

VAPOR HYDRATION AND SUBSEQUENT LEACHING OF
TRANSURANIC-CONTAINING SRL AND WV GLASSES

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VAPOR HYDRATION AND SUBSEQUENT LEACHING OF TRANSURANIC-CONTAINING SRL AND WV GLASSES

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Prior to contact by liquid water and subsequent leaching, high-level nuclear waste glass subject to disposal in the unsaturated environment at Yucca Mountain, Nevada, will be altered through contact with humid air. Conditions could range from temperatures as high as 200°C to ambient repository temperature after cooling and relative humidities up to 100% depending on the air flow and heat transport dynamics of the waste package and near field environments. However, under any potential set of temperature/humidity conditions, the glass will undergo alteration via well-established vapor phase hydration processes [1,2,3]. In the present paper, the results of a set of parametric experiments are described, whereby vapor phase hydrated glasses were subjected to leaching under static conditions. The purpose of the experiments was to 1) compare the leaching of vapor phase altered glass to that of fresh glass, 2) to develop techniques for determining the radionuclide content of secondary phases that formed during the hydration reaction, and 3) to provide a basis for performing long-term saturated and unsaturated testing of vapor hydrated glass.

The glasses studied were a SRL black frit based glass that had been doped with the transuranic elements Np, Pu, and Am (SRL glass) and ATM-10 glass (WV glass) that contained the radioactive elements U, Th, Np, Pu, Am, and Tc. The glasses were vapor hydrated at temperatures between 90° and

200°C. This range of temperatures was used to investigate reactive kinetics and the stability of secondary phases because the potential exists in the repository for waste form/humid air contact at temperatures above 90°C, and because such conditions also can be used to accelerate the hydration process in a way that does not alter the mechanism of hydration. The glasses were hydrated as pairs (one SRL and one WV glass per hydration vessel) in batch experiments that extended for a maximum time period of 180 days. In this way glasses with varying degrees of hydration were produced. The vapor hydration matrix is shown in Table 1.

Table 1. Conditions Under Which Glasses Were Vapor Phase Hydrated

Test #	Glass Type	Temp °C	Time (days)	Estimated Reaction (um) (SRL/WV)
H-161	SRL	200	10	12/20
	WV			
H-162	SRL	200	16	17/25
	WV			
H-163	SRL	200	22	22/15
	WV			
H-164 ^a	SRL	200	44	35/70
	WV			
H-165	SRL	150	30	<1/<1 ^b
	WV			
H-166	SRL	150	80	<1/<1 ^b
	WV			
H-167	SRL	150	98	<1/<1 ^b
	WV			
H-168	SRL	150	143	<1/<1 ^b
	WV			
H-169	SRL	90	37	<1/<1
	WV			
H-170	SRL	90	101	<1/<1
	WV			
H-171	SRL	90	180	<1/<1
	WV			

^a Their samples were not leached but were saved to determine the actinide content of the secondary phases.

^b Hydration inhibited by lack of precipitate formation.

Vapor hydration of glass results in penetration of water into the glass, thereby transforming the glass surface into a hydrated reaction zone of measureable thickness; and in the formation of secondary phases on the glass surface. The extent of the reaction can be determined by establishing a relationship between the reaction time and reaction thickness at a given temperature, and/or by correlating the surface secondary phase formation with layer thickness. In the present experiments both methods were used to estimate the extent of hydration in the vapor hydrated glasses.

The relationship between reaction zone thickness and reaction time for both glasses reacted at 200°C is shown in Figs. 1a,b. Here it is shown that although there is scatter in the data, a general trend exists in that the thickness of the reaction zone increases with time. The cause for the scatter in the data is that the reaction progress is promoted by the formation of secondary phases on the glass surface, and that the onset of nucleation of these phases introduces a degree of nonreproductability to the reaction. The appearance of glass surfaces that have been reacted at 200°C are shown in Figs. 2a, b. The identification of the secondary phases is also shown in Fig. 2. The estimated extent of vapor hydration for the samples that were subsequently leached is given in Table 1. The samples that reacted at 150° and 90°C did not exhibit the same secondary phase formation and extent of reaction because the reaction periods were not long enough.

