EXPERIMENTAL HYDRATION STUDIES OF NATURAL AND SYNTHETIC GLASSES

JOHN K. BATES, TEOFILO A. ABRAJANO, JR., WILLIAM L. EBERT, JAMES J. MAZER,
AND THOMAS J. GERDING

Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439

The submitted manuscript has been authorized by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

ABSTRACT

The results of a series of hydration experiments on natural glasses (Hawaiian basalt, obsidian) and the nuclear waste glass WV-44 done to examine laboratory methods of accelerating reaction processes are summarized. The glasses were reacted in hydrothermal solution and in saturated vapor water. It was found that different reaction rates and processes were found using the differing conditions, and that laboratory efforts to accelerate and duplicate natural processes must account for the physical processes that occur naturally.

CONF-8804134--3

INTRODUCTION

DE88 011986

Of the technical issues facing the eventual licensing of a high-level nuclear waste repository, the projection of materials performance to times representative of the repository lifetime is the most difficult. Materials of interest range from the metals used in the container, to the waste forms, of which borosilicate glass will represent about 40% of the anticipated 118,000 waste containers. To help project the performance of glass in the repository environment, natural glasses have been used as analogues, and the reaction rates and alteration products that occur in nature compared with those generated in laboratory experiments. The eventual hope is to develop an experimental method that accelerates the reaction of glasses in such a manner so as to replicate long-term interactions found in nature.

This is similar to the problem facing geologists or archaeologists who wish to experimentally derive hydration rate constants that can be used to date either obsidian artifacts or natural basalts. The difference is simply whether one wishes to go forward or backward in time.

The problem of finding the best method to accelerate the reaction deserves special attention. For natural basaltic glasses, layer growth has been described in terms of both first order [1] and zeroth order [2,3] kinetics. The thickness of the palagonite layer that forms is very dependent on localized conditions, and variations of layer thickness within individual samples may make a kinetic relationship very difficult to define. Accelerated laboratory dating methods using reaction in hydrothermal fluid also refer to reaction rates that slow with time [4] or are proportional to time [5], while experiments done in vapor report $t^{1/2}$ kinetics [6].

For obsidian, hydrothermal fluid reaction yields $t^{1/2}$ kinetics, arguably matching that found in nature. However, water diffusion, ion exchange, and congruent dissolution of the glass have all been noted to occur [7-9]. Additionally, it has been reported that the reaction of obsidian is independent of the relative humidity of the burial site, but the rate of reaction is affected by the temperature and composition of the glass [10].

For both types of natural glass, most of the reported work has been done to establish an empirical relationship that fits the reaction kinetics as determined by independent methods, and not to explicitly examine the mechanism of reaction. Thus, as a basis to project the performance of waste glass, the existing data on natural glasses offers a starting point, but does not provide more than a guide to experimentation.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

JMP

The Nevada Nuclear Waste Storage Investigations (NNWSI) project is investigating the tuff beds of Yucca Mountain, Nevada, as a potential site for a high-level nuclear waste repository. This site is hydrologically unsaturated, which means that the glass, after failure of the metal container, may be contacted by either water vapor or liquid water. Temperatures could range downward from a maximum near 150°C if there were premature container failure for vapor contact, and 96°C (the local boiling point of water) for liquid contact. The lowest temperature expected would be near 37°C, the ambient temperature of the host rock. Thus, the glass could be exposed to a variety of conditions that will change with time. Such is also the case with natural glasses. The important question is what accelerated experimental method will best reproduce interactions and reaction rates expected for long exposure times.

To address this question, we have used elevated temperatures (≤240°C) and a range of conditions from hydrothermal submersion of the glass to reaction of glass in water vapor with relative humidities between 60 and 100% [11,12]. In this paper we contrast the results of these different methods as applied to a nuclear waste glass, a basaltic glass, and an obsidian.

EXPERIMENTAL

The glasses used were a prototype glass developed for the West Valley Demonstration Project referred to as WV-44, a synthetic basaltic glass modeled after Hawaiian glass [13], and a natural obsidian from Nevada. The compositions of these glasses are given in Table I.

