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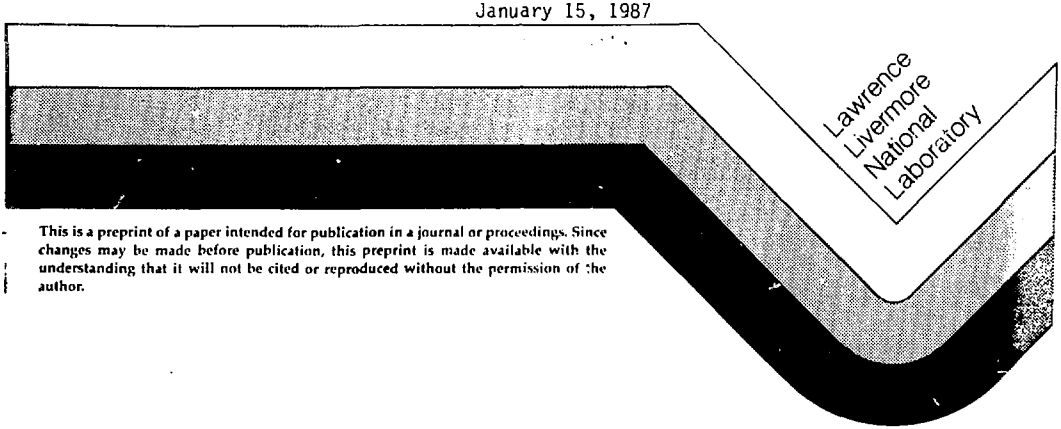

HYDROGEN SPECIATION IN HYDRATED LAYERS ON NUCLEAR WASTE GLASS

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ABSTRACT

The hydration of an outer layer on nuclear waste glasses is known to occur during leaching, but the actual speciation of hydrogen (as water or hydroxyl groups) in these layers has not been determined. As part of the Nevada Nuclear Waste Storage Investigations Project, we have used infrared spectroscopy to determine hydrogen speciations in three nuclear waste glass compositions (SRL-131 & 165, and PNL 76-68), which were leached at 90°C (all glasses) or hydrated in a vapor-saturated atmosphere at 202°C (SRL-131 only). Hydroxyl groups were found in the surface layers of all the glasses. In addition, molecular water was found in the surface of SRL-131 and PNL 76-68 glasses that had been leached for several months in deionized water, and in the vapor-hydrated sample. The water/hydroxyl ratio increases with increasing reaction time; molecular water makes up most of the hydrogen in the thick reaction layers on vapor-phase hydrated glass while only hydroxyl occurs in the least reacted samples. Using the known molar absorptivities of water and hydroxyl in silica-rich glass the vapor-phase layer contained 4.8 moles/liter of molecular water, and 0.6 moles water in the form hydroxyl. A 15 micrometer layer on SRL-131 glass formed by leaching at 90°C contained a total of 4.9 moles/liter of water, 2/3 of which was as hydroxyl. The unreacted bulk glass contains about 0.018 moles/liter water, all as hydroxyl.

The amount of hydrogen added to the SRL-131 glass was about 70% of the original Na + Li content, not the 300% that would result from alkali-hydronium ion (H_3O^+) interdiffusion. If all the hydrogen is then assumed to be added as the result of alkali-H^+ interdiffusion, the molecular water observed may have formed from condensation of the original hydroxyl groups according to:

$$2OH = H_2O \text{ molecular} + O^0$$

where O^0 refers to a bridging oxygen, and OH refers to a hydroxyl group attached to a silicate polymer. The hydrated layer on the nuclear waste glasses appears to be of relatively low water content (4 to 7% by weight) and is not substantially hydroxylated. Thus, these layers do not have many of the properties associated with "gel" layers.

INTRODUCTION

The concept of a "gel" layer forming on nuclear waste glass after reaction with water has been broadly accepted (e.g. [1]), and is an important part of discussions of waste glass leaching presented in several other papers in this symposium [2,3]. The gel layer is widely believed to be hydrated, of low density, and depleted in soluble components, particularly alkalis. The depletion in alkalis is thought to occur through exchange of hydrogen from solution. If this were the only mechanism for hydration and the hydrogen was not introduced as a complex such as H_3O^+, the gel layer would contain only hydroxide,

and at the same concentrations as the original alkali elements. In this paper we discuss the speciation of hydrogen in the gel layer, as determined by infrared (IR) spectroscopy. This work was conducted as part of glass waste form testing (Waste Package task) for the Nevada Nuclear Waste Storage Investigations project.