All of the vapor hydrated samples except for those from the 44 day/200°C hydration, were leached for 28 days at 90°C. The leaching

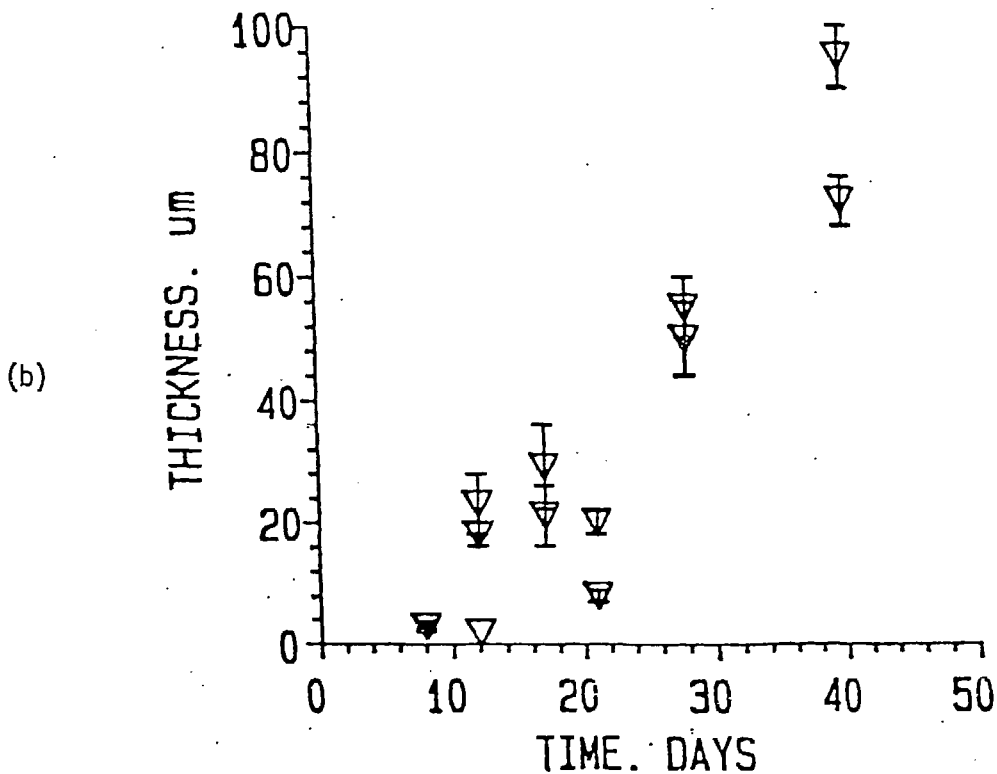
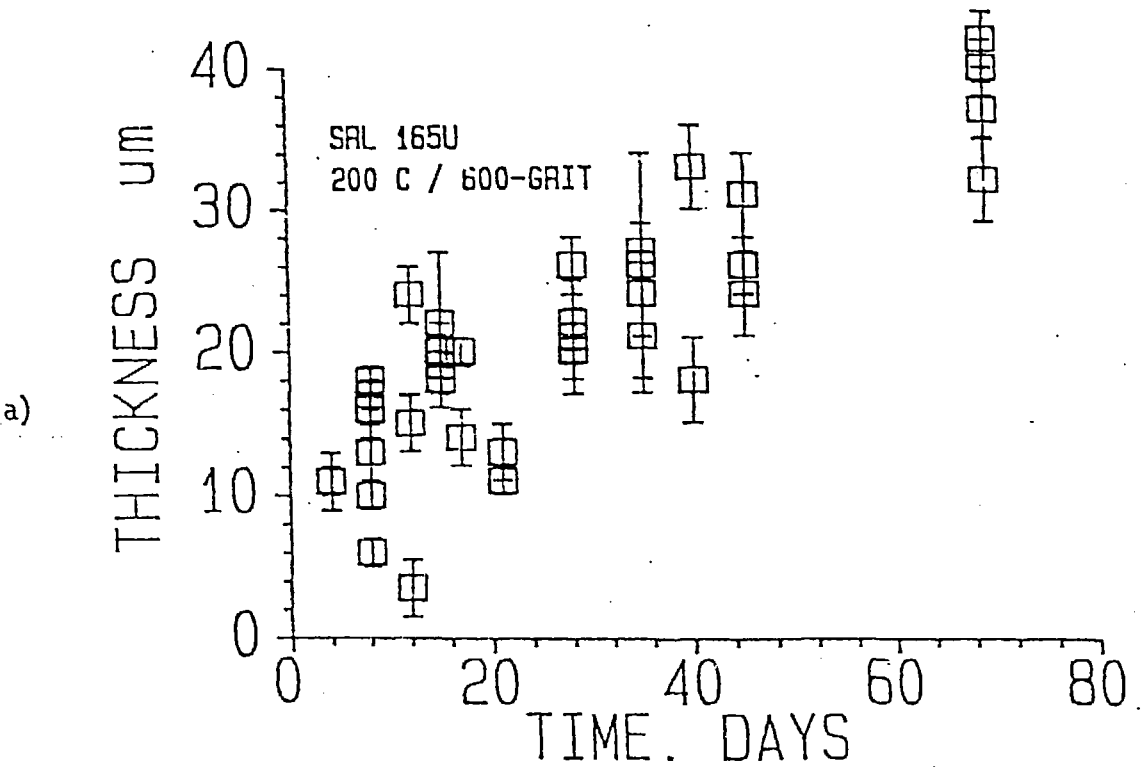


