2) determination of the relationship between the release of radionuclides from a glass waste package and performance assessment of the repository. However, these tasks will not be completed until application is made for a repository license, several years after the DWPF begins production of waste for storage and disposal. The Unsaturated Glass Testing Program is being undertaken 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 that will characterize glass performance under a range of bounding conditions relevant to the potential repository, as 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

The predicted repository environment at Yucca Mountain has been described by the YMP as 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 the information regarding what is known about these conditions has not been synthesized for use within the waste glass research community. Thus, the need to perform such a critical review was identified and review is currently underway.

During the projected lifetime of an unsaturated repository, 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 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 temperature, ratio of glass surface area to solution volume (SA/V), radiation field, glass composition, and alteration phases resulting from glass hydration. Detailed critical reviews to document how each of these parameters affects waste glasses are being performed. Each review will be issued as a stand-alone document, and these documents will be integrated into a summary compendium document. The results will be used to support startup of the DWPF and WVDP.

A preliminary critical review had previously been performed in order 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 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 (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 dependencies 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 laboratory experiments.

The next parameter to undergo a detailed critical review is the glass composition. This review is in progress. Models of glass structure are being studied in order to help understand the fundamentals of how water may interact with glass. Brief reviews of models of glass dissolution are combined with this information to form a basis for critically reviewing theoretical and empirical 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 water environments) are in progress, and drafts of each report will be completed in the upcoming year.

B. Long-Term Testing of Fully Radioactive Glass

The detailed descriptions of the tests involving fully radioactive and simulated (nonradioactive) waste glasses have been given earlier.⁵ Three groups of glass compositions, designated 165/42, 131/11, and 200, are being used. The fully radioactive (R) waste glasses were made in the DWPF in-cell minimelter, and the simulated (S) glasses were made to have the same compositions as the R glasses, but with no radioisotopes. The glasses are being tested at 90°C in EJ-13 water (repository groundwater equilibrated with tuff rock) at SA/V = 340 m⁻¹ (monolith), 2000 m⁻¹ (powder), and 20,000 m⁻¹ (with glass 200 powders only). Tests have been underway for up to 560 days.

The comparison of the normalized release of B, Li, Na, and Si for all the glass compositions tested at 340 and 2000 m⁻¹ showed similar leach behavior for both R and S glasses, with differences being less than 170%. While the differences that are 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 and S).

However, the leach behavior of the 200-based composition at 20,000 m⁻¹ indicates a large difference in the long-term reactivity between R and S glasses. 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. Moreover, the pH of 200S is 12.29 at 364 days, which is 0.6 unit higher than the corresponding pH of 200R at 364 days. The 200S glass at 20,000 m⁻¹ initially has a similar leach rate as 200R, but there is a large reaction acceleration between 182 and 364 days.

The surface layers are also significantly different before and after the reaction acceleration for 200S at 20,000 m⁻¹. The surface layer before acceleration is a single-layer structure. The layer thickness grows slowly with time, being about 150-nm thick at 98 days and about 300-nm thick at

182 days. After acceleration, the surface layers increased to about 6500 nm in thickness, with two distinct regions: a crystalline region (thickness of about 2000 nm) and a large amorphous alteration region (more than 4500 nm in thickness) below the crystalline region. Several types of phases have been identified in the crystalline region. The dominant phase contained elongated prism-shaped crystals with a composition and electron diffraction pattern matching those of a clinoptilolite.^{6,7} The phases in the other region are a typical iron-rich clay; an almost pure amorphous silicon phase, which was isolated from but in close proximity to the clay phase; and a Si-Ca phase, which is a button-like mass.

The surface layer thickness of 200R glass reacted for 364 days is 150-300 nm, which is similar to that of 200S at 182 days. In addition, the composition of the surface layer in the 364-day sample of 200R is also similar to the layer composition of 200S before acceleration.

The accelerated glass reaction for 200S can 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 acceleration) and 200R (up to 560 days) decreased with time, while the leach rate of 200S (during acceleration) greatly increased with time when the leachate had a pH value of higher than 12.0. The leachate pH is known to be one of the dominant effects on nuclear waste glass reaction.^{8,9} The leach rate for 200R at 20,000 m⁻¹ is always lower than the corresponding 200S, and the corresponding leachate pH for 200R is also always lower than that of 200S. The 200S glass leachates had pH values of 11.82 ± 0.05 at 15, 56, 98 and 182 days, while the 200R had pH values of 11.65 ± 0.13 between 15 and 560 days. The pH of 200R leachate at 560 days is still similar to its pH at the beginning of the test and showed no sign of pH excursion. This lower pH of 200R may retard the onset of increased glass reaction rate. We expect no reaction acceleration for 200R if the radiation effect of this glass can maintain the leachate pH below 11.8. The consequences of a pH effect are important because, in a repository setting, there is likely to be minimal water content with the waste glass (while the radiation field will result in a significantly lower reaction rate).

Another possible explanation for the observed rate acceleration is the formation of a suite of crystalline phases. As the glass reaction progresses, the concentration of leached elements in solution increases. The increased solution concentration lowers the glass reaction affinity,¹⁰ and the glass reaction rate decreases with time before acceleration. When the solution concentration reaches solubility limits of some secondary phases and the nucleation barrier is overcome, the formation of secondary phases reduces the solution concentration (activity) and increases the glass reaction affinity, resulting in glass reaction acceleration. Examination of the 200S surface shows a gradual increase in the formation of surface precipitates. At 98 days, there were few surface precipitates. The amount of surface precipitates increased at 182 days. The surfaces were fully covered with white precipitates at 364 days. The dominant phase of clinoptilolite in the 330, 364, and 390-day samples was rarely seen at 182 days, and this zeolite phase may be a main contributor to the acceleration.

In summary, static tests at 340 and 2000 m⁻¹ up to 560 days with three nuclear waste glass compositions have shown little difference in reactivity between radioactive and simulated nuclear waste glasses with similar chemical compositions. However, within one year, a large difference in reactivity (up to a factor of 40 in leach rates of boron) was observed between 200R and 200S when tested at SA/V of 20,000 m⁻¹. The accelerated glass reaction rate with 200S is associated with the formation of crystalline phases, such as clinoptilolite, 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 the increased reaction rate. These results suggest that radioactive glass 200R may be much more durable than 200S if the leachate pH of 200R can be kept lower than that of 200S. In modeling the performance of glass, all factors that influence glass reaction, such as the radiation-induced pH reduction in the leachate discussed above, must be accounted for to make adequate long-

term predictions. 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 m⁻¹ to determine whether the leach rate of the radioactive glass will eventually catch up to 200S. More emphasis will be placed to the analyses of the surface layers of the terminated samples, especially on the radioactive samples. Data will be generated to compare the identities and formation 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 used to further compare the reactivity of the R and S glasses and provide a data base for validation of glass performance models.