The reactions were performed for time periods up to 182 days, at temperatures between 187 and 200°C. The hydrothermal experiments were performed in Teflon^{TM}-lined Parr reaction bombs using a SA/V (surface area of glass to volume of liquid) of 1 cm⁻¹. The reacted samples were air dried at room temperature, measured for mass change, and then analyzed using SEM/EDS/WDS, SIMS, and optical microscopy to determine the thickness and elemental profiles of the reacted portion of glass. The basaltic and waste glasses were reacted as disks that had been core drilled from bulk samples, with both faces polished to a 600 grit finish. The obsidian was reacted as both cut disks with a 0.25 μm finish and as chips flaked from the bulk sample.

TABLE I
Composition of Reacted Glasses

Glass Type	Oxide wt %											
	Si	Na	Al	Ca	Fe ^a	K	Mg	Ti	Li	B	P	Others ^b
WV-44	44.8	9.9	6.6	8.9	11.8	3.2	1.2	0.9	2.8	9.0	2.3	6.9
Hawaiian Basalt	58.7	4.6	11.8	10.6	13.1	0.7	0.7	1.9	-	-	-	
Nevada Obsidian	77.8	3.4	13.6	0.7	1.6	3.7	0.4	0.2	-	-	-	

^aFe as Fe₂O₃.

^bIncludes Ba, Co, Cr, Cs, Mn, Nd, Ni, S, Th, U, and Zr.

The vapor phase reactions were conducted using specimens prepared as described above, except that two notches were cut in the sample to allow the samples to be suspended with a Teflon^{TM} thread from a 1/16" 304L stainless steel rod that was fabricated to span the upper portion of the vessel. The glass/hanger assembly was placed in a 22 cc 304L stainless steel Parr vessel to which enough water (0.25 mL at 200°C) had been added to insure saturation of the gas phase at the reaction temperature. Steel with low impurity levels of carbon, nitrogen, and sulfur was used to lessen the effects of outgassing on the composition of alteration products. The glass/hanger assembly was preheated to temperature prior to emplacement in the vessel. This is because vapor phase reaction refers to reaction between a thin film of water that forms on the glass surface and the glass. Preheating was done to lessen the possibility of water condensing on the glass during the time when the system was being heated to temperature. It was found in earlier experiments [13,15] that without preheating a droplet of water could form on the glass. When this occurred, the droplet remained on the glass during the reaction period and the extent of reaction on such samples was not uniform. However, with preheating the normal variations in temperature ($\pm 1^\circ\text{C}$) were not great enough to result in a distinctly measurable effect.

RESULTS AND DISCUSSION

WV-44

Vapor Phase

The nuclear waste glass reacted to form a distinct altered layer penetrating into the glass with alteration products forming on the surface of the glass. A typical cross-section of the reacted glass is shown in Fig. 1. The layer thickness increased with time as shown in Fig. 2. There was an initial period where no distinct layer was observed in the SEM and no alteration products formed on the glass. However, after four days at 200°C the glass began to react more rapidly, with extensive phase formation occurring as the layer became thicker. At least seven different phases formed, including analcime, apatite, and phases that incorporate both uranium and thorium [14].

Similar reaction trends have been observed for the early generation waste glasses SRL 211 and 131. For these glasses the more rapid reaction appears to correspond to the formation of tobermorite [$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] on the glass surface [15]. However, for the waste glass PNL 76-68, no reaction products are formed on the glass surface under the conditions used to react WV-44 glass, and no distinct reaction layer is observed through 16 days of reaction [16]. This is despite the fact that PNL 76-68 glass is the least resistant of the glasses noted above when leached at 90°C.

The diversity in vapor phase reaction of the different glasses appears to be related to the chemistry of the thin film of water present at the glass surface. As the reaction proceeds, the thin film of water becomes rapidly enriched in those elements whose release can be linked to an ion exchange process, e.g., Li, Na, B. Boron is not released via direct ion exchange but appears to be released along with Li and Na as the glass matrix becomes hydrolyzed.

The hydrothermal film on the glass surface further reacts with the hydrated glass. If stable phases form, based on the chemistry of the hydrothermal "soup," the reaction can proceed. If, as in the case of tobermorite formation, a stable phase is formed which can act as a sink for released species, the reaction rate may increase. However, if no secondary phases form, the chemical potential of alkalis on the surface

Fig. 1. The Cross-Section of WV-44 Glass Reacted in (a) Vapor for 14 Days at 200°C, and (b) Hydrothermally at 200°C. Magnification 200X.

