Distribution Category:
Nuclear Waste Management
(UC-70)

ANL--82-11

DE83 002320

ANL-82-11

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

THE HYDRATION PROCESS OF NUCLEAR-WASTE GLASS:
AN INTERIM REPORT

by

J. K. Bates, L. J. Jardine, and M. J. Steindler

Chemical Engineering Division

DISCLAIMER

This report was prepared for the U.S. Department of Energy by the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for government purposes, not withstanding any copyright notation that may appear hereon. The U.S. Government does not warrant the quality of the information contained herein, nor does it accept any liability for damages, including consequential damages, which may result from its use. The U.S. Government is authorized to reproduce and distribute reprints for government purposes, not withstanding any copyright notation that may appear hereon.

July 1982

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.

JB

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
I. INTRODUCTION	1
II. APPROACH	2
A. Theory	2
B. Experimental	3
III. RESULTS AND DISCUSSION	6
A. Mineral Formation	6
B. Hydration Kinetics	25
IV. CONCLUSIONS	29
REFERENCES	31

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Photomicrographs of SRL 131 Glass Hydrated at 240°C for Specified Time Periods and Saturated Water Vapor Conditions	10
2.	Photomicrographs of SRL 211 Glass Hydrated at 240°C for Specified Time Periods and Saturated Water Vapor Conditions	11
3.	Photomicrographs of SRL 131 Glass Hydrated at 202°C for Specified Time Periods and Saturated Water Vapor Conditions	12
4.	Photomicrographs of SRL 211 Glass Hydrated at 202°C for Specified Time Periods and Saturated Water Vapor Conditions	13
5.	Photomicrographs of SRL 131 Glass Hydrated at 120°C for Specified Time Periods and Saturated Water Vapor Conditions	14
6.	Photomicrographs of SRL 211 Glass Hydrated at 120°C for Specified Time Periods and Saturated Water Vapor Conditions	15
7.	Typical Sodium Line Profile of Hydrated Layer	16
8.	EDAX Spectra of As-Cast Glasses SRL 131 and SRL 211	17
9.	EDAX Spectra of Identified Minerals Formed during the Hydration of Nuclear Waste Glasses	18
10.	EDAX Spectra of Unidentified Minerals Formed during the Hydration of Nuclear Waste Glasses	20
11.	Elemental Line Profiles of the Hydrated Layers Formed on SRL 131 Glass during the Initial Hydration Stage	21
12.	Elemental Line Profiles of the Hydrated Layer Formed on SRL 131 Glass during the Second Hydration Stage	22
13.	Elemental Line Profiles of the Hydrated Layers Formed on SRL 211 Glass during the Initial Hydration Stage	23
14.	Elemental Line Profiles of the Hydrated Layer Formed on SRL 211 Glass during the Second Hydration Stage	24

LIST OF FIGURES (contd)

<u>No.</u>	<u>Title</u>	<u>Page</u>
15.	The Relationship Between the Thickness of the Hydrated Layer and Time for Glasses Hydrated at 120, 202, and 240°C	26
16.	Arrhenius Plot of Hydration Data for SRL 131 Glass	28

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Compositions of Defense Waste Glasses Used in the Current Hydration Studies and a Composition Range for Naturally Occurring Obsidian	4
2.	The Saturation Pressure of Water Vapor as a Function of Temperature Used for Hydration	4
3.	The Experimental Design and Some Results and Observations for the Hydration Tests	7
4.	Hydration Layer Thickness and Rate Constants, k, for Hydration of SRL Glass	27

THE HYDRATION PROCESS OF NUCLEAR WASTE GLASS:
AN INTERIM REPORT

by

J. K. Bates, L. J. Jardine, and M. J. Steindler

ABSTRACT

Aging of simulated nuclear waste glass by contact with a controlled-temperature, humid atmosphere results in the formation of a double hydration layer penetrating the glass, as well as the formation of minerals on the glass surface. The hydration process can be described by Arrhenius behavior between 120 and 240°C. Results suggest that simulated aging reactions are necessary for demonstrating that nuclear waste forms can meet projected Nuclear Regulatory Commission regulations.

I. INTRODUCTION

A repository designed for storage of nuclear waste may be described as two separate but interacting parts--the waste package and the geologic media. The waste package consists of the waste form, the canister, overpack and sleeve, and the backfill; the geologic media, as yet undefined, may be basalt, tuff, granite, or salt. Although the waste package is located within the geologic media, a practical distinction between the two has been drawn by regulations proposed by the Nuclear Regulatory Commission [NRC]. These require that there be no release of radioactivity from the waste package for the first 10^3 y of storage and that thereafter, the maximum release be equal to no more than 10 ppm of the amount remaining.

The ramifications of these regulations are that, although groundwater contact is still the major release scenario by which radioactivity will be transferred from the repository to the biosphere, there is likely to be no contact between groundwater and the waste form for at least 10^3 y. When contact does occur, the waste form will no longer be in the same condition as when the repository was closed, but its state will have been altered by various aging processes. Aging will begin immediately after the repository is closed and will consist of processes such as devitrification, radionuclide transmutation, radiation effects on the waste form and surroundings, and chemical reactions including hydration. The effect of many of these processes on the physical properties of the waste package has been studied [MENDEL-1981A]. However, little work has been reported on the effects of hydration on the waste form.

In the present context, hydration is defined as contact between the waste form and a humid atmosphere. It will be applied only to glass waste forms and can be differentiated from leaching, or typical hydrothermal studies, in that there is no contact with aqueous solution. Given the conditions that may exist in a repository for the initial 10^3 y, hydration by water vapor is expected to be the most common aging process for solid waste [SEITZ]. This is because the canister, overpack, sleeve and clay backfill are designed to exclude most of the water. Some water vapor may exist in the sealed containers

or leak through tiny holes in the barrier. Additionally, hydration would be the dominant aging process in a repository located in unsaturated sediments such as the Nevada test site [WINOGRAD].

