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THE REACTION OF SYNTHETIC NUCLEAR WASTE GLASS IN STEAM AND HYDROTHERMAL SOLUTION

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ABSTRACT

Glass monoliths of the WVCM 44, WVCM 50, SRL 165, and SRL 202 compositions were reacted in steam and in hydrothermal liquid at 200°C. The glass reaction resulted in the formation of leached surface layers in both environments. The reaction in steam proceeds at a very low rate until precipitates form, after which the glass reaction proceeds at a greater rate. Precipitates were formed on all glass types reacted in steam. The assemblage of phases formed was unique to each glass type, but several precipitates were common to all glasses, including analcime, gyrolite, and weeksite. Reaction in steam occurs in a thin layer of condensed water which becomes saturated with respect to the observed phases after only a few days of reaction. The reaction in steam is accelerated relative to reaction in hydrothermal liquid in the sense that secondary phases form after a shorter reaction time, that is, after less glass has reacted, because of the smaller effective leachant volume present in the steam environment. A knowledge of the secondary phases which form and their influence on the glass reaction rate is crucial to the modeling effort of the repository program.

INTRODUCTION

The U.S. Department of Energy is studying the feasibility of locating a repository for the isolation of high-level nuclear waste and spent reactor fuel in the volcanic tuff beds of Yucca Mountain, Nevada. Experiments are being performed in many laboratories to project the behavior of various waste forms in the tuff environment over the thousands of years the waste must be isolated from the biosphere. The primary means of nuclide release will be through the ingress of groundwater and subsequent reaction to free and transport radionuclides from the waste containers. The tuff geology being studied by the Yucca Mountain Project (YMP) is unique among sites previously studied in that it is hydrologically unsaturated [1]. The thermal load of the emplaced waste will ensure that liquid water will not contact the waste throughout the 300/1,000-year containment period. During this time, only water vapor and small amounts of pore-trapped water will exist near the waste. At longer times, the repository will cool sufficiently that small amounts of liquid water may accumulate.

Since leaching from the waste is a major means of nuclide release and liquid water is required to transport released nuclides away from the waste form, most laboratory experiments are performed with large volumes of water relative to the glass surface area. The glasses are found to degrade at a high rate initially but the rate decreases as the solution becomes more concentrated until a low "final rate" is reached [2]. The initial and final rates have been used to model the reaction of several waste glass compositions.

A credible scenario of the repository environment permits small volumes of liquid water to contact the waste for long periods of time, such as water condensed from the vapor phase. Reaction between the waste glass and this water may lead to highly concentrated solutions. Because of the long reaction times required to reach the "final rate" of glass reaction in typical leaching experiments, little is known regarding the long-term behavior of the glass in concentrated solutions. Experiments performed at low glass surface/leachant volume (SA/V) ratios and the models they support

may not accurately simulate a system of high leachate concentrations. In order to project the results of short-term laboratory experiments to long times relevant to the repository, a thorough understanding of glass corrosion under such conditions is necessary.

By increasing the glass surface area/leachant volume ratio, the amount of glass that must react to attain high solution concentrations decreases. We describe here reactions performed in a steam environment wherein very high SA/V ratios are attained. These experiments permit direct testing of the glass corrosion in highly concentrated leachates and are equivalent to extremely long static leach tests. The reaction occurs in a thin film of condensed water which becomes saturated after very little glass reacts and so the "final rate" of glass reaction may be reached within a few days. The experiments described here are repository relevant as they do not involve large volumes of water. Similar experiments may be performed under varying degrees of vapor saturation although reaction in saturated steam proceeds at a greater rate. Because water is a reactant as well as a solvent, sufficient water must be present to allow the reaction to proceed. The high reaction temperature is relevant to times shortly after emplacement but more importantly allows the reaction to proceed to a measurable extent within a short period of time. Other experiments are being performed at lower temperatures to study the accelerating influence of the temperature on the reaction in steam for extrapolation to lower temperature relevant to the long-term repository environments. Several glass compositions have been reacted in saturated and unsaturated vapor environments to better understand the behavior of waste glass in highly concentrated leachate solutions. Some results of unsaturated vapor experiments are presented elsewhere in this symposium [3]. The experimental technique for reactions performed in saturated steam and the methods of analysis are discussed below, and the results of experiments performed using several different glasses are presented.