Fig. 2. Layer Thickness of Vapor and Hydrothermally Reacted WV-44 Glass (200°C); (□) hydrothermal, (●) vapor.

approaches that in the bulk glass, and the depletion of alkalis slows. It is believed that for PNL 76-68 glass, which contains low (>0.5 oxide %) amounts of aluminum compared to the other glasses, the ion exchange reaction slows because no aluminosilicate phases (e.g., analcime) are stabilized.

Hydrothermal

A distinct reaction layer also forms in the hydrothermal experiments (Fig. 1). Unlike the vapor experiments, no distinct secondary phases form on the reacted surface. The layer increases in thickness at a fairly

uniform rate (Fig. 2) and does not show the change in slope observed in the vapor experiments. Depending on the length of reaction, the layer thickness produced in the vapor experiments may exceed those formed hydrothermally. The relatively large solution volume available in the hydrothermal experiments does not provide the saturation constraints described above for the vapor phase experiments.

Hawaiian Basaltic Glass

Vapor Phase

An extensive series of hydrothermal and vapor experiments have been conducted [13]. The vapor samples generated a range of alteration products on the surface including analcime, gyrolite, thomsonite, and smectite. These phases have all been identified with naturally altered basaltic glass. The thickness of the reacted layers have recently been measured and are shown in Fig. 3. There is a wide variance in the thicknesses as a result of the slightly different experimental conditions used. In these experiments considerably more water than required to produce saturation was used, and the glass/hanger assembly was not preheated. This resulted in condensation on the glass surface and subsequent uneven reaction.

Hydrothermal

The layers that form in the hydrothermal experiments are thicker than that observed in the vapor experiments (Fig. 3) for the reaction times tested. The layers are uniform in appearance and no surface precipitates have been observed on the reacted glass surface through 182 days of reaction. The appearance of a cross-sectioned layer is similar to that shown for WV-44 glass (Fig. 1).

Nevada Obsidian

Vapor Phase

The appearance of the reacted obsidian surface as observed in a binocular microscope or with the SEM is no different from the unreacted sample. No reaction products can be identified and the sample retains its reflectant appearance. However, when the sample is thin sectioned and observed in transmitted light, the birefringent layers are sharp, intense, and easily measurable. The layer thicknesses are plotted in Fig. 4.

The surfaces were also examined using SIMS. Selected profiles are shown in Fig. 5. These profiles are representative of those taken from samples reacted between 1 and 16 days at 200°C. Sodium, silicon, and calcium are slightly enriched on the sample surface, but no depletion of any element from the glass can be detected. This is despite the observation of a continually increasing thickness in the birefringent layer. This suggests that in these experiments water was able to diffuse into the glass without resulting in marked movement of other elements.

Hydrothermal

Both prepared disks and obsidian chips were reacted hydrothermally. In the disk experiments, the surface lost its original reflectance and became covered with a white residue. This residue was enriched in Al, Ca,

Fig. 3. Layer Thickness of Vapor and Hydrothermally Reacted Basaltic Glass (187°C); (□) hydrothermal, (●) vapor.

Fig. 4. Layer Thickness of Vapor and Hydrothermally Reacted Obsidian (200°C); (□) hydrothermal disk, (Δ) hydrothermal chip, (●) vapor disk.

Fig. 5. SIMS Profiles for (a) Vapor and (b) Hydrothermally Reacted Obsidian (200°C, 16 days). The birefringent layer on sample (a) is 6 μm thick and for sample (b) is 2.5 μm.

Ti, and Fe, and produced a pattern corresponding to the dioctahedral mica celadonite and an alumino-oxy-hydroxide phase when examined with XRD. Similar alteration has also been observed by Karhanis [9], who reported muscovite on hydrothermally reacted obsidian. The white residue also

formed in the experiments done with chips, forming predominantly in regions of high stress. The weight loss of both types of samples was normalized to the sample surface area and the resultant values increased nearly linearly with time. The samples were cross-sectioned and examined with the SEM. Dissolution of the glass was clearly evident in the cracks and on the surface of the circular rims, with the residue described above remaining. Evidence for dissolution was also found on the flat surfaces, although the number of cracks penetrating into the bulk was less than on the rims.