Hydration is also closely related to the archaeological problem of dating natural artifacts, and an understanding of the processes involved in aging of natural glasses may provide a reasonable basis for predicting the durability of nuclear waste glasses over extended time periods [EWING]. As a dating technique, hydration has been studied extensively [FRIEDMAN-1960, -1966, -1976, TAYLOR, ERICSON], and the chemistry of the hydration process has been developed [LANFORD, TSONG, HOUSER]. These studies indicate that the process is one in which alkali metal ions (Na^+ or K^+) in the glass network are replaced by a charged hydrogen species, either H^+ or H_3O^+ . The kinetics can be described by

$$D = kt^x \quad (1)$$

where D is the thickness of the hydrated layer (μm), k is the hydration rate constant ($\mu\text{m}^2/1000 \text{ y}$), and t is the time (y). Since hydration is known to be a diffusion process, x , the exponent of t , is often found to be $1/2$, and this relationship has been applied both to field samples [FRIEDMAN-1960, -1966, -1976] and to laboratory-induced hydration studies [FRIEDMAN-1966, -1976, LANFORD, TSONG, ERICSON]. However, other investigators [TAYLOR] find that the time dependence varies between $t^{1/3}$ and t^3 . The disparity for these results has been attributed to an incomplete knowledge of weathering conditions and to less-than-rigorous segregation of glasses having different compositions. Clearly, composition, temperature, and water vapor concentration all affect layer formation, and it has been concluded [TAYLOR] that the dating of natural specimens on the basis of hydration is valid only if the glass compositions and past climatic conditions are specified and if the hydration kinetics of the glass are established.

In this report, knowledge gained from the hydration studies of natural analogues has been applied to nuclear waste glasses. A method of hydrating nuclear waste glass is described, and it is shown that the results can be extrapolated to match long-term repository conditions. In addition, avenues of future study are discussed that would allow a complete description of release that may occur from a repository after 10^3 y .

II. APPROACH

A. Theory

As shown in Eq. 1, for a given glass sample and a prescribed set of hydration conditions, the hydration rate can be described as a function of the thickness of the hydration layer and of time. To obtain k for a given set of conditions, experiments are run for different time intervals and the thickness of the layer is determined. The relationship between D and t can be obtained by fitting Eq. 1 to the data.

If hydration experiments are performed at different temperatures, keeping other conditions constant, a value of k can be determined for each temperature. It is then possible to solve the Arrhenius equation to establish the

relationship between hydration rate and temperature. The Arrhenius equation is

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

where k is the hydration rate constant ($\mu\text{m}^2/1000 \text{ y}$), A is a constant, E_a is the activation energy of the hydration process (cal/mol), R is the gas constant ($\text{cal/K}\cdot\text{mol}$), and T is the absolute temperature (K). The empirical constants, E_a and A , can be deduced from the slope and intercept of the appropriate plot of the values of k at different temperatures. It is generally accepted that a linear relationship over a range of temperatures indicates that the mechanism of the reaction has not changed in that temperature range.

B. Experimental

Those variables that may affect the hydration rate of a waste glass sample are temperature, glass composition, total pressure, and degree of saturation of the air in contact with the waste form. Degree of saturation is defined as $P_{\text{H}_2\text{O}}/P_{\text{H}_2\text{O}}^{\text{sat}}$ (saturation). Previous studies [FRIEDMAN-1966, -1976] have indicated that total pressure has little effect on hydration rate. Accordingly, most of the effort in the present experiments has been to determine the effects of the other variables.

Two glass compositions were used throughout the experiments. A third was used only in the initial testing. The glasses extensively studied were Savannah River Laboratory (SRL) defense glasses 131 and 211. SRL 131 was used as supplied; 211 was modified by adding an amount of simulated waste elements. The third glass studied was Pacific Northwest Laboratory (PNL) glass 76-68. The compositions of the SRL glasses are given in Table 1, together with a typical composition of the natural glass, obsidian.

The degree of saturation was set at 100%, and only enough water was used to produce this condition when operating temperatures were reached. The goal was to produce saturated conditions with as little chance for condensate formation as possible. Temperatures used were 120, 202, and 240°C. The relationship between saturation pressure and temperature is shown in Table 2. One experiment (not listed in the tables) was done with 10% saturation.

SRL 131 glass was prepared for hydration by crushing and melting a 500-g batch of starting frit that was supplied by PNL. This batch was melted at 1050°C in a platinum crucible and was poured into water, making a frit. Forty grams of this frit was remelted in a platinum crucible and held at 1050°C for four hours. The glass was then poured into a Pt-10% Au crucible and annealed at 500°C for two hours. The annealed glass was then cooled slowly to room temperature. PNL 76-68 glass was prepared in a similar fashion. For SRL 211 glass, there was an additional melting, crushing, and a mixing step in which the waste oxides were added.

The glass samples used for hydration were cut from a larger ingot, using an Isomet saw with a low concentration diamond wafering blade and using water as the cutting fluid. The final size of the samples was not carefully controlled, but generally samples were 10 x 5 x 1 mm. The rough-cut samples were

Table 1. Compositions of Defense Waste Glasses Used in the Current Hydration Studies and a Composition Range for Naturally Occurring Obsidian

Oxide	SRL 131, wt %	SRL 211, wt %	Obsidian, wt %
SiO ₂	44.0	42.9	62-81
Na ₂ O	13.7	15.2	3-4
Fe ₂ O ₃	14.3	14.2	0.1-3
B ₂ O ₃	10.9	7.9	---
CaO	1.4	5.2	0.2-2
MnO	3.1	3.2	<0.01
Al ₂ O ₃	3.5	3.8	12-14
Li ₂ O	4.2	3.2	---
NiO	1.8	1.7	<0.01
TiO ₂	0.7	---	0.1-0.2
MgO	1.6	---	0.05-0.2
ZrO ₃	0.4	---	<0.01
La ₂ O ₃	0.4	---	<0.01
K ₂ O	---	---	4-5
Waste Additives^a			
Cs ₂ O	---	0.1	---
SrO	---	0.4	<0.01
BaO	---	0.06	<0.1
CeO ₂	---	0.8	<0.01
Nd ₂ O ₃	---	0.9	<0.01
Eu ₂ O ₃	---	0.1	<0.01
RuO ₂	---	0.5	---

^aThe levels for obsidian represent its natural composition, not waste additives.