EXPERIMENTAL

Experiments were performed using SRL 165 black frit and SRL 202 frit doped with Cs, Sr, and U, referred to as SRL 165U and SRL 202U, respectively, and two glasses which simulate the waste glass to be produced by the West Valley ceramic melter, WVCM 44 and WVCM 50. The glass compositions are given in Table I. The SRL 202U glass is similar to that being characterized by the Westinghouse Savannah River Company and the WVCM 50 glass is similar to that being characterized by the West Valley Demonstration Plant for waste disposal. Other glass compositions have been reacted in steam to better understand the reaction mechanism, and not all glasses studied are being considered for waste disposal in the repository. Samples are cut into discs about 1.1 cm in diameter and 1.5 mm thick and have geometric surface areas of about 2 cm^2. The faces of the disks were ground to a 600-grit finish in these experiments.

Experiments are performed by sealing a small amount of water and two glass samples in a small reaction bomb. Samples are suspended from a steel rod by Teflon™ thread and 0.25 g of deionized water is added to the vessel. About 0.15 g of water is required to saturate the gas phase at 200°C and about 0.05 g of water may condense on each of the two samples in the vessel without dripping off. The samples are preheated to about 200°C prior to vessel assembly to reduce the amount of thermal condensation on the sample which would otherwise remain the coolest available surface. Vessels are sealed using a copper gasket and a compression fitting and placed in an oven. At the conclusion of an experiment, the vessel is removed from the oven and the vessel bottom is cooled in a water bath to recondense the water vapor inside the vessel. The samples are then removed from the vessel and allowed to air dry, the water remaining in the vessel is weighed, and the pH measured. High pH values (near 10) usually indicate water has dripped from the sample during the reaction. Because this

TABLE I
Glass Compositions as Analyzed at ANL

	WVCM 44[a]	WVCM 50[a]	SRL 165U[b]	SRL 202U[b]
Al_2O_3	6.14	9.86	4.08	4.76
B_2O_3	8.42	12.27	6.76	8.06
BaO	0.05	0.19	0.06	-[c]
CaO	0.99	0.82	1.62	0.79
CeO	0.06	0.70	<0.05	-
Cr_2O_3	0.03	0.14	<0.01	-
Cs_2O	0.07	0.07	0.07	0.07
Fe_2O_3	11.40	11.93	11.74	12.05
K_2O	3.63	1.60	-	3.21
Li_2O	2.80	2.22	4.18	4.69
MgO	1.38	0.79	0.70	1.47
MnO_2	1.29	1.21	2.79	3.47
Na_2O	9.10	9.79	10.85	6.75
NiO	0.42	0.30	0.85	1.03
P_2O_5	2.20	2.47	0.02	-
SiO_2	45.80	39.60	52.86	51.22
SrO	-	0.02	0.11[d]	0.13[d]
ThO_2	3.30	3.52	-	-
TiO_2	0.88	0.82	0.14	1.32
UO_2	0.70	0.61	0.92[d]	1.08[d]
ZrO_2	0.29	0.39	0.66	-
TOTAL	98.95	99.32	98.47	100.12

[a]Analyzed at CUA.
[b]Analyzed at ANL.
[c]Not determined or below detection limit.
[d]Values are as-doped concentrations.

removes leached components from the leachate and so changes the leachate chemistry and reduces the extent of precipitate formation, tests with high pH values are considered anomalous.

RESULTS AND DISCUSSION

Hydration results in the alteration of the glass in the surface region due to selective leaching. Some samples are cross-sectioned and the depth of the altered region measured using an SEM; the depth is used as a measure of the extent of reaction. Reacted samples usually contain precipitates formed from components leached from the glass. The samples are analyzed using an SEM with associated EDS and WDS to compositionally analyze the precipitates. When possible, precipitates are removed and structurally analyzed using x-ray diffraction (XRD).