C. Effect of Radiation

1. Introduction

Radiation effects on high-level waste glasses are an important consideration for radionuclide immobilization because of the potential to influence the glass stability. Radiation may affect the long-term performance of waste glass 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 gases to form reactive radicals and new molecules. Dissolved molecular nitrogen and carbon dioxide in the water may also undergo radiolytic decomposition by a several-step recombination of the dissociation products with oxygen, water, and other associated radiolytic products to form nitrogen and carboxylic acids, respectively.¹¹⁻¹³ 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) by the absorption of 100 eV of radiation energy. Because the solubility of nitrogen in water is low, G values for nitric acid production in air-saturated water will be small, ranging from zero to less than 0.2.^{14,15} The G values for radiolytic production of nitric acid from moist air or two-phase (air/water) systems are ~2.0 for gamma, alpha, electron, and mixed neutron-gamma irradiation studies.¹⁴⁻¹⁶

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.^{11,14-16} Significant changes in the leachate pH and glass dissolution rates were not observed when glass samples were irradiated in the presence of bicarbonate groundwaters. 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.^{13,17}

The overall purpose of this effort is to determine if radiation has a significant effect on glass durability under the high SA/V conditions that are expected for an unsaturated repository site. Data will be collected in three separate studies. The first examines the effect of radiation on moist air systems, without the presence of glass (blank experiments), and on the locations and concentrations of radiolytic products. Variables to be tested include radiation type (alpha vs. gamma), temperature, dose rate, and gas/liquid volume (G/L) ratio. The second study examines glass reaction rates in unsaturated conditions as a function of glass composition 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 study examines the influence of radiation and the radiolysis environment on the stability and formation of secondary mineral phases.

2. Technical Approach

Blank experiments have been carried out in several sample configurations, with each test conducted in duplicate. Base-line blank tests under gamma irradiation were conducted in 22 mL stainless steel Parr test vessels, with enough deionized water (DIW) added to achieve a G/L ratio of 100 at 25°C. These tests will be used as a comparison between NO_3^- yields in a high SA/V environment, as is expected for an unsaturated environment, relative to results previously obtained at lower SA/V ratios (0.1 to 18).¹⁴ The experimental matrix for the gamma blank tests includes external gamma dose rates of $\sim 3 \times 10^3$ to 1×10^5 rad/h; temperatures of 25, 90, and 200°C; and G/L ratios of 10 and 100.

Also being conducted are alpha blank tests, which use 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. This foil assembly was inserted and sealed into a 1.9-L glass vessel with enough DIW added to achieve a gas/liquid ratio of 100. These tests examine the effects of the much longer-lived alpha-emitting actinide elements on altering the radiolytic environment. Results correlated with the gamma blank tests from this study and the neutron source tests of Linacre and Marsh¹⁴ provide a comparison of the effects of different types of ionizing radiation on radiolytic production formation. In the gamma and alpha blank tests, aliquots for anion, pH, and carbon determinations are removed from the solution collected in the bottom of the test vessel and obtained from a "rinse solution" produced by spraying the surfaces of the test vessels and components with DIW to collect any condensed radiolytic products.

Experiments with glass monoliths were also performed in the same type of 22 mL stainless steel test vessels used in the gamma blank tests. Samples of SRL 131, 165, and 202 glass monoliths doped with actinide and technetium were cut into $\sim 1 \times 10$ mm wafers and immersed in 2 mL of EJ-13 water at an SA/V ratio of 340 m^{-1} and a temperature of 90°C. The SRL 202 glass is similar to that projected for waste disposal, while the SRL 131 and 165 glasses represent glasses that are less and more durable, respectively, relative to the 202 glass. This batch test design allows for the highest SA/V ratio attainable, yet still permits the glass monoliths to be completely immersed in water. It also allows for the collection of enough solution aliquots to complete all desired analyses. As with the gamma blank tests, these experiments included exposure to an external gamma source of ~ 3500 rad/h. Thus, these samples were subjected to an internal alpha-beta and external gamma source. This dose rate was chosen as an upper bounding condition and is used to evaluate whether radiation affects glass reactions. Cumulative gamma exposures for the 56-day tests were $\sim 5 \times 10^6$ rad. Solution aliquots were taken from these tests to determine pH, carbon, cations, anions, and filtered size distributions of actinides. Results from these irradiated tests will be directly comparable to 340 m^{-1} nonirradiated tests from the high SA/V experiments (Sec. I.D).

3. Results and Discussion

a. Blank Tests

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

The tests run at 25°C with an alpha radiation source indicated 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 were run at 25, 90, and 200°C to measure the formation of radiolytic products as a function of temperature (dose rate of ~ 3500 rad/h, $G/L = 100$). Results indicate that NO_3 production varies inversely with temperature, with the lowest quantities being detected for the higher temperature experiments (Fig. 1). The $G(\text{NO}_3)$ 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 $G(\text{NO}_3) = 1.9$ values obtained by Linacre and Marsh in tests conducted at 80°C.¹⁴ The results indicate that NO_3 yields for the 90°C experiments are $\sim 40\%$, while the 200°C yields are $\sim 10\%$ of those that characterize the 25°C results. 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 in the repository history may mitigate against large decreases in pH resulting from radiolysis effects.

Fig. 1. Average NO_x ($\text{NO}_3 + \text{NO}_2$) Production as Function of Cumulative Exposure and Temperature in Gamma Blank Experiments. Rinse fraction represents total NO_x production for each test. Dashed lines show best fit to measurements. The 80°C line is from data of Linacre and Marsh.¹⁴

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

b. Batch Tests with Glass Monoliths

The batch tests with actinide-doped glass monoliths (SRL 202A, 165A, and 131A) examined the cumulative effects of radiolytic product formation on the alteration of the glass. Anion and cation solution analyses have been done for batch leach tests conducted with ^{99}Tc - and actinide-doped glass at 90°C and $\text{SA/V} = 340 \text{ m}^{-1}$, under an external gamma irradiation field, for time periods of up to 360 days. Results show invariant concentrations of most anions (F^- , Cl^- , SO_4^{2-} , COOH^- , and $\text{C}_2\text{O}_4^{2-}$) over time for solutions in contact with the glasses. This suggests that the presence of reacting glass in the tests does not have a major influence on the anion chemistry of the leachate. An exception to this generalization is the concentration of nitrogenous species. Nitrate is depleted relative to EJ-13, whereas nitrite is significantly enriched. The decrease in the $\text{NO}_3^-/\text{NO}_2^-$ ratio for irradiated solutions in contact with glass samples results in a $\text{NO}_3^-/\text{NO}_2^-$ ratio that is lower (0.34 ± 0.33) than the ratio for the starting EJ-13 solution (~ 165) and the ratio derived from results of gamma blank tests at 90°C (3.09 ± 2.12). The decreased $\text{NO}_3^-/\text{NO}_2^-$ ratio of irradiated solutions in the presence of glass may be attributed to the stability of the NO_2^- radical in the presence of an alkali solution buffered by the reacting glass.¹⁴ The lower H^+ activity in these buffered solutions results in decreased rates for the following two NO_2^- consumption/ NO_3^- production reactions:

The NO produced in Eq. 1 should be rapidly oxidized to NO_2 in the oxygenated conditions of the test vessels. This NO_2 will then react with water to form equivalent amounts of NO_3^- and NO_2^- , with the NO_2^- reforming to nitrous acid and repeating the cycle. Equation 2 also demonstrates that increased NO_2^- radical stability may be influenced by catalytic decomposition of radiogenic H_2O_2 by iron and manganese oxides forming on the altered glass surface.¹⁸

While the data show some scatter, pH analyses of SRL 131A and 202A samples indicate a leveling or slight decrease in pH to ~ 9 after displaying peak pH values at 56 and 180 days, respectively (Fig. 2a). These trends are interpreted to 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 present in the glass are released in concentrations greater than that necessary to neutralize the H^+ ions dissociated from radiolytic acids. In the later test intervals, a buildup of radiolytic acids in the leachate results from a decrease in the rate of ionic exchange with the glass as the reaction layer thickens and the glass reaction rate decreases. The cation solution trends indicate a decrease in the rate of Na, Li, and B release to solution after 180 days for the SRL 202A glasses (Fig. 2b to 2d). 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 providing supporting evidence for a change in the rate of the ionic exchange process.

The SRL 165A glass samples display pH values that ranged from ~ 8 to 9.5 throughout the first 360 days of the testing cycle, despite the observation that Na, Li, and B release rates decreased after 180 days of testing (Figs. 2a to 2d). Since the SRL 165A glass is more leach resistant than the 131A and 202A glasses, we had expected that the lower overall glass reaction rates would fail to offset the production of radiolytic acids in these tests, resulting in lower overall pH values. The SRL 165A glass reactions are characterized by initially low pH values, but the 360-day solution trends are indistinguishable from those of the SRL 202A glass.

Fig. 2. Solution pH and Normalized Mass Release (NL_i) for 340 m⁻¹ Batch Leach Tests at 90°C. In these tests, SRL 202A, 165A, and 131A samples were doped with 23 $\mu\text{Ci/g}$ alpha radiation source and exposed to an external gamma dose rate of ~ 3500 rad/h; SRL 202U samples (dotted line) represent average value for U-238 doped glass reactions without any external gamma exposure: (a) pH values, (b) $NL(\text{Na})$, (c) $NL(\text{Li})$, (d) $NL(\text{B})$, and (e) $NL(\text{Si})$.

Results for the reaction trends of SRL 202A gamma-irradiated and SRL 202U nonirradiated tests indicate that the former tests are characterized by slightly lower pH and Na, Li, and B release values after 180 days of reaction (Figs. 2a to 2d). These differences can be attributed to radiolytic acid formation and a resultant decrease in the solubility of silica acids in the lower pH solutions (Fig. 2e).

Alpha counting results for unfiltered, 50 Å filtered, and acid strip aliquots from the 340 m⁻¹ batch tests indicate that Am and Pu release is dominated by the acid strip component, with the <50 Å fraction being negligible for most time periods (Figs. 3a and 3b). These data indicate that most of the Am and Pu released from the glass subsequently plates out on the stainless steel vessel walls, while the remainder of the released fluid is dominated by particulates >50 Å in size. These results indicate that (1) stainless steel waste canisters may act as a barrier to Am and Pu release in a repository scenario, and (2) iron oxide particulates and colloids present in natural groundwaters may serve as carriers for actinide migration.

An accurate spectroscopic determination of the aliquot concentrations of neptunium is complicated by the relatively small ²³⁷Np peak heights and an overlap of the ²³⁷Np with the ²³⁹Pu peaks. Despite this difficulty, the neptunium release appears to be dominated by the <50 Å size fraction (Fig. 3c). Recovery of a plate-out fraction of neptunium is generally negligible, although some increase is noted in the 360-day tests. These trends indicate that neptunium release is dominated by a soluble or fine colloidal (<50 Å) suspension in these tests.

D. Relationship between High SA/V Experiments and MCC-1

1. Introduction

Static leach tests are being performed in CMT to characterize the reaction behavior of various compositions for candidate borosilicate waste glass to be employed in vitrification of high-level radioactive waste. Such tests will be used to monitor the product consistency of waste glasses generated at the DWPF and other processing facilities and may be used to qualify glass waste forms for repository disposal. Several test parameters are defined by the likely environment of the waste glass, including the temperature and groundwater composition, while other test parameters reflect constraints at the processing facility, such as the need for radioactive shielding, remote operation, and minimal sample preparation. Another important variable in static leach tests is the SA/V ratio. The preponderant effect of the SA/V ratio is dilution of the reaction products: tests at higher SA/V have less solution available to dilute components released from the glass.¹⁹ The response of a glass in a static leach test is usually monitored by measuring the release of soluble glass components into the solution. Because the solution composition is known to affect the rate of glass reaction,²⁰⁻²³ tests at different SA/V ratios will result in different glass reaction rates. Tests are in progress in CMT to assess the effects of the SA/V ratio on the mechanism and rate of the glass reaction.

Interpretation of test results may require other effects to be considered. For example, changes in the solution composition or the gas phase may occur during a static leach test due to interactions with the reaction vessel, in addition to those due the glass reaction. Most static leach tests are performed in either stainless steel vessels or in PFA (perfluoroalkoxy) Teflon vessels. Neither vessel is inert with respect to the solution composition: the steel surface may adsorb components released from the glass or may corrode to release metal ions into solution.²⁴ Teflon may release HF into solution,²⁵ which may accelerate the glass corrosion and acidify the leachate. Teflon is also pervious to carbon dioxide, which may affect the solution pH.²⁶ It is important to account for effects related to vessel interactions during leach test results to accurately measure the extent of glass reaction.

Fig. 3. Actinide Release from 340 m^{-1} Batch Leach Tests of 202A Glasses. Data presented in total nanograms released as a function of time: (a) Am release, (b) Pu release, and (c) Np release.

The objective of this work is to assess the influence of the SA/V ratio used in static leach tests performed with high-level waste glasses on the mechanism and rate of the reaction. Tests are being performed to provide insight into the effects on the glass reaction of the SA/V ratio, the glass composition (including the presence of radionuclides), the leachant composition, and the test vessel. This report will discuss the effects of the initial leachant composition and the vessel material used in the test on the extent of glass reaction.