Table 2. The Saturation Pressure of Water Vapor as a Function of Temperature Used for Hydration

Temperature, °C	Saturation Vapor Pressure of Water, mm	Mass of Water, ^a g
120	1489	0.025
202	12155	0.17
240	25100	0.33

^aThis is the amount of water required to reach saturation in the present experiments. The volume of the reaction vessel is 21.3 cm³.

further polished on both sides and one edge, using 600-grit Al_2O_3 paper with kerosene. The final samples were cleaned ultrasonically in ethanol to remove accumulated Al_2O_3 . The cleaned samples were then air-dried and weighed.

The reaction vessel was a tantalum-lined stainless steel bomb made by Parr, Inc. (Cat. No. 4547). The vessel consisted of a body, lid, and Teflon washer; the washer was compressed by a pressure fitting to form a seal between the body and lid. The volume of each vessel was 21.3 cm^3 . There was no pressure monitoring or control mechanism. Thus, the final pressure and degree of saturation were calculated from the amount of water added to the vessel at the beginning of each experiment and from the amount of water remaining after the experiment terminated. An amount of water slightly in excess of that necessary to give 100% saturation was added to offset losses during heating.

The samples were suspended from a 5-mil Teflon thread tied around the sample and attached to a Teflon support. The Teflon support had been pretreated by an established procedure [MENDEL-1981B]. Samples of each glass were contained in each hydration vessel to ensure they were exposed to identical hydration conditions. Care was taken so that no pieces of glass were touching other samples or the sides of the vessel.

Careful positioning of the samples was necessary to ensure that no condensation occurred. Condensation can be detected by visual examination of the sample after hydration and by monitoring the pH of the water at the conclusion of the experiment. When the samples were properly positioned, the required amount of deionized water (pH 6) was added and the container was sealed and weighed.

The containers were placed in a constant-temperature ($\pm 1.5^\circ\text{C}$) oven, Blue M No. OV-490A-2, and held for predetermined periods of time. The temperature was monitored with a thermometer calibrated by NBS and a thermocouple combined with an X-Y recorder to monitor temperature fluctuations.

An experiment was terminated by removing the container from the oven, allowing it to cool for five minutes, then quenching the lower portion in water. The time period was taken to be the interval between the time the reaction vessel was placed in the oven and the time the vessel was opened (approximately ten minutes after it was removed from the oven). This procedure was found to be effective in eliminating condensation during hydration and upon cooling. Any condensation that occurred during cooling would not alter the thickness of the hydration layer but would alter the surface topography.

The containers were weighed and opened, and the pH of the remaining water was determined with pH paper. The samples were observed for condensation and general appearance, then dried in air for 48 h. Next, the Teflon thread was removed and the sample weighed. Each sample was split into two parts; one was mounted for surface evaluation by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX), and the other was mounted on edge in a resin mold. The polished edge was faced down and polished, using first, 600 grit carborundum paper and finally, $0.05 \mu\text{m}$ Al_2O_3 in kerosene. The final sample was washed ultrasonically in kerosene, rinsed with water, and gold-coated for examination with SEM and EDAX. Some of the surface layers were

also submitted for examination by X-ray diffraction (XRD). A complete account of the experimental design, together with some results and observations, is shown in Table 3.

III. RESULTS AND DISCUSSION

Both the thickness and the surface features of the hydrated layer were investigated. The general appearance of the glass surface ranges from a rainbow-type reflectance to complete coverage by a white (SRL 211) or off-white (SRL 131) matted fibrous material, as the hydration becomes more extensive. Photomicrographs of each glass that had been surface hydrated under various conditions are shown in Figs. 1 through 6. In each of these figures, the photomicrograph of the sample surface is to the right of the corresponding photomicrograph of the cross section.

The cross section of the hydrated layer could easily be observed and measured for layer thicknesses greater than 1 μm . Thinner layers may be observable if mounting and polishing techniques are refined. Hydrated layers could be seen for SRL 211 and SRL 131 glasses but not for PNL 76-68 glass. For this reason, extensive hydration testing was not continued or reported for PNL 76-68 glass.

The hydrated layer was defined as the distance between the glass surface and the furthest penetration of water into the glass. Usually, the interface between the bulk glass and the hydrated layer was sharp and easily distinguished by contrast difference; also, confirming evidence was provided by a elemental line profile obtained using EDAX (Fig. 7). This is possible since water penetration is known to be marked by sodium depletion [LANFORD, TSONG]. The sodium line profile (Fig. 7) indicates sodium removal from the hydrated layer.

As is evident in Fig. 1(b), the hydrated region of glass consists of two parts: (1) a thinner outer layer, which can be observed only after it becomes well enough developed, is marked by striations perpendicular to the surface and (2) a thicker inner layer which is more uniform in general appearance but is sometimes cracked and separated from the surface. Cracking occurs during drying, as is shown by cracks in surface minerals which are a continuation of cracks in the surface layer (Fig. 4e). Whether cracking also occurs during hydration is not obvious, but cracking is expected due to layer expansion that occurs as water is incorporated into the glass. Water gain should be measurable by determining the weight increase, but hydration of 30- μm thickness will provide a calculated weight increase of only 0.0001 g; this cannot be detected by readily available techniques. Layer thickness includes both layers, but not the structure that forms on the surface.

A. Mineral Formation

The surface structure is shown in Figs. 1 through 6. As the degree of hydration increases, the variety and size of surface structure increases. Features on both SRL 131 and SRL 211 glasses are similar.