The alteration depths produced in experiments performed in saturated steam at 200°C with SRL 165U, SRL 202U, WVCM 44, and WVCM 50 glasses are plotted vs. the reaction time in Figs. 1a-d. Symbols are plotted at representative depths and the error bars show the range measured on a given sample. Although there is considerable scatter in the results for some glasses, a common trend of increasing alteration depths with reaction time is shown for all glasses. All glasses show an increase in depth with time. The SRL 165U results have a near $t^{1/2}$ dependence, in agreement with previous experiments in saturated steam [4]. Both WVCM glasses and

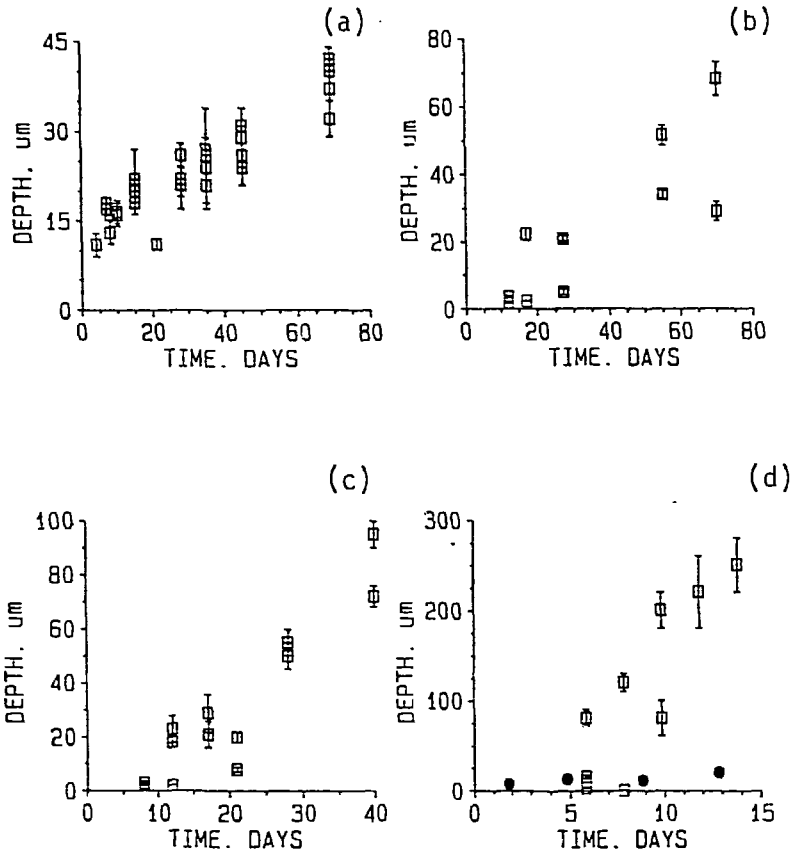

Figure 1. Measured Layer Thickness as a Function of Reaction Time for (a) SRL 165U, (b) SRL 202U, (c) WVCM 44, and (d) WVCM 50 Glass at 200°C in Steam (□) or in Hydrothermal Solution (●)

SRL 202U glass show little reaction for the first few days (points on X-axis not shown for clarity) and then react at a single high rate over the reaction times tested. This behavior is due to the limited amount of water available to the reaction.

The amount of water available for reaction in the steam environment is restricted to that which condenses on the glass surface. Several monolayers of water are known to condense on clean glass surfaces [5] under saturated vapor conditions. We have measured the sorption isotherm of water on several simulated waste glasses, including WVCM 50 and SRL 165U, at room temperature and found that between 5 and 10 monolayers typically sorb at high relative humidities [6]. Assuming a monolayer thickness near 0.3 nm [7,8], this results in a water layer about 3 nm thick and an SA/V ratio near 3E8 m^{-1} for an initial coverage of 10 monolayers. Reaction to release alkali from the glass will increase the hydroscopicity of the surface film and so more water will condense as the vapor pressure of the film decreases. Considering the limit where all available water except that required to maintain saturated vapor is condensed on the sample, an SA/V ratio of about 4000 m^{-1} may be achieved in these experiments (2 cm^2/0.05 mL on each sample).