2. Technical Approach

Static leach tests were performed using a reference glass of the DWPF, which is referred to as SRL 202, at several SA/V ratios to assess the effects of the initial leachant composition and reaction vessel material on the measured extent of reaction. Tests were performed using both monolith samples and crushed glass and followed slight modifications of the MCC-1²⁷ or PCT²⁸ protocols at SA/V ratios of 340, 2000, and 20,000 m^{-1} . Either deionized water (DIW) or EJ-13 groundwater solution, which is the reference groundwater for the Yucca Mountain repository site, was

used as the leachant, and tests were performed in either 304L stainless steel or Teflon vessels at 90°C. The Teflon vessels were carefully cleaned prior to use to preleach HF from the Teflon. Blank tests with leachant only were performed in both Teflon and steel vessels for times up to one year to monitor long-term vessel interactions. These tests were conducted as part of a larger experimental matrix designed to characterize the effects of the SA/V ratio used in a static leach test on the glass reaction.²⁹⁻³¹

Leachates from tests with crushed glass were immediately filtered upon test termination through pre-heated 0.45 μm polycarbonate filters. Aliquots of the leachates from tests with monolith samples and of the filtrates from tests with crushed glass were then analyzed for pH, anions, and cations. Aliquots of the leachates from some tests were passed through 6 nm filters, and these filtrates were analyzed for cations. The reacted glass was gently rinsed with DIW and allowed to dry at room temperature or in a 60°C oven. Reacted glass samples were analyzed using scanning electron microscopy (SEM) and analytical electron microscopy (AEM) to assess the extent and nature of the alteration due to reaction.

3. Results and Discussion

The results of tests analyzed to date are summarized elsewhere.²⁹⁻³³ Representative results are included here, which illustrate the general trends observed in tests at different SA/V ratios.

a. Blank Tests

The leachate pH values and fluoride concentrations of blank tests with DIW or EJ-13 in Teflon vessels and EJ-13 in steel vessels showed some effects of the vessel. Test solutions with DIW in Teflon became acidified relative to the initial solution pH (about 5.6), while tests with EJ-13 in Teflon or steel vessels had leachates that were more basic than the initial EJ-13 solution (which was about 8.2) at all times; the pH was slightly higher in tests with Teflon vessels. The leachant volume in the blank tests did not affect the final pH in tests with either DIW or EJ-13. The fluoride concentration of the initial EJ-13 leachant was measured to be about 2 to 3 ppm. Tests with DIW in Teflon had measurable fluoride in the leachate, about 1 ppm, at all times tested, although the level did not increase with time. Tests with EJ-13 in Teflon also had measurable fluoride levels, again the level did not appear to increase with the reaction time. Tests with EJ-13 in Teflon vessels showed the release of between 0 and 10 ppm fluoride, while no fluoride was released from the steel vessels.

Analysis of the EJ-13 leachant gave a total carbon concentration of about 20 ppm and an organic carbon concentration of about 2 ppm. The total carbon and organic carbon levels in DIW were both between 0.5 and 3 ppm at all reaction times in tests with 3 and 6 mL of leachant. The blank tests with EJ-13 solution had total carbon levels of about 30 ppm and organic carbon levels of about 10 ppm at all times. The levels were similar for tests with 3 and 6 mL of leachant and did not vary significantly with the reaction time. The leachate composition differences with respect to glass components are small for the most part and are negligible compared to the concentrations attained in tests with glass (see below).

b. Tests with Glass

The results of tests performed with DIW or EJ-13 and SRL 202 glass at common SA/V ratios can be compared to assess the effects of the leachant composition and vessel interaction on the glass reaction. Figure 4 shows the leachate pH and the Li, Na, B, and Si concentrations measured in the 0.45 μm filtrate solutions for tests at 2000 m^{-1} . The curves in the figures are drawn through the data for tests in DIW to distinguish them from the EJ-13 tests, but do not represent

Fig. 4.

Results of Tests with SRL 202 Glass at 2000 m^{-1} : (a) pH, (b) Lithium (filled circle) and Sodium (open square) Concentrations, and (c) Boron (open diamond) and Silicon (open triangle) Concentrations.

Open symbols represent tests with DIW in Teflon vessels and filled symbols tests with EJ-13 in 304L stainless steel vessels. Curve drawn through DIW data.

analytical fits to the data. At 2000 m^{-1} , the pH values of tests with EJ-13 in steel vessels are slightly lower than those with DIW in Teflon vessels through 70 days, but the pH is higher in tests with EJ-13 in steel vessels beyond 70 days. The results from tests with EJ-13 solution have been corrected for background concentrations that were measured in blank tests with EJ-13 in steel or Teflon vessels. The solution concentrations of Li and B are the same in all tests, within analytical error, regardless of the leachant or vessel used. The background-corrected concentration of sodium is also similar in tests with DIW and EJ-13. The silicon concentrations in tests with DIW are about 50 ppm higher than those in tests with EJ-13 at all times tested, which is about equal to the amount of silicon that was subtracted as the background level of the initial EJ-13 leachant.

These results show that the initial leachant composition does affect the releases of some glass components. The measured release of different glass components from the glass is related to their concentrations in the leachant: Li and B have low concentrations in the leachant, and the release from SRL 202 is the same in DIW and EJ-13. On the other hand, Na and Si have relatively high concentrations in the EJ-13 leachant, and the amounts released from the glass are lower in tests with EJ-13 than in tests with DIW. The total amount of sodium measured in solution is similar in tests with DIW and EJ-13, however. The overall glass reaction rate is the same in EJ-13 and DIW based on boron release, but greater in DIW based on silicon release. High leachant silicon levels have been reported to reduce the boron release in other experiments,³⁴ but the silicon concentration in EJ-13 does not measurably reduce the boron release in the present tests over long time periods.

The leachate pH reflects the influence of several species released from the glass. The release of alkali metals via ion-exchange reactions leads to a pH increase during glass reaction, while the released boric and silicic acids buffer the pH against excursions above about pH = 9. Carbon dioxide dissolved in the solution will decrease the pH, and degassing the solution will increase the pH. Blank tests with DIW in Teflon showed the pH to decrease from the initial value near 5.6 to as low as 4 after one year. The decrease may be due to vessel interactions to release HF. The low ionic strength of DIW makes pH measurements sensitive to CO₂ dissolution during the measurement, which will lower the pH. Blank tests with EJ-13 in Teflon vessels showed the pH to increase to about 9 after one year. The initial EJ-13 leachant had a pH of about 8.2. The pH rise may be due to outgassing of the leachant solution and a net decrease in dissolved carbonic acid. These results suggest that infusion of CO₂ into the Teflon vessels and the release of HF from the vessel did not significantly affect the final pH in EJ-13.

Conclusions were also reached by comparing the results at different SA/V ratios. Tests with glass in DIW had higher pH values than tests in EJ-13 at SA/V = 2000 m⁻¹, while tests run at SA/V = 340 m⁻¹ with EJ-13 had higher pH values than those run with DIW. This suggests that the EJ-13 solution mitigated the pH rise due to the glass reaction (particularly the ion-exchange reactions to release sodium), while the DIW had little or no buffering capacity. The reaction at SA/V = 340 m⁻¹ has apparently not progressed to the extent where the pH rise due to the glass reaction has reached the effective buffer pH of the EJ-13. Changes in the leachate chemistry due to the glass reaction dominate any changes due to vessel interaction in either Teflon or steel vessels.