Table 3. The Experimental Design and Some Results and Observations for the Hydration Tests

Test Number	Glass Type	Temp, °C	Time Interval, h	Initial Sample Mass, g	Final Sample Mass, g	Initial Water Mass, g	Final Water Mass, g	Final pH	Layer Thickness, ^a μ m	Comments ^b
1	211 131	202	6	0.0489 0.0745	0.0490 0.0747	0.2669	0.2416	7	1.2 3.7 $\pm$ 0.3	analcime (12), sponge, puffy analcime (17), sponge, no second layer obvious
2	211 131	202	24	0.0520 0.0807	0.0522 0.0807	0.2722	0.2529	7	2.1 6.9 $\pm$ 0.6(0.8)	analcime (25), sponge, small round spheres analcime (30), sponge, some puffy
3	211 131	202	24	0.0470 0.1506	0.0471 0.1507	0.2645	0.2087	7	2.0 5.3 $\pm$ 0.8(1.0)	no surface picture no surface picture
4	211	202	36	0.0568	0.0570	0.2603	0.2124	6	14.4 $\pm$ 2(1.4)	analcime (45), tobermorite coverage 95%
5	211 131	202	48	0.0763 0.0666	0.0764 0.0664	0.2707	0.2535	8	12.1 $\pm$ 1.6(1.6) 9.2 $\pm$ 0.6(1.2)	analcime (43), tobermorite coverage 50% analcime (29), sponge, puffy
6	211 131	202	96	0.0348 0.1782	0.0348 0.1780	0.2844	0.2549	9	30 $\pm$ 2(2.3) 12.3 $\pm$ 0.5(2.6)	analcime (42), tobermorite coverage analcime (38), sponge, some puffy
7	211 131	202	144	0.0672 0.1485	0.0676 0.1483	0.2697	0.1400	6	35 $\pm$ 8 13.8 $\pm$ 1.6(3.4)	analcime (85), tobermorite coverage 15% analcime (63), some tobermorite
8	131	202	170	0.0773	0.0772	0.2694	0.2481	8	15.9 $\pm$ 2.0(3.4)	analcime (39), sponge, some puffy covering analcime
9	211 131	202	192	0.0440 0.0863	0.0465 0.0866	0.2681	0.2133	7	82 $\pm$ 5 27 $\pm$ 1.5(4.9)	tobermorite coverage 100% analcime (85), some tobermorite
10	131	202	233	0.0609	0.0608	0.2678	0.2422	8	18 $\pm$ 1(3.7)	no surface picture
11	131	202	336	0.0380	0.0358	0.2825	0.2294	8	68 $\pm$ 7	analcime (97), round puffballs, no tobermorite
12	211 131	240	1.6	0.0176 0.0593	0.0175 0.0592	0.3696	0.3552	6	ND ^c 1.4	sponge, no analcime analcime (4)
13	211 131	240	4	0.0231 0.0661	ND ND	0.3479	0.3300	7	3.4 4.2	no surface picture no surface picture

(contd)

Table 3. (contd)

Test Number	Glass Type	Temp, °C	Time Interval, h	Initial Sample Mass, g	Final Sample Mass, g	Initial Water Mass, g	Final Water Mass, g	Final pH	Layer Thickness, ^a μ m	Comments ^b
14	211 131	240	4	0.0263 0.0951	0.0259 0.0946	0.3747	0.3206	7	1.8 3.5(0.5)	analcime (13), round puffballs (5), sponge analcime (39), sponge
15	211 131	240	4.4	0.0311 0.1342	ND ND	0.3639	0.3400	7	5.1(0.4) 5.6(0.4)	analcime (51), tobermorite 100% analcime (37), sponge and some small needles
16	211 131	240	7	0.0330 0.0890	0.0329 0.0886	0.3668	ND	ND	4.8? 5.6(1.0)	analcime(6), round puffballs(8), tobermorite(50%) analcime (9)
17	211 131	240	11.5	0.0301 0.0518	0.0302 0.0519	0.3603	0.3439	7	5.0 4.4	analcime (20), round puffballs (20) analcime (16), smaller forms
18	211 131	240	7	0.0491 0.0890	0.0490 0.0886	0.3668	ND	ND	10.0 5.6(1.0)	analcime(18), round puffballs(20), tobermorite(50%) analcime (9)
19	211 131	240	11.5	0.0301 0.0518	0.0302 0.0519	0.3603	0.3439	7	5.0 4.4	analcime (20), round puffballs (20) analcime (16), smaller forms
20	211 131	240	16	0.0491 0.0910	0.0490 0.0910	0.3449	0.2648	8	10.0 10.0(0.9)	analcime(18), round puffballs(20), tobermorite(50%) analcime (18), tobermorite (30%), sponge
21	211 131	240	16	0.0644 0.1301	0.0638 0.1297	0.3698	0.3518		26.6 $\pm$ 3(2) 11.1 $\pm$ 0.5(1.5)	analcime (44), tobermorite (100%) analcime (?), sponge, tobermorite (2%)
22	211 131	240	24	0.0294 0.0928	ND ND	0.3799	0.3665		21.2(1.1) 9.5(1.2)	analcime(34), round puffballs(10), tobermorite(95%) analcime (22), puffy coverage
23	211 131	240	24	0.0294 0.0684	ND ND	0.03598	0.3495		15.5(2.0) 8.9 $\pm$ 0.3(1.9)	analcime(42), round puffballs(35), tobermorite(70%) analcime (31), puffy coverage

(contd)

Table 3. (contd)