Also shown in Fig. 1d are results of hydrothermal experiments performed with WVCM 50 glass in deionized water. These experiments were performed using SA/V ratios of about 10 m^{-1}, a factor of about 400 less

than the ratio of the hydrothermal experiments. These results are included to demonstrate that the reaction of some glasses may proceed at a rate much greater in steam than in hydrothermal liquid at lower SA/V ratios. Other experiments have shown the reaction to proceed at a greater rate in hydrothermal liquid [4]. Although the reaction paths are probably the same, the amount of glass reacted and the "progress of reaction" is different in the two environments (steam or hydrothermal liquid). Species are initially released into solution in both environments. Saturation of the leachate is reached after very little glass has reacted in the steam environment due to the very small solution volume available. As the solution becomes more concentrated, the glass reaction rate slows as the "final rate" is approached. Saturation is reached very early in the steam environment and the reaction proceeds at a low rate for about three to ten days for WVCM 50, WVCM 44, and SRL 202U. SRL 165U does not show the initial low rate of reaction. Saturation of the leachate is not reached during the hydrothermal experiments shown in Fig. 1b, and no precipitates are seen on the sample surfaces.

The reaction in the highly concentrated solution present in the steam environment can progress only if precipitates form to reduce the ion concentrations in the solution. If precipitates cannot form due to unfavorable nucleation kinetics or an improper solution chemistry, the reaction can only proceed at the very low "final rate." This has been observed in the steam hydration of PNL 76-68 glasses which have only a trace amount of aluminum. The inability to form analcime ($NaAlSi_2O_6$) results in the glass reacting at an immeasurably low "final rate" [4]. The identity of the precipitates which do form may influence the observed rate of reaction. For example, in the steam hydration of SRL 131 glass, the reaction rate increases with the formation of tobermorite [9]. Only two rates are seen in Figs. 1b-d, the low rate occurring prior to precipitate formation when the leachates are near saturation (5-10 days for the glasses in Fig. 1b,d), and the high rates which occur after the formation of precipitates. The observed rate depends on the glass and leachate compositions, the latter is influenced by the precipitates which form. Figure 2 shows a photomicrograph of a cross-sectioned WVCM 44 sample. The altered region can be clearly seen adjacent to the bulk glass and several precipitates are seen clustered at the corner of the sample.

Table II lists the precipitates formed on the four glass types. Precipitates were identified by x-ray fluorescence analysis (EDS) in the SEM and by x-ray diffraction analysis of precipitates removed from reacted samples. No precipitates were observed on the surfaces of samples reacted in hydrothermal solution. Analcime is usually the first precipitate formed on all glasses and is the primary sink for released sodium. Potassium is contained by both orthoclase and an unidentified zeolite. Gyrolite is the initial calcium-containing precipitate formed on all glasses though small amounts of tobermorite may form on some SRL 165U and SRL 202U glasses at long reaction times. Tobermorite was a major calcium-containing phase on some long-term samples in previous experiments with SRL 211 and SRL 131 glass [9]. Both WVCM compositions contain phosphorus which forms Li_3PO_4 and hydroxy-apatite precipitates on these glasses. The sodium analog of weeksite is the only uranium phase found on all glasses reacted to date. Potassium-containing glasses show partial substitution of sodium in the weeksite formed. A photomicrograph of some precipitates formed on SRL 202U glass reacted in saturated steam at 200°C is shown in Fig. 3. Note that the different precipitates have distinct morphologies which simplify identification, and that they often nucleate in close proximity to other precipitates. A detailed description of the precipitates formed will be presented elsewhere.