Fig. 1 The relationship between reaction zone thickness and reaction time for (a) SRL and (b) WV glasses reacted at 200°C.

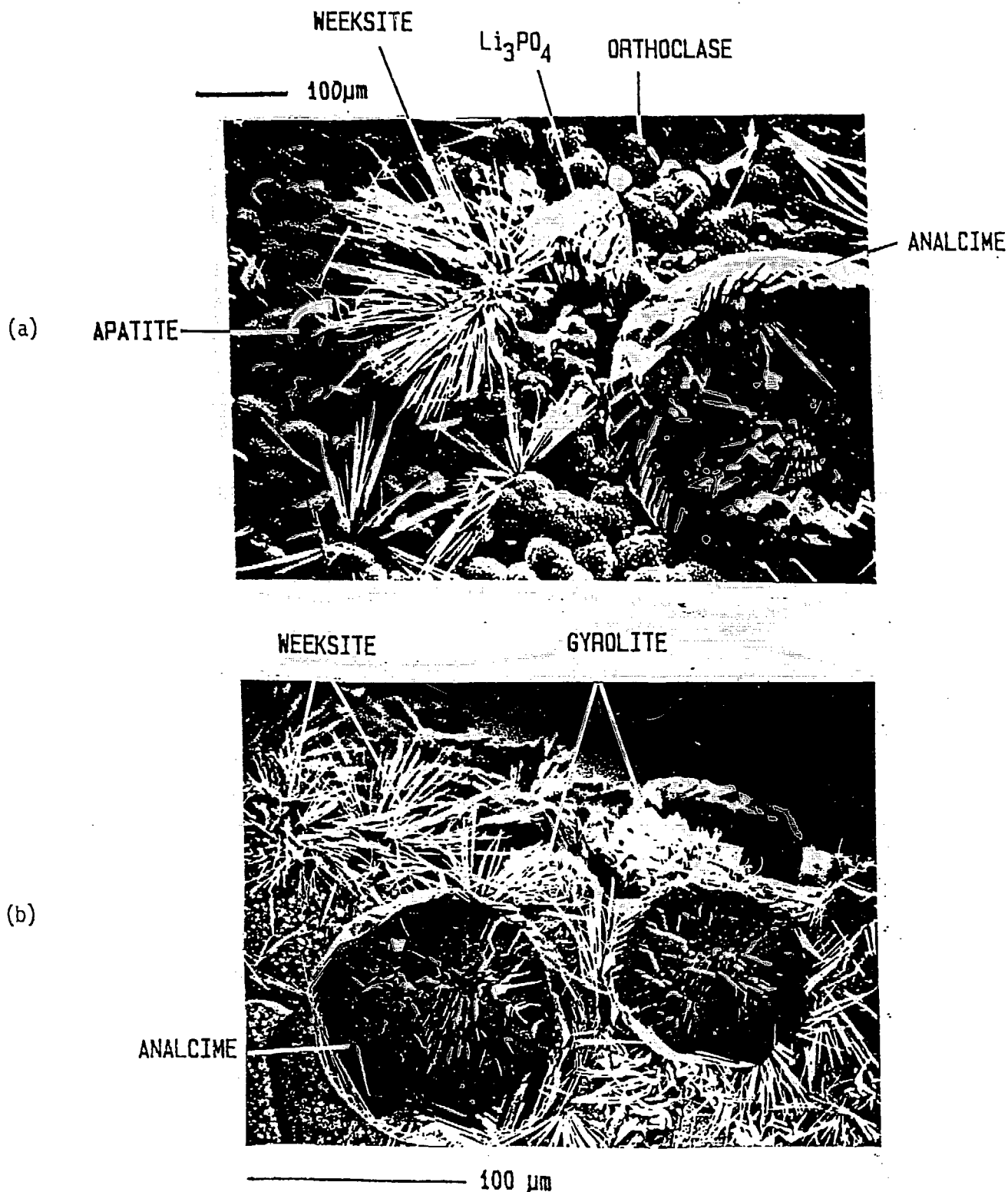


Fig. 2 Photomicrographs of (a) SRL and (b) WV glasses reacted in saturated water vapor at 200°C. The secondary phases formed during the reaction are identified in the micrograph.

conditions were chosen to generate results that would be comparable with data obtained previously on non-hydrated glasses of the same compositions. The SRL glass was leached using equilibrated EJ-13 water with a SA/V ratio of $\sim 0.3 \text{ cm}^{-1}$, while the WV glass was reacted using deionized water with a SA/V of $\sim 0.1 \text{ cm}^{-1}$.

At the termination of the tests the solutions were analyzed for pH, carbon, anion, cation and radionuclide content. The transuranic release was measured in the unfiltered solutions, solutions filtered through an 18 \AA filter, and an acid wash of the vessel and other metal components. Examination of the leachate upon opening the vessels indicated there were solids on the vessel bottom of the samples that had the greatest extent of pre-hydration (the 200°C samples). For the SRL glass, the solids ranged up to mm size and had a rust colored appearance. For the WV glass, the solids were of a finer nature and had a tan color. There appeared to be more solids produced in the SRL samples than the WV samples, and the amount of solids increased with the extent of hydration.