The effect of the initial leachant composition on the amounts of Li, Na, B, and Si released from the glass is similar in Teflon and steel vessels. The vessel itself had little effect. The primary effects of Teflon vessels were reduced by (1) carefully cleaning the vessels before use to minimize the release of HF during the test and (2) performing the tests with the vessel in a water bath. The water bath was used to minimize the water loss due to vessel leakage. While vessels were not totally submerged in the water bath, the vapor head space above the water level in the water bath probably had a very low CO₂ partial pressure, which may have reduced the amount of CO₂ that diffused into the vessel. The steel vessels formed an air-tight seal, which prevented water loss and any infiltration of carbon dioxide.

In summary, these results show a small effect of the leachant composition on the glass reaction but no effects of the vessel. Hydrofluoric acid is released from the Teflon vessel even after thorough pre-leaching and cleaning of the vessel, but does not affect the glass reaction compared to identical tests performed in 304L stainless steel vessels. The initial leachant composition affects the releases of some glass components, such as silicon and sodium, but the release of other components that are commonly used as indicators of the extent of glass reaction, such as boron and lithium, are not affected by the leachant composition. The structure of the layer formed on the glass as a secondary phase is affected only slightly by the leachant composition.

4. Future Progress

Long-term tests in Teflon and steel vessels are still in progress. These tests will show if the long-term reaction continues at the accelerated rate seen between about 182 and 364 days. The results of tests in Teflon will also be used for comparison to the results of computer simulations being developed at Lawrence Livermore National Laboratory. Results will also be compared to those obtained in other tests being performed (Sec. I.B and C).

E. Analytical Electron Microscopy

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 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, including very small inclusions, small crystallites, colloidal size particles, and thin reaction and diffusion layers.

Self-supporting samples of this thinness are difficult to produce, and considerable effort is expended in preparing and surveying samples. In addition to this preparation work, new ideas for sample preparation are developed.³⁵

Work during this reporting period has concentrated on the analysis of reaction layers, the underlying glass, and the colloidal particles generated during these reactions of samples from the tests reported in Secs. I.B and D. Techniques to prepare samples of micelles for examination in the TEM were also developed in this reporting period.

1. Analysis of "Long-Term Testing" Glass

The "Long-Term Testing" Task (Sec. I.B) seeks to evaluate the long-term performance of fully radioactive glass and compare this performance with that of nonradioactive glasses with the same nominal composition. The test matrix is designed to allow investigation of several variables which may affect glass reaction, including SA/V·t scaling, glass composition, and inclusion of radionuclides in the glass.^{36,37} Samples have been prepared of all nonradioactive tests terminated to date in this test matrix, and preparation of radioactive samples has begun.

The alteration layer in most samples examined to date is a poorly crystallized smectite intermediate with a composition between montmorillonite and nontronite, a dioctahedral smectite. Such intermediates are common in natural samples.³⁸ Samples from long-term reactions (>100 days) give diffraction patterns 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 inconclusive. Identification of the clay phase developing on the 165 glass is based on the results from the longer term tests.

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 were investigated.³⁰ In some of these samples, a backbone structure had formed with clay crystallites growing out from both sides of the backbone. The composition above, below, and on the backbone was investigated, and no significant differences were observed.

2. Analysis of "Effects of SA/V" Glass

A detailed analysis of a 202A glass reacted in EJ-13 for 364 days at 20,000 m⁻¹ was completed for the "Effects of SA/V" Task (Sec. I.D). In summary, sections of this sample contained three clay layers with different morphologies but essentially the same composition and electron diffraction.³⁰ The different morphologies suggest different deposition environments and rates.

Within one of the layers, a large ($\sim 2 \mu\text{m}$ particles) crystalline phase was observed. The diffraction and composition of these particles suggest that this phase is clinopyroxene, which usually forms at high temperature. On short duration tests (30 days), similar phases have been observed, suggesting that these crystallites may be devitrification products.

3. Analysis of Micelles

Other groups within CMT are applying biphasic extraction techniques to problems of extraction of micelle plutonium contaminants.³⁹ These micelles, which are primarily silica, are extremely small ($\sim 50 \text{ nm}$). Questions about the morphology of the particles produced, size distributions, and the way in which plutonium is absorbed into each micelle are difficult to answer with conventional analysis techniques but might be addressed with AEM methods. Using nonradioactive samples, we have worked out a sample preparation technique that satisfactorily disperses the silica particles produced on a TEM grid.

4. Analysis of Colloids from Nuclear Waste Glass Reactions

There is increasing interest in determining whether colloids will greatly increase the release rate of radionuclides from buried nuclear waste into the environment.⁴⁰⁻⁴² An AEM study has been carried out to characterize colloidal particles produced during waste glass dissolution. Clay colloids can be readily identified by TEM, as they often produce oblique textured electron diffraction patterns (OTED) when tilted.⁴³ The most common type of colloid observed in the leachate was a smectite clay which is similar to that found in the reacted layers, although evidence suggests that these colloids are not derived from the layer. Although obtaining data on size distributions was not possible with the specimen preparation technique used, amounts of colloidal material were estimated.³⁰

From the "Long-Term Testing" Task (Sec. I.B), a limited number of leachates have been examined for colloids. Samplings of leachate have occurred at long reaction times, which has prevented the observation of trends in colloid development, except in a few cases. The leachate from 200R glass reacted at $\text{SA/V} = 340 \text{ m}^{-1}$ displayed a steady increase in complexity and amount of clay colloidal material with time. At 56 days no clay material was found. By 182 days a few crystalline clay colloids were found. These were so thin that EDS composition data were difficult to obtain. The clay was found to be a Na-Fe-K-Al silicate. The material was so crystalline at 364 days that electron diffraction information on the 00 l lines was obtained, and lattice fringe images were possible. The composition was the same as that in the colloids in the 182-day test leachate. In contrast, the leachate from 200S glass reacted at $\text{SA/V} = 20,000 \text{ m}^{-1}$ showed little evidence of colloids after 100 days of reaction.

In contrast, a representative number of leachates from the "Effects of SA/V" Task (Sec. I.D) have been examined over the test duration. Tests have involved SRL 202U glass reacted at different SA/V ratios (340, 2000, 20,000 m^{-1}). These experiments have permitted an investigation of the effect of some waste glass test parameters on colloid formation. In general, a smaller amount of colloidal material was found in tests run at $\text{SA/V} = 20,000 \text{ m}^{-1}$. For the short-term (30 days) experiments, the material was only weakly crystalline. Electron diffraction has revealed some differences in clay colloidal material with reaction time. Less long-range order was observed in the samples reacted for shorter times; the inner rings were much more diffuse. The morphology of the clay colloids was also altered between tests. As more colloidal material was present in the leachate, flocculation resulted in the c-axis spacing becoming visible. Samples reacted for longer times (>100 days) have been found to possess the most colloidal material. All tests have shown an increase in both the amount of material and the degree of crystallinity of the material with time. Glass reacted in EJ-13 groundwater appeared to have an overall increase in colloidal material.