Test Number	Glass Type	Temp, °C	Time Interval, h	Initial Sample Mass, g	Final Sample Mass, g	Initial Water Mass, g	Final Water Mass, g	Final pH	Layer Thickness, ^a μ m	Comments ^b
24	211 131	240	29.4	0.0270 0.0483	0.0270 0.0474	0.3668	0.3475		37 $\pm$ 2(1.3) 13.0 $\pm$ 1.8(3.5)	tobermorite (100%) no picture of surface
25	211 131	240	31.8	0.0253 0.0613	0.0250 0.0610	0.3665	0.3450		37 $\pm$ 2 19.6(3.5)	tobermorite (100%) no picture of surface
26	211 131	240	40.1	0.0275 0.0459	0.0278 0.0461	0.3750	0.3597		41 $\pm$ 4(2.0) 24.3 $\pm$ 2.5(1.8)	analcime(38), round puffballs(38), tobermorite(100%) analcime (49), tobermorite (100%)
27	211 131	120	192	0.0547 0.1205	0.0547 0.1203	0.0533	0.0292	7	1.4 2.0	sponge sponge
28	211 131	120	384	0.0405 0.1241	ND ND	0.0556	0.0541	7	ND 3.15 $\pm$ 0.1(0.3)	sponge, small bumps
29	211 131	120	811	0.0414 0.1299	0.0415 0.1302	0.0541	0.0296	ND	2.6 $\pm$ 0.2 ND	rough with bumps and spikes
30	211 131	120	984	0.0407 0.1540	ND ND	0.0517	ND	8	ND 5.1 $\pm$ 0.8	rough with bumps sponge
31	211 131	120	2208	0.0406 0.1611	0.0405 0.1611	0.0568	ND	ND	5.4 $\pm$ 0.4 7.2 $\pm$ 0.2	analcime (80), crystalline plates

^aSecond layer thickness, if observed, is given in parentheses.

^bThe average diameter (μ m) of a crystal or the percentage coverage of the surface by that mineral type is given in parentheses.

^cNot determined.

Fig. 1. Photomicrographs of SRL 131 Glass Hydrated at 240°C for Specified Time Periods and Saturated Water Vapor Conditions: (a) 1.6 h, mm = 8.9 μm ; (b) 24 h, mm = 5 μm ; (c) 40.1 h, mm = 5 μm ; (d) 1.6 h, mm = 7.8 μm , the trapezohedral crystals are analcime; (e) 24 h, mm = 7.7 μm , note the analcime crystals and the sponge-like surface; and (f) 40.1 h, mm = 7.7 μm , note the analcime crystals, the smaller round isotropic mineral form in center foreground, and complete tobermorite coverage of the surface. The symbol "mm" is the "micron marker." The length of the rightmost segment of the line on each photomicrograph represents the indicated number of micrometers.

Fig. 2. Photomicrographs of SRL 211 Glass Hydrated at 240°C for Specified Time Periods and Saturated Water Vapor Conditions: (a) 4.4 h, mm = 8.5 μm ; (b) 24 h, mm = 8.5 μm ; (c) 40.1 h, mm = 5 μm , note the analcime crystal on the surface; (d) 4.4 h, mm = 8.5 μm , note the analcime crystal in the center foreground, the round isotropic crystals in the center, and the sponge-like appearance of the surface; (e) 24 h, mm = 8.1 μm , note the peak-shaped but unidentified mineral form in the left foreground and the nearly complete tobermorite coverage; and (f) 40.1 h, mm = 8.2 μm . The symbol "mm" is the "micron marker." The length of the rightmost segment of the line on each photomicrograph represents the indicated number of micrometers.

Fig. 3. Photomicrographs of SRL 131 Glass Hydrated at 202°C for Specified Time Periods and Saturated Water Vapor Conditions: (a) 6 h, mm = 5 μ m; (b) 24 h, mm = 5 μ m; (c) 192 h, mm = 8.5 μ m; (d) 6 h, mm = 50 μ m, analcine crystals; (e) 24 h, mm = 50 μ m; and (f) 192 h, mm = 95 μ m, note the round fuzzy mineral form in the center background. The symbol "mm" is the "micron marker." The length of the rightmost segment of the line on each photomicrograph represents the indicated number of micrometers.

Fig. 4. Photomicrographs of SRL 211 Glass Hydrated at 202°C for Specified Time Periods and Saturated Water Vapor Conditions: (a) 24 h, mm = 7.9 μm ; (b) 144 h, mm = 5 μm ; (c) 192 h, mm = 8.5 μm ; (d) 24 h, mm = 8.5 μm , note the analcime and the smaller unidentified segmented crystals; (e) 144 h, note the peak-like crystals and the cracked round mineral form in the left background that demonstrates that cracking occurs during drying; and (f) 192 h, mm = 8.9 μm , note the complete tobermorite coverage. The symbol "mm" is the "micron marker." The length of the rightmost segment of the line on each photomicrograph represents the indicated number of micrometers.

Fig. 5. Photomicrographs of SRL 131 Glass Hydrated at 120°C for Specified Time Periods and Saturated Water Vapor Conditions: (a) 192 h, mm = 5 μm ; (b) 384 h, mm = 5 μm ; (c) 2208 h, mm = 5.1 μm ; (d) 192 h, mm = 8.5 μm ; (e) 384 h, mm = 8.5 μm ; and (f) 2208 h, mm = 13.2 μm , note the large analcime crystal, the crystalline plates, and the smaller round minerals on the surface. The symbol "mm" is the "micron marker." The length of the rightmost segment of the line on each photomicrograph represents the indicated number of micrometers.

Fig. 6. Photomicrographs of SRL 211 Glass Hydrated at 120°C for Specified Time Periods and Saturated Water Vapor Conditions: (a) 192 h, mm = 8.6 μm ; (b) 811 h, mm = 5 μm ; (c) 2208 h, mm = 5.1 μm ; (d) 192 h, mm = 5 μm ; (e) 811 h, mm = 8.1 μm , and (f) 2208 h, mm = 8.6 μm , note the large analcime crystal in the right center, the crystalline plates in the left center that are rich in Nd, the round mineral on the right that are rich in Cs and Ce, and the smaller mineral forms on the surface. The symbol "mm" is the "micron marker." The length of the rightmost segment of the line on each photomicrograph represents the indicated number of micrometers.