The same trend is observed in the pH and normalized weight loss measurements shown in Table 2. Those samples with the greater extent of pre-hydration had higher pH values and a larger $(\text{NL})_{\text{wt}}$. For those samples pre-hydrated to a lesser extent (90 and 150°C), the amount of reaction was similar to that of the fresh glass. The amount of transuranic release found in the unfiltered SRL leachates also shows an increase of Np($10x$), Pu($300x$), and Am($300-500x$) compared to fresh glass. For WV glass, the increases are Np($3x$), Pu($10x$), and Am($4-10x$). The smaller increase in transuranic content of the solution for the WV glass compared to the SRL

Table 2. Ph and Normalized Weight Loss Values for Hydrated/Leached SRLA and WVA Glasses.

Glass (Extent of Hydration)	pH	(NL) _{wt}
SRL (Fresh)	8.1	0.6
SRL (12um)	9.1	9.1
SRL (17um)	9.2	26.5
SRL (22um)	9.2	18.1
SRL (<1um)	8.2	0.7
ATM-10 (Fresh)	8.7	4.8
ATM-10 (15um)	9.0	12.4
ATM-10 (20um)	9.1	15.8
ATM-10 (25um)	9.2	21.3
ATM-10 (<1um)	8.7	4.9

glass is attributed to the fact that the hydrated layers produced after 28 days of reaction remain more intact for WV glass than for SRL glass, and that the fresh WV glass is more reactive than fresh SRL glass.

These results indicate that glass that has been pre-hydrated in water vapor to the extent that significant alteration has occurred (as measured by reaction zone thickness and secondary phase formation) will react more rapidly than non-hydrated glass when exposed to liquid water. The increase in reaction depends on the extent of hydration, with the largest effect observed in the release of transuranic elements into solution. Additional work is underway to monitor the release from hydrated glass as a function of time, water contact mode (dripping water or total immersion), and degree of pre-hydration.

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