Uranium phases were only detected in the samples reacted at $SA/V = 20,000 \text{ m}^{-1}$. Small uranium phases were located by contrast due to backscattering electrons.

The most common types of clay colloidal phases found appeared to be smectite; however, kaolinite and mica have also been observed. Other phases identified included calcite, dolomite, titanium oxide, manganese oxide, and iron oxide. The SA/V ratio has an important role in colloidal development through its effect on solution chemistry. Results, so far, indicate that colloids eventually disappear from solution by flocculation and sedimentation. However, as secondary phase formation either on the glass or within the leachate will act as sinks for ions in solution, colloids may arise at longer reaction times. This work has demonstrated that colloids are produced during waste glass dissolution, and that these will contain actinide elements. The TEM has been shown to be a useful tool for characterizing colloidal material. Further studies will examine the formation of colloids at longer reaction times (>300 days).

5. Future Work

In the future, detailed characterizations of phases found on the "Long-Term Testing" Glass and "Effects of SA/V " Glass will continue. This detailed characterization will entail identification of the secondary phases produced on the glass surface, and observation of compositional gradients within the glass caused by the reaction process.

Colloidal studies will continue with identification of the phases that make up this particulate matter and a search for those colloidal phases which bear radionuclides and elements of potential environmental impact.

F. Natural Analogues

We have developed a natural analogue approach for relating water diffusion observed in long-lived natural rhyolitic glasses to water diffusion in nuclear waste glasses.⁴⁴ The natural analogue approach relates natural glasses to glass waste forms by a detailed experimental study of reaction mechanisms. The goal of these studies is to relate the reaction mechanism in natural glasses of great age to that found in nuclear waste glasses. The approach is graphically illustrated in Fig. 5.

The first step is to develop a means of experimentally altering natural samples by the same reaction mechanism as occurs in nature. Because this is necessarily performed at accelerated rates, it is crucial to establish that the reaction mechanisms are identical. This is checked by investigating both the reaction products and the reaction kinetics. Once experimental techniques for natural samples are developed, then the nuclear waste glasses of interest are experimentally altered by the same techniques. Detailed surface characterizations and studies of the reaction kinetics for the glass waste forms then provide information about durability under conditions experienced by the natural analogue materials.

The information derived from a natural analogue study can be used to assess the long-term importance of a particular reaction process. The reaction process found in the natural analogue of great age may not be dominant in a nuclear waste glass in short-term experiments. However, an understanding of the natural analogue's reaction process can help modelers to assess when, if ever, the process may become important for a nuclear waste glass.

The other major link in the natural analogue approach for tektite and nuclear waste glass reaction has been previously discussed: the comparison between tektite alteration produced in nature and by experiment.⁴⁵ There we demonstrated that the alteration of naturally weathered tektites,

Fig. 5. Graphic Depiction of a Natural Analogue Approach

including those found at the 65-million-year old Cretaceous-Tertiary boundary, could be duplicated by reacting tektites in a water vapor atmosphere (high SA/V).

Tektites are derived from a meteoritic impact event. Tektites are strewn throughout the world: the Australasian [0.7 million years (My) old], the Ivory Coast (1 My old), the Czechoslovakian (14.8 My old), and the North American (35 My old).⁴⁶ Recent discoveries of tektites in Haiti have been dated at 65 million years old.^{47,48} Since durability for 10^5 - 10^6 years is desired for nuclear waste glasses, it is of interest to understand how these glasses have survived.

The compositional parameter that most strongly affects molecular water diffusion in rhyolitic obsidians and tektites can be quantitatively related to the initial total water content in the glass.⁴⁹ Obsidians generally contain between 0.05 and 2.0 wt% intrinsic water, while tektites contain ~0.01 to 0.1 wt%.

A large number of tektites have been found in subaerially exposed environments. For this reason, we decided to perform tektite experiments in vapor environments, as these are more representative of naturally altered tektites. This is consistent with results obtained for naturally and experimentally altered obsidians.^{50,51} Furthermore, water vapor experiments have been shown to alter nuclear waste glasses similarly to naturally altered basalt glasses.^{52,53}

With this approach, we postulated 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 have been presented.⁴⁴ These experimental results are summarized in Table 1.

Water diffusion was found to be the rate-determining process in all experiments. The reaction resulted in the formation of a birefringent hydration layer that increased in thickness as a function of the square root of time. Birefringent layer formation on tektite has not been previously reported, either under natural or experimental conditions.^{51,54,55} The temperature dependence of the reaction was quantified, resulting in an activation energy of hydration of 91 kJ/mol.⁴⁴

These experimental results were extrapolated to repository-relevant conditions for nuclear waste glass, resulting in a value of $0.01 \mu\text{m}/\text{days}^{1/2}$ at 90°C and 100% relative humidity. This value is significantly lower than the observed final or long-term rate observed for nuclear waste glass reactions.

Table 1. Hydration Tests of Indochinite Tektite at 100% Relative Humidity*

Sample No.	Temperature, °C	Duration, days	Rim Thickness, μm
225-1	225	4	1.71
225-2	225	10	2.52
225-3	225	18	3.40
225-4	225	48	4.83
200-1	200	10	1.34
200-2	200	23	2.11
200-3	200	36	2.59
200-4	200	120	4.27
175-1	175	22	1.22
175-2	175	81	2.20
175-3	175	128	2.16
150-1	150	71	0.87
150-2	150	120	1.01
150-3	150	256	1.81
150-4	150	400	2.11

*The hydration constants determined from linear regression fits to these data and their corresponding correlation coefficients, R, are: 225°C, 0.697 ($\mu\text{m}/\text{day}^{1/2}$), 0.994; 200°C, 0.390 ($\mu\text{m}/\text{day}^{1/2}$), 0.997; 175°C, 0.208 ($\mu\text{m}/\text{day}^{1/2}$), 0.981; 150°C, 0.096 ($\mu\text{m}/\text{day}^{1/2}$), 0.997.

This would seem to indicate that the water diffusion process may not be rate-controlling for waste glass alteration. However, at lower temperatures (<150°C) or under conditions in which processes such as ion exchange or dissolution are suppressed, the reaction mechanism for the nuclear waste glass may change and become dominated by water diffusion; however, these results indicate that this would not reduce the glass durability.⁴⁴ Furthermore, it seems likely that physical evidence for water diffusion in nuclear waste glasses can be obscured or altered by other competing reaction processes.