Fig. 7. Typical Sodium Line Profile of Hydrated Layer. EDAX Spectrum

Chronologies of the surface-topography changes for both SRL 211 and SRL 131 glasses are shown in Figs. 1 through 6. For SRL 211 glass the initial surface changes are the appearance of trapezohedral crystals, together with an alteration such that the surface acquires a sponge-like appearance (Fig. 2). The trapezohedral crystals become larger, and round isotropic crystals (together with smaller, irregular peak-like structures) begin to form. Finally, a white fibrous material begins to cover the surface and eventually attains total coverage. Both the trapezohedral and isotropic crystals reach diameters of $\sim 50 \mu\text{m}$.

SRL 131 glass exhibits the same general behavior except that mostly trapezohedral crystals form on the surface and the final matted coverage is off-white. These surface features have been partially identified, using XRD and EDAX. To allow comparison, the EDAX spectra of as-cast SRL 211 and SRL 131 are shown in Figs. 8a and 8b.

XRD was done using a section of hydrated layer (including the surface features) from the 202°C , 336-h hydration test. Three distinct patterns were identified but since it was a mixed sample, no XRD pattern was free of interferences. These three patterns were matched with known mineral patterns and were correlated to the actual surface features with the aid of EDAX and the known physical description of the minerals.

The trapezohedral crystals, evident after only six hours of hydration at 202°C , Fig. 3d, have been identified by XRD as analcime, a mineral belonging to the zeolite family and having the composition, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. An EDAX spectrum of an analcime crystal is shown in Fig. 9(a). The elemental compositions of the crystals that form on SRL 211 and SRL 131 glasses are very

(a)

(b)

Fig. 8. EDAX Spectra of As-Cast Glasses (a) SRL 131 and (b) SRL 211. For each of the EDAX spectra, the insert is an expanded scan of that energy region

Fig. 9. EDAX Spectra of Identified Minerals Formed during the Hydration of Nuclear Waste Glasses: (a) Analcime, (b) SRL 211 tobermorite, (c) SRL 131 tobermorite, (d) SRL 211 montmorillonite, and (e) SRL 131 montmorillonite (stevensite)

similar. Analcime may contain excess SiO_2 and H_2O , apparently as $\text{SiSi}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ in crystal solution. It may also contain excess Al_2O_3 , K_2O , and CaO . In nature it is usually found as a secondary mineral, often associated with zeolites or possibly as an alteration product of nepheline or sodalite. The cesium analogue to analcime is pollucite, and a continuous series of Na, Cs compositions is possible during mineral formation. Once incorporated, however, the cesium is locked in the mineral and is nonexchangeable.

The fibrous materials that appear as needle-like crystals (Fig. 3f) only after hydration has proceeded for a period of time and then cover the surface with a matted layer have been identified by XRD as tobermorite, $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$. Tobermorite is one of the main constituents of concrete. EDAX spectra of tobermorite as found on SRL 211 and SRL 131 glasses are shown in Figs. 9(b) and 9(c). The composition of the mineral differs somewhat, depending on the composition of the base glass. SRL 211 tobermorite has concentrated the K and Ba which, although present in the as-cast glass, cannot be detected with EDAX (Fig. 8). SRL 211 also contains some Na. SRL 131 tobermorite (Fig. 9c) contains less Na and more heavy metals. However, these heavy metals may be an artifact of the X-ray collection system, being actually representative of the surface layer rather than tobermorite.

The glass surface itself is altered by hydration. It has a sponge-like appearance in the surface photomicrographs and a striated appearance in the cross sections. This is named the second layer in further discussion. It has not been identified unambiguously, but belongs to the montmorillonite group of clay minerals. XRD indicates the layer to be similar to stevensite, $(\text{Mg}_{2.88}, \text{Mn}_{0.02}, \text{Fe}_{0.02})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot (\text{Ca}, \text{Mg})_{0.07}$. EDAX spectra of this layer that is common to all samples is shown in Figs. 9d and 9e. For SRL 211 glass, this layer is depleted in Na, Al, Ca, Ni, and the rare earths; for SRL 131 glass, it is depleted in Na, Ca, and Ni.

The structure of montmorillonite-type minerals is always unbalanced due to atomic substitutions in their expandable layer structure. The resulting deficiency of net positive charge is balanced by exchangeable cations adsorbed between the unit layers and around their edges. This montmorillonite layer may have the capability of incorporating certain waste radionuclides into its structure.

The other features seen on SRL 211 glass have not been identified but have been analyzed with EDAX. The round isotropic crystals (Fig. 2f) give the energy spectrum shown in Fig. 10a, while the smaller peak-like structures have the spectrum shown in Fig. 10b. Both minerals contain Si, Ca, and Na in varying amounts, but the exact identification of each must be obtained using XRD or electron microprobe analysis.

The above minerals were identified on glass that had been hydrated at 202 and 240°C. In addition, the surface of SRL 211 glass weathered at 120°C for 90 days provides two additional unidentified minerals whose EDAX spectra are shown in Figs. 10c and 10d. The first appears as crystalline plates that are Ca-rich and contain lesser amounts of Si, Na, Nd, Mn, Fe, and Ni. Interestingly, this mineral has been able to incorporate a considerable amount of Nd yet contains no Ce. The second mineral, which is round and fuzzy, is rich in Si and Al and contains lesser amounts of Na, Ca, Ce, Cs,

Fig. 10. EDAX Spectra of Unidentified Minerals Formed during the Hydration of Nuclear Waste Glasses: (a) round isotropic minerals, see Fig. 2f; (b) peak-like structures, see Fig. 2e; (c) crystalline plates, see Fig. 6f; and (d) round minerals, see Fig. 6f

Mn, Fe, and Ni. In this mineral, there is little or no Nd. This is the only mineral in which Cs has been identified, although its amount is not constant between different crystals on the same surface.