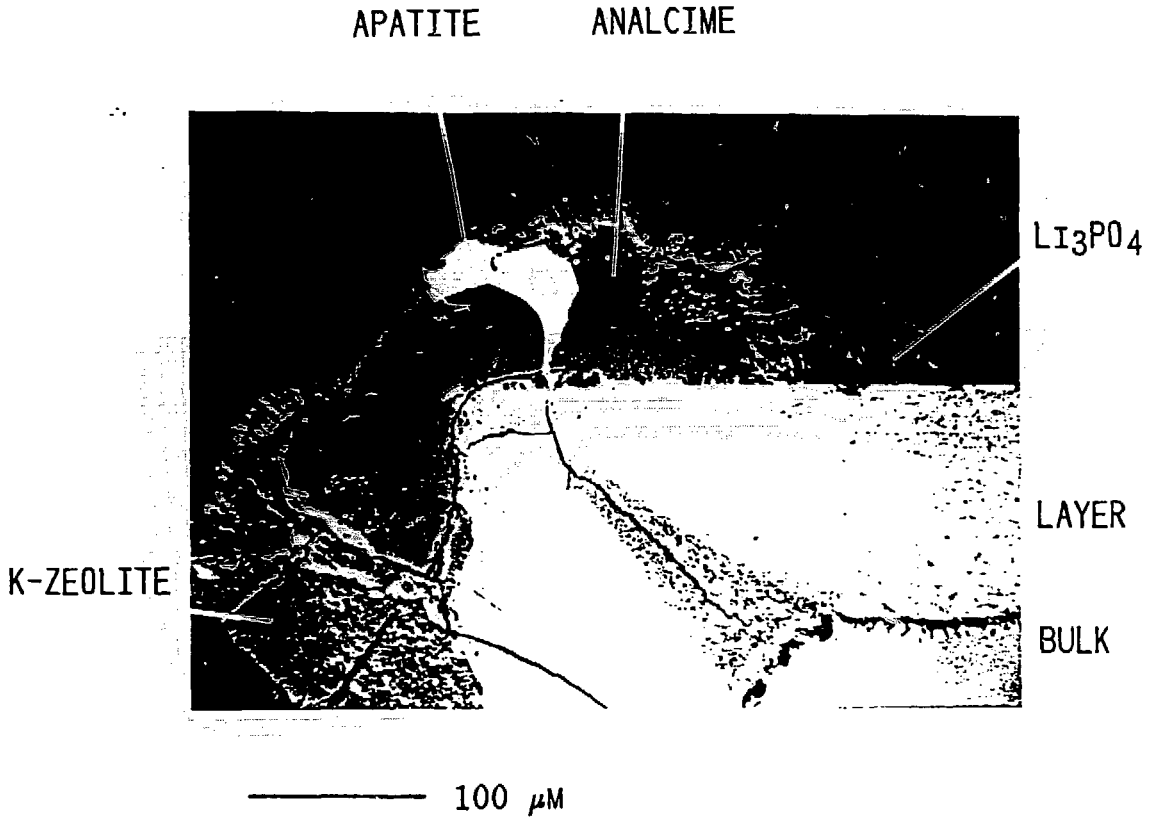

Figure 2. Photomicrograph of Cross-Sectioned WVCM 44 Glass Reacted 40 Days in Saturated Steam at 200°C Showing the Altered Layer and Several Precipitates. The phase labeled "k-zeolite" has not yet been identified.

TABLE II
Precipitates Which Form on Various Simulated Nuclear Waste Glasses

Precipitates		Glass			
		WVCM 44	WVCM 50	SRL 165U	SRL 202U
Analcime	$[NaAlSi_2O_6 \cdot H_2O]$	√	√	√	√
Gyrolite	$[Ca_4(Si_6O_{16})(OH)_2 \cdot 3H_2O]$	√	√	√	√
Li_3PO_4		√	√		
Orthoclase	$[KAlSi_3O_8]$	√	√		√
OH-Apatite	$[Ca_5(PO_4)_3OH]$	√	√		
Tobermorite	$[Ca_5(OH)_2Si_6O_{16} \cdot 4H_2O]$			?	?
Weeksite	$[K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O]$	√	√	√*	√

√ - found in abundance on most reacted samples.

? - found in scarcity on one or two samples.

*Sodium analog $[Na_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O]$.