II. GLASS STUDIES FOR YUCCA MOUNTAIN PROJECT

The Yucca Mountain Project (YMP) is investigating the tuff beds of Yucca Mountain, Nevada, 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 (1) development and performance of a test to measure waste form behavior in unsaturated conditions, (2) performance of experiments to study the behavior of waste package components in an irradiated environment, (3) development of test methods to study the reaction of glass in water vapor and, subsequently, in liquid water, (4) development of static leaching tests to provide long-term release data to the glass modeling effort, and (5) detailed characterization of reacted glass surfaces.

The YMP Unsaturated Test Method (see ANL-91/26, pp. 188-189) 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 but without shielding. Since the N4 test series will be conducted with "fully" radioactive sludge-based glass, the test method will have to be modified. These tests will be performed as part of the long-term testing program (see Sec. I.B).

The N2 continuing tests (SRL 165 glass) have been completed through 316 weeks. All the batch tests have been completed, and three continuous tests and one blank test are ongoing with samplings at yearly intervals.

The N3 Unsaturated Test uses ATM-10 glass (simulated West Valley glass containing actinides plus ^{99}Tc) that was received from the Materials Characterization Center (MCC) and remelted to obtain the required form of the glass. This ongoing test was started July 6, 1987, according to the Unsaturated Test Method, and has been completed through 246 weeks.

III. UNSATURATED LEACH TESTS WITH SPENT FUEL

A. Introduction

Permanent disposal of spent fuel is possible in the repository that may be located in the volcanic tuff beds near Yucca Mountain, Nevada. During the post-containment period, the spent fuel could be exposed to water condensation since the cladding may fail. Under anticipated unsaturated conditions, spent fuel would be contacted by small amounts of water that trickle through the spent fuel container. Spent fuel leach (SFL) tests have been initiated to simulate and monitor the release of radionuclides from spent fuel under unsaturated conditions.

The reactivity of spent fuel will be determined by measuring solution composition, the type and extent of secondary phase formation, and gas evolution as a function of time. The results from these tests will be used by the waste community to (1) identify important spent fuel degradation modes and/or processes that will affect spent fuel performance and radionuclide release rates under unsaturated conditions, (2) provide data that can be used to develop and to validate models that predict the long-term behavior of spent fuel within the repository, (3) provide data which, in conjunction with thermodynamic data, can be used to identify needed speciation studies, (4) provide information regarding the distribution of radionuclides in solution, and (5) provide a technical basis for determining the source term for radionuclide release in a tuff repository. This latter information will be required for the Nuclear Regulatory Commission licensing process.

The spent fuel specimens will be two well-characterized samples, ATM-103 and ATM-106, from a pressurized water reactor (PWR). The core geometry, irradiation history, and characterization of the two fuel specimens are given elsewhere.⁵⁶⁻⁵⁷ Some of the characteristics of these two PWR fuels are shown in Table 2. They have different burnups, different fission gas releases, and different grain sizes, but both will be present as fragmented materials.

Table 2. Characteristics of Irradiated UO₂

Characteristic	ATM-103	ATM-106
Initial Density, %TD	94.4-95.6	91.7-94.0
Burnup, MW-day/kg U	30	43
Discharge Date	10/80	04/82
Fission Gas Release, %	<1	10
Grain Size, μm	>5	>10
Pellet Height, cm	1.14	1.651
Pellet Diameter, cm	0.9563	0.965
Cladding Thickness, cm	0.066	0.066

The water used in the tests will originate from well J-13 located near Yucca Mountain, whose chemistry approximates that of the repository pore fluid. This water will be equilibrated with Topopah Spring tuff. The projected composition of EJ-13 water is shown in Table 3.

In the unsaturated tests, the spent fuel is inside a Zircaloy-4 cladding tube, which rests on a Zircaloy-4 support stand. The base of the Zircaloy-4 support stand will contain a Zircaloy-4 filter (20 μm thick) to separate the spent fuel from the leach solution. This assembly will be inside a test vessel. The test vessel and its matching cap will be constructed of 304L stainless steel and will be sealed with a copper gasket. Each test will be done in an oven held at a fixed temperature (90° or 150°C).

Table 3. Composition of EJ-13 Water (pH = 8.1)

Species	Content, $\mu\text{g/mL}$	Species	Content, $\mu\text{g/mL}$
B	0.2	Al	0.6
Fe	0.0	Ca	9.1
Li	0.04	K	NA ^a
Na	50	Mg	1.0
Sr	0.04	Si	45
F	2.4	U	0.0
NO ₃ ⁻	7.6	Cl	7.2
SO ₄ ²⁻	17	NO ₂	<0.5
C (inorg)	26	HCO ₃ ⁻	135
C (org)			5.0

^a NA = not available.

B. Experimental Operation

A typical test matrix is shown in Table 4. For most tests, EJ-13 water will be periodically dripped on the spent fuel specimens at a water injection rate of 0.075 mL or 0.75 mL, each being injected every 3.5 days. (In an unsaturated test, a water injection rate of 0.075 mL/3.5 days is equivalent to a water infiltration rate of 0.5 mm/yr.) A ten-fold range is used because the available spent fuel has a high radiation field, which causes heating and potential evaporation of the dripped water. The saturated vapor tests (S3-V1 and S6-V1) will have an atmosphere of saturated water vapor, but no liquid water will be injected. The reference test, R6-1J1, will be used to measure the pressure rise in the test vessel during a test cycle and to obtain a sample of the gases present. This capacity will permit one to determine the extent to which radiolysis changes the test environment and also the composition of the gaseous products. The control test (CC-1J1) will verify that the leach solutions are not contaminated by either actinides or fission products and will account for the effect of the stainless steel vessel on the solution chemistry. The results from a test pair in which the only variable will be the fuel type (e.g., S3-1J1 and S6-1J1) should provide insight on the importance of this variable on radionuclide release and the extent of fuel alteration. The tests will be run in six-month periods until steady state is reached.

During testing, aliquots of the leach solutions will be taken at predetermined intervals to determine the rate and extent of radionuclide leaching. The total solution in each test vessel will be removed at the end of each six-month period. The vessel will then be acid-stripped, and appropriate aliquots taken to account for all leached material.

Table 4. Conditions for UO_2 Unsaturated Leach Tests

Test Number	Fuel	Water Form	Inject Rate, ^a mL
S3-1J1	ATM-103	Inject	0.075
S6-1J1	ATM-106	Inject	0.075
S3-2J1	ATM-103	Inject	0.75
S6-2J1	ATM-106	Inject	0.75
S3-V1	ATM-103	Vapor	---
S6-V1	ATM-106	Vapor	---
CC-1J1	None	Inject	0.075
R6-1J1	ATM-106	Inject	0.075

^a Injected every 3.5 days.

The solutions will be characterized as to pH, cation and anion content, elemental composition, and radionuclide speciation between dissolved and suspended material periodically and at test termination. At test termination, the spent fuel samples and/or the alteration products will also be characterized (e.g., X-ray diffraction, Auger, electron-microprobe, metallography, TEM, SEM). The nature of the alteration products formed in the tests with saturated water vapor will be compared to those in which liquid water is injected. In addition, the results will be compared with those from unsaturated tests with unirradiated UO_2 and those from saturated tests with spent fuel. The results will also be compared with the calculated results from a predictive model, designated EQ3/6.