The elemental line profiles of the surface cross sections also give some indication of the composition of the hydrated layers in comparison to the bulk glass composition and demonstrate the partitioning of glass components during the hydration process. The EDAX spectra and line profiles shown in Figs. 11 through 14 are semiquantitative, and no matrix corrections have been made. The apparent intensity of an energy peak is dependent on the density of the matrix, and light elements are more susceptible to surface profile changes and to density differences than are heavy elements. Thus, the intensity peaks near the crack in the glass for sodium and silicon, and the heavy

Fig. 11. Elemental Line Profiles of the Hydrated Layers Formed on SRL 131 Glass during the Initial Hydration Stage: (a) photomicrograph of polished cross section; note the horizontal trace showing the beam path. The black vertical line is a burn in the photo CRT; (b) Si; (c) Na; (d) Al; (e) Ca; (f) Mn; (g) Fe; and (h) Ni.

Fig. 12. Elemental Line Profiles of the Hydrated Layer Formed on SRL 131 Glass during the Second Hydration Stage: (a) photomicrograph of the scanned layer, (b) Si; (c) Na; (d) Al; (e) Ca; (f) Mn; (g) Fe; and (h) Ni.

Fig. 13. Elemental Line Profiles of the Hydrated Layers Formed on SRL 211 Glass during the Initial Hydration Stage: (a) photomicrograph of the scanned layer, (b) Si; (c) Na; (d) Al; (e) Ca; (f) Mn; (g) Fe; and (h) Ni.

Fig. 14. Elemental Line Profiles of the Hydrated Layer Formed on SRL 211 Glass during the Second Hydration Stage: (a) photomicrograph of the scanned layer, (b) Si; (c) Na; (d) Al; (e) Ca; (f) Mn; (g) Fe; and (h) Ni.

element intensity differences between the layer and the bulk glass near the crack in the glass (Fig. 3) may not reflect the factual elemental composition. However, the sodium, silicon, aluminum, iron, and nickel intensity differences that occur within the hydrated layer are real.

These elemental line profiles indicate that more diffusion occurs within the glass than has previously been described [TSONG]. For SRL 131 glass shown in Fig. 11, two layers are evident in both the micrograph (Fig. 11a) and in the line profiles (Fig. 11b-11h). In comparison to the first layer, the thinner second layer has a greater concentration of Si and Fe at the expense of Ca, Ti (not shown), and Ni. In comparison to the bulk glass, the first layer appears to be enriched in Ca, Fig. 11e. Other elemental intensity differences between the bulk glass and the layers are probably caused by matrix effects and may not be real.

SRL 131 glass that has been hydrated for a longer period of time has only a thick, single hydration layer (Fig. 12a). This layer is significantly depleted in Al, Ca, and Na. The Ca depletion is the reverse of what is observed for shorter hydration periods (Fig. 11e) but is not unexpected due to the extensive mineral formation on the surface.

SRL 211 glass hydrated for short time periods also displays two layers (Fig. 13). The second layer is enriched in Si, Al, Fe, and Ca while depleted in Ni. The first layer, when compared to the bulk glass, is depleted in Si, Ca, and Al. Thicker hydrated layers (Fig. 14) have EDAX spectra similar to those of corresponding layers of SRL 131 glass.

Although no detailed mechanistic description of the hydration process is given here, it seems reasonable that in addition to the simple diffusion of "water" into the glass and Na^+ out of the glass, there is a driving force established, due to the formation of stable minerals, that promotes the diffusion and distribution of other elements.

B. Hydration Kinetics

The thickness of the total hydration layer varies generally by $\pm 10\%$. This could be due to surface roughness or the formation of minerals. The layer is thinner where large minerals are present. In some samples, there is no variation in layer thickness; in others, there is up to 20% variation. The layer thicknesses have been measured and are given in Table 4. The relationships between thickness and hydration time for hydrations done at 120, 202, and 240°C are given in Fig. 15. At 202 and 240°C, each relationship consists of two parts, an initial curve linear with $t^{1/2}$, and a second curve with a significantly greater rate for which the functionality has not been determined. At 120°C, only one curve, linear in $t^{1/2}$, is evident. At all three temperatures, hydration of SRL 211 occurs slower initially, but at 202 and 240°C soon exceeds the rate of SRL 131 glass. The latter behavior is anticipated at 120°C if the experiments are performed for a long enough duration.

The values of k determined for each temperature using the initial portion of the curves are given in Table 4 and are plotted for SRL 131 glass in Fig. 16 as $\ln k$ vs. $1000/T$, K. Although the data are limited, the relationship is linear and for SRL 131 glass yields an activation energy of

Fig. 15. The Relationship Between the Thickness of the Hydrated Layer and Time for Glasses Hydrated at 120, 202, and 240°C. Each line represents the best fit through all points, including zero

Table 4. Hydration Layer Thickness and Rate Constants,
k, for Hydration of SRL Glass

Glass Type	Temperature, °C	Time Interval, h	Layer Thickness, μm	k^a $\mu\text{m}^2/1000 \text{ y}$
SRL 131	120	192	2.0	2.37×10^5
		384	3.15 ± 0.1	
		784	5.1 ± 0.08	
		2208	7.2 ± 0.2	
SRL 211	120	192	1.4	1.17×10^5
		811	2.6	
		2208	5.4 ± 0.4	
SRL 131	202	6	3.7 ± 0.3	1.21×10^7
		24	6.1 ± 0.6	
		48	9.2 ± 0.6	
		96	12.3 ± 0.5	
		144	13.8 ± 1.6	
		169	15.9 ± 2.0	
		235	18.1 ± 0.5	
		192	27.0 ± 1.5	
		336	67.6 ± 6.0	
SRL 211	202	6	1.2	1.57×10^6
		24	2.1	
		36	14.4	
		48	12.1	
		96	30	
		144	35	
		192	82	
SRL 131	240	1.6	1.5 ± 0.2	4.57×10^7
		4	3.9 ± 0.4	
		4.4	5.6 ± 0.3	
		7	5.6 ± 0.5	
		11.5	7.4 ± 0.5	
		16	10.0 ± 0.3	
		19.6	11.1 ± 0.5	
		24	9.3 ± 0.4	
		29.4	13.0 ± 1.8	
		31.8	19.6 ± 2	
		40.1	24.3 ± 2.5	

(contd)

Table 4. (contd)

Glass Type	Temperature, °C	Time Interval, h	Layer Thickness, μm	$\mu\text{m}^2 k,^a$ /1000 y
SRL 211	240	1.6	ND	2.07×10^7
		4	2.8 ± 0.8	
		4.4	9.1	
		7	4.8	
		11.5		
		16	10.0	
		19.6	26.6 ± 3	
		24	18.3 ± 2.7	
		29.4	26.6 ± 2	
		31.8	37 ± 2	
		40.1	42 ± 2.5	

^aValues were determined from data points which comprise the initial portion of each curve.