The hydrothermally reacted surfaces were also examined with SIMS (Fig. 5b). It is evident that there is a slight depletion of Na and Si in the near surface (300 Å), but Na was not depleted throughout the region of observed birefringence. The measurements of the birefringent layers are shown in Fig. 4, where it can be seen that the layers produced in the hydrothermal reaction are thinner than those produced in the vapor reaction. Additionally, the hydrothermally layers are not as well defined or bright as those found on the vapor samples.

The experiments were repeated with the same results, which suggests that a real difference in layer thickness occurs depending on what method of accelerated reaction is used. Dissolution of the glass matrix in the hydrothermal experiments results in underestimating the actual thickness of reacted glass. Potential methods of reducing the dissolution of obsidian when performing accelerated laboratory experiments include performing the hydrothermal reaction in a silica saturated solution [17], or measuring weight gains in hydrated glass powders [18].

CONCLUSIONS

The results of vapor and hydrothermal hydration of the glass types presented indicate differences are observed in the reaction rates depending on the reaction media. For nuclear waste glasses, the vapor reaction may form layers at different rates depending on the constitution of secondary phases that form on the surface and the chemical potential gradient for each element across the glass vapor interface. When no stable reaction products are observed, the formation of an ion exchange layer is restricted, although it is possible that molecular water is still diffusing into the glass. If reaction products form which act as sinks for the released glass components, the reaction rate in the vapor reaction may be greater or less than that observed in hydrothermal solution.

For basaltic glass, the vapor reaction produces alteration products that are similar to those found in naturally altered basaltic glass, but are different from those formed via hydrothermal reaction. The layers produced in the hydrothermal reaction are always thicker than those produced in vapor. The similarity of reaction products suggests the vapor reaction may be a useful technique to accelerate basaltic glass reaction; however, a functional relationship between reaction rate and time must still be established for the vapor reaction and compared to that for natural samples.

In the case of obsidian, the birefringent layers formed in the vapor were always thicker and more clearly defined for equivalent reaction times compared to the hydrothermal samples. This difference could be attributed to dissolution of the glass matrix in the hydrothermal experiments. The implication of the obsidian results for dating artifacts is that care must be taken when conducting accelerated experiments to properly reproduce the processes that occur in nature.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Geologic Repositories, Nevada Nuclear Waste Storage Investigations Project, under Contract Number W-31-109-38.

REFERENCES

1. J. G. Moore, U.S. Geol. Survey Prof. Paper 550D, p. D163-D171 (1966).
2. J. G. Moore, D. J. Fornari, and D. A. Clague, U.S. Geol. Survey Bull. 1663 (1985).
3. M. Morgenstein and T. J. Riley, *Asian Perspectives* 17, 145 (1975).
4. H. Furnes, *Mineral. Petrol.* 50, 105-113 (1975).
5. J. L. Crovisier, J. Honnorez, and J. P. Eberhart, *Geochim. et Cosmochim. Acta* 51, 2977-2990 (1987).
6. C. D. Byers, M. J. Jercinovic, R. C. Ewing, and K. Keil, in *Scientific Basis for Nuclear Waste Management* 44, 583-591 (1985).
7. W. A. Lanford, *Science* 196, 975-976 (1977).
8. I. S. T. Tsong et al., *Science* 201, 339-341 (1978).
9. S. N. Karhanis et al., *Nature* 284, 435-437 (1980).
10. I. Friedman and F. W. Trembour, *Amer. Scientist* 66, 44-51 (1978).
11. J. K. Bates, L. J. Jardine, and M. J. Steindler, *Science* 218, 51-54 (1982).
12. J. K. Bates et al., Lawrence Livermore National Laboratory report UCRL-15801 (1988).
13. C. D. Byers, M. J. Jercinovic, and R. C. Ewing, U.S. Nuclear Regulatory Commission report NUREG/CR-4842 (1987).
14. W. L. Ebert and J. K. Bates, "NNWSI Waste Form Testing at Argonne National Laboratory, Semiannual Report, July-December 1987," in press.
15. J. K. Bates, L. J. Jardine, and M. J. Steindler, Argonne National Laboratory report ANL-82-11 (1982).
16. T. A. Abrajano and J. K. Bates, in preparation.
17. C. M. Stevenson, Archaeological and Historical Consultants, Inc., personal communication.
18. W. Ambrose, in *Advances in Obsidian Glass Studies*, edited by R. E. Taylor (Noyes Press Publishers, Park Ridge, NJ, 1976), p. 81.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.