EXPERIMENTAL

The speciation of hydrogen in glasses and silicate solids may be readily determined by infrared spectroscopy [e.g. 4-9]. Figure 1 shows a typical spectrum for a hydrated silica-rich glass, in the regions providing the most information about hydrogen speciation. The absorptions at 4300-4600 and 5200 cm^{-1} are the most useful in determining hydrogen speciation, as they are uniquely due to hydroxyl and water, respectively. The exact location of the hydroxyl absorption varies slightly as a function of its local environment [4]. The absorptions at 3500 cm^{-1} are intense (Figure 2), and are useful in determining total water content (irrespective of speciation) in relatively dry glasses where the near-infrared absorptions are not intense enough to use quantitatively. The absorption at 1620 cm^{-1} due to molecular water requires care in use, because of underlying absorptions due to the anhydrous glass.

Infrared spectra presented in this paper were obtained using a Nicolet 60SX Fourier transform infrared spectrometer, with a Hg-Cd-Te Liquid N_2 cooled detector and a KBr beamsplitter. Transmission spectra were obtained in the normal sample compartment, and in a highly-focused (f 1.0) microbeam compartment. Stainless steel apertures were placed in contact with the samples to restrict light to only the region desired. Spectra were also obtained by diffuse reflectance using the Barnes-Nicolet diffuse reflectance apparatus, with an aluminum surface-coated mirror as the reference. In this technique, parabolic mirrors focus and re-collect reflected light from a large solid angle

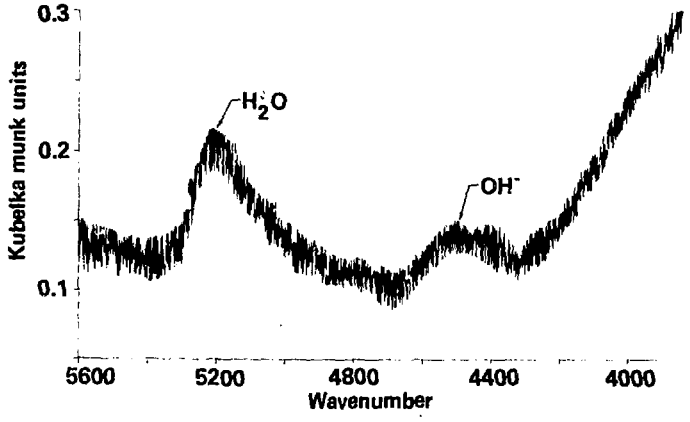

Figure 1. Near-Infrared spectrum of hydrated ATM 1-c glass. The absorption at 4500 cm^{-1} is assigned to combined oxygen-hydrogen stretch and wagging of hydroxyl (X-OH); the absorption at 5200 cm^{-1} to combined stretching and scissoring of molecular water. Diffuse reflectance on powder, reacted in DIW 28 days S/V=4/cm at 90°C.

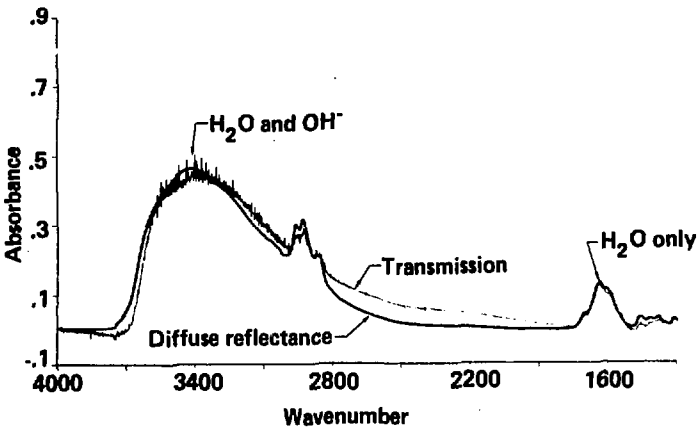

Figure 2. Comparison of the infrared transmission and diffuse reflectance spectra of a thin flake of a hydrated layer from SRL-131 glass, hydrated in DIW under MCC-1 conditions (90°C, S/V=0.1/cm) for 183 days. The absorption at 1620 cm^{-1} is assigned to the scissor (bending) motion of molecular water; the absorption at 3500 cm^{-1} to oxygen-hydrogen stretching in both hydroxyl and molecular water. Light path was parallel to the layer growth direction, thickness 15 μm. Kubelka Munk data have been scaled to match the intensity of the absorbance data at 3500 cm^{-1}; Kubelka Munk intensity was 2.3 units.

[10]. Diffuse reflectance spectra are reported in Kubelka-Munk units (inversely proportional to the square of the reflected light intensity) which are proportional to the amount of absorbing species in a similar, but less rigorous, fashion as the Beer-Lambert law for transmission [10]. Glass samples used for both methods are held in a dry N_2 atmosphere during the measurement and are never subjected to vacuum. Similar samples subjected to high vacuum during nuclear reaction analysis [2] show minor dehydration. This suggests that our samples have not dehydrated significantly, but we cannot rule out