Raw analytical data will be analyzed to determine the total mass released from the fuel matrix for fission and actinide species, the rate of individual radionuclide and actinide release, elemental concentrations in solution, water chemistry, species form, and species type (ion, colloid, etc.). Raw analytical data will include (1) the thickness of the alteration layer, (2) the elemental composition of the alteration layer, and (3) the compounds in the alteration layer.

The duration of the tests will be flexible, depending on the nature of the observed reactions, but each test will be designed as a long-term test (≥ 2 years) based on experience with unsaturated tests with unirradiated UO_2 .

C. Water as a Parameter

Two issues were considered in choosing the three water environments: (1) the amount of evaporation which would occur due to the decay heat of the spent fuel and (2) the effect of a higher water drip rate in the repository, i.e., a factor of ten higher than that associated with an infiltration of 0.5 mm/yr.

The decay heat produced by one pellet (11.6 g) of 10-yr-old ATM-106 fuel is of the order of 0.017 W and arises primarily from fission products.⁵⁸ This corresponds to a heat rate of 60 J/h (0.057 Btu/h). With this as a heat source, the temperature rise at the pellet surface was calculated for three representative heat transfer coefficients: 4.1, 6.1, and 10 J/(h·cm²·°C). The temperature rise was respectively, 2.6, 1.7, and 1°C, all sufficient to evaporate the water drops injected at the fuel surface. To establish a worse case, the minimum time required to evaporate the injected water was

calculated for each injection rate; it is 10.2 s for the 0.075 mL drops and 102 s for the 0.75 mL drops. The higher injection rate thus permits water to percolate and/or diffuse into the spent fuel. For these limiting cases, most of the water may not percolate down through the spent fuel. However, these are boundary calculations and ignore factors such as surface tension and the presence of saturated water vapor.

D. Oxygen Content - Radiolysis Effects

One concern in the tests is the oxygen content in the test vessel, since the formation of alteration products is limited by the amount of oxygen present. The UO_2 present in one ATM-106 pellet is 0.049 mol, so that the minimum oxygen needed to convert 1% of the UO_2 to U_2O_5 is 1.25×10^{-4} mol.

Since the test vessels will be sealed, the maximum amount of oxygen present will be the sum of the amount originally in the test vessel plus that introduced during water injection and/or vessel opening for sampling. The test vessel volume when empty is ~60 mL; thus, the maximum amount of oxygen present at room temperature in an air environment will be 5×10^{-4} mol. As the total amount of water injected into the vessel increases, the vessel free volume will decrease, and since the vessel will be vented, the total oxygen content will decrease. The amount of oxygen introduced each 3.5 days during an injection is 7×10^{-6} mol (which is the amount in 500 μL of air) and will not appreciably increase the total oxygen content.

The effect of radiolysis of water, liquid and vapor, within the test vessel was considered, specifically its effect on the oxygen content. The radiolysis products from water will be hydrogen and peroxide. However, the G value for water varies not only due to the form of the water but also the form of the radiation. For gamma radiation, the $G(\text{H}_2)$ is 0.43 for liquid water⁵⁹ and 0.02 for vapor.⁶⁰ For alpha radiation, the $G(\text{H}_2)$ is 2 for liquid water⁶¹ and 5.9 for vapor. If one considers the gamma radiation field and the alpha radiation field of 10-year-old fuel, the alpha field is ten times less than the gamma field.

The maximum amount of hydrogen produced from radiolysis of liquid water by gamma irradiation in these tests will be 7.5×10^{-10} mol/s or 6.5×10^{-5} mol/day (because that from vapor will be twenty times less, it is ignored). Since the maximum amount of oxygen in the vessel is 5×10^{-4} mol, the introduction of significant amounts of hydrogen due to water radiolysis is an issue of concern. In 30 days if recombination does not occur, the hydrogen content could be 2×10^{-3} mol, which could result in a lower oxygen potential at the fuel surface.

The effect of the radiation field on the nitrogen atmosphere was considered. The radiolysis product will be nitrate, NO_3 , a species which incorporates oxygen and which can decrease the pH of water. Oxygen depletion could result, but this could not be quantified since either the oxygen atmosphere or by-products from water radiolysis could be the oxygen source. If the pH of the solution and/or that at the fuel surface decreases, the speciation of ions in solution will change, as will the alteration products formed.

Other materials in the test vessel could react with the available oxygen, the Zircaloy-4 test stand, and the inner wall of the stainless steel vessel. To evaluate the amount of oxygen which might react with these surfaces, this amount was estimated to be 0.24 mol for Zircaloy-4 and ~0.29 mol for a stainless steel layer that is 0.13-cm thick. If 0.01% of these surfaces reacted with oxygen, one would use 6×10^{-5} mol of oxygen.

If one considers the oxygen content in the test vessel, the effects of radiolysis, oxidation of vessel surfaces, and the requirements of stoichiometric oxidation of UO_2 , tests done in a static atmosphere may be conducted under oxygen-deficient conditions, even though the test vessel will be opened periodically for solution sampling.

IV. TESTS WITH UNIRRADIATED UO_2

Leachate samples have been collected for the 5.5-to-6.8 year interval unsaturated drip tests (PMP8U series) with UO_2 samples supported by Teflon stands. These tests are being conducted to determine the feasibility of using the unsaturated test method with unirradiated UO_2 samples and are intended to act as pilot tests for unsaturated spent fuel studies. During the course of testing, the surfaces of all four samples have displayed a well-developed alteration profile, where the uraninite pellets are progressively altered first to uranyl oxide hydrates, followed by uranyl silicates, and finally to alkali and alkaline earth uranyl silicates. This alteration sequence is identical to that observed in oxidized zones of natural uranium deposits. Thus, these experimental investigations correlate with those of natural deposits.

Aliquots from the leachates were collected for determination of pH and content of carbon, anions, and cations (including uranium). The pH values for all tests were fairly consistent, with a mean value and standard deviation of 7.0 ± 0.2 . These values are similar to those that have characterized the leachates over the last four years and are lower than the $\text{pH} = 8.22$ value of the starting EJ-13 injectant. Carbon analyses indicated that trends observed during earlier test intervals are continuing. Average total carbon and inorganic carbon concentrations have decreased to 16.2 ± 3.6 and 4.8 ± 1.7 ppm, respectively. Organic carbon concentrations increased rapidly during the first four years of testing, but have since decreased to 11.4 ± 2.9 ppm.

Solution results for anions and cations have yet to be received. Holey-carbon TEM analyses of the filtered leachates have indicated the presence of titanium oxides, calcium silicates, and uranium phases as colloidal materials, while dynamic light scattering analyses have identified average particulates from the four tests that range in size from 0.10 to 0.65 μm .

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