Fig. 16. Arrhenius Plot of Hydration Data for SRL 131 Glass

17,900 cal/mol and an A of $1.9 \times 10^{15} \mu\text{m}^2/1000 \text{ y}$. This suggests that the mechanism of the initial hydration reaction does not change between 120 and 240°C. This suggestion is reinforced by the same surface features being observed for glass hydrated at the three temperatures.

Neither the cause nor the functionality of the second rate curve has been established, but correlation of surface topography with layer thickness suggests that the onset of the increased rate and the formation of tobermorite needles occur simultaneously.

One experiment was conducted in which the effect of the degree of water vapor saturation at one-tenth saturation and 202°C for eight days was determined. No layers could be observed on either SRL glass, although analcime formation was seen on SRL 131 glass.

IV. CONCLUSIONS

Although the results are preliminary, this work raises two points relevant to the disposal of nuclear waste.

(1) The Arrhenius behavior that has been observed for the hydration of defense waste glass allows the hydration process to be cautiously extrapolated to various time/temperature conditions, provided that saturated but noncondensing conditions exist and that the hydration follows the kinetics noted in the initial hydration curve. Such extrapolation allows the aging of SRL glass to be accelerated so that reasonable time-temperature scenarios may be simulated. For example, after storage under hydrating conditions for 1000 y at 90°C, SRL 131 glass would have a hydrated layer 170 μm thick and would be covered with a thick mineral layer.

If this hydrated glass was then contacted by groundwater, leaching would occur, but the initial leaching would be from hydrated glass, not from fresh glass. This is important because most research on glass-leaching mechanisms done on fresh glass may not be directly useful in establishing the long-term release of nuclides from aged glass.

(2) During the process of hydration and drying, extensive cracking of hydrated layers occurs. If such humid/dry cycling is a possible scenario for long-term burial of nuclear waste, it would have a different effect on the degradation of the glass than just hydration or just leaching by liquid water solutions.

By use of the hydration processes described in this report, realistic long-term aging of glass may be simulated. Such tests, done in combination with other simulated aging reactions would be valuable in demonstrating the performance of a waste form in relation to projected NRC regulations.

These results also have applicability to the age dating techniques used for natural glasses. The activation energies derived from the initial portion of the SRL 131 glass hydration curves are very similar to those calculated for obsidian by Friedman [FRIEDMAN-1976] who reports that E ranges from 19,200 cal/mol to 21,600 cal/mol, with A ranging from 1.4 to $18 \times 10^{15} \mu\text{m}^2/1000 \text{ y}$. The $t^{1/2}$ kinetics are also the same as those determined by Friedman and

Long [FRIEDMAN-1976]. However, if the present results are replotted using the error limits pertinent to previous data [TAYLOR], a single rate, linear in $t^{3/2}$ can be obtained, in concert with other reported values [TAYLOR]. Clearly, care must be exercised when determining the time-temperature relationship for glass hydration.

REFERENCES

Ericson

J. E. Ericson, Durability of Rhyolitic Obsidian Glass Inferred from Hydration Dating Research, Materials Research Society Symposium D, Scientific Basis for Nuclear Waste Management, Vol. 3, 283 (1981).

Ewing

R. C. Ewing and R. F. Haaker, Naturally Occurring Glasses: Analogues for Radioactive Waste Forms, Pacific Northwest Laboratory Report PNL-2776 (1979).

Friedman-1960

I. Friedman and R. L. Smith, A New Dating Method Using Obsidian: Part I, The Development of the Method, Am. Antiq. 25, 476 (1960).

Friedman-1966

I. Friedman, R. L. Smith, and W. D. Long, Hydration of Natural Glass and Formation of Perlite, Geo. Soc. Am., Bull. 77, 323 (1966).

Friedman-1976

I. Friedman, and W. Long, Hydration Rate of Obsidian, Science 191, 347 (1976).

Houser

C. A. Houser, J. S. Herman, I. S. T. Tsong, and W. B. White, Sodium-Hydrogen Interdiffusion in Sodium Silicate Glasses, J. Non-Cryst. Solids 41, 89 (1980).

Lanford

W. A. Lanford, K. Davis, P. Lamarche, T. Laursen, and R. Groleau, Hydration of Soda-Lime Glass, J. Non-Cryst. Solids 33, 249 (1979).

NRC

Fed. Reg. 48(130), 35280 (1981).

Mendel-1981A

J. E. Mendel et al., A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms, Pacific Northwest Laboratory Report PNL-3802 (1981).

Mendel-1981B

J. E. Mendel, Nuclear Waste Materials Handbook, DOE/TIC 11400 (1981).

Seitz

M. G. Seitz, Repository-Analog Experiments on Nuclear Waste Leaching and Migration, presented at the Int. Symp. on Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle, Knoxville, Tennessee, July 27-31, 1981.

Taylor

R. E. Taylor, Ed., Advances in Obsidian Glass Studies, Noyes Press, Park Ridge, New Jersey (1976).

Tsong

I. S. T. Tsong, C. A. Houser, W. B. White, and G. L. Power, Glass Leaching Studies by Sputter-Induced Photon Spectrometry (SIPS), J. Non-Cryst. Solids 38, 39, 649 (1980).

Winograd

I. J. Winograd, Radioactive Waste Disposal in Thick Unsaturated Zones, Science 212, 1457 (1981).