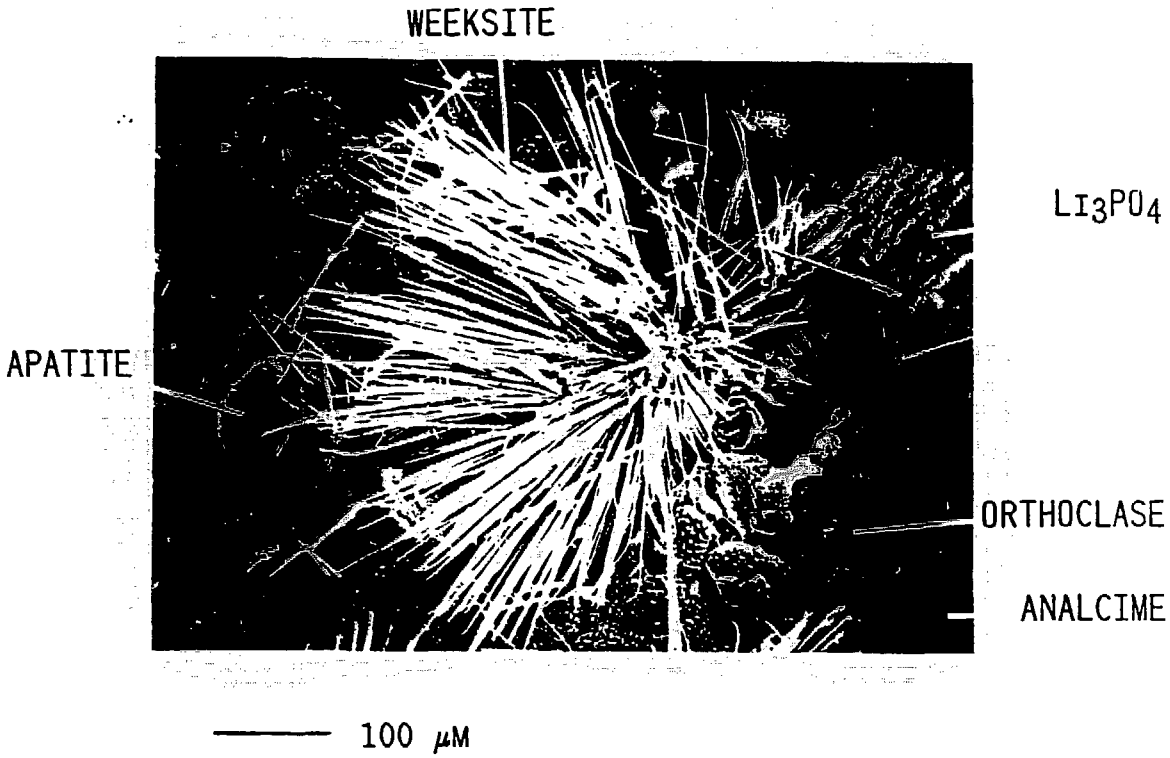

Figure 3. Photomicrograph of SRL 202U Glass Reacted in Saturated Water Vapor at 200°C. The secondary phases formed during the reaction are identified in the micrograph.

It is possible that the phases found to form in these short-term experiments are not stable over long times. Other phases may evolve after longer reaction times. The reaction temperature may also influence the assemblage of secondary phases formed. Other experiments are in progress at lower temperatures that will more clearly define the stability range of these secondary phases and their effects on the reaction rates of different glasses. While the leachate solutions in the steam experiments are not currently analyzed, identification of the precipitates formed provides valuable information to modeling efforts. The phases identified in this work are being compared to those predicted using EQ3/6 modeling at LLNL, and the results will be presented elsewhere.

CONCLUSIONS

Hydration reactions have been performed in a steam environment at elevated temperatures using four synthetic nuclear waste glasses. The amount of glass reacted in steam may be greater for some glasses than that reacted in a hydrothermal liquid environment as evidenced by elemental depletion depths. This is interpreted to be due to the large difference in the SA/V ratio. Saturation of the very small leachate volume in the steam reactions initially quenches the reaction, but the formation of precipitates allows the reaction to proceed at a greater rate. Which precipitates form depends on the glass composition and may influence the rate of glass reaction. These results show that the "final rate" obtained in hydrothermal experiments due to leachate saturation does not accurately describe the long-term behavior of waste glasses because it does not account for the influence of precipitate formation on the glass reaction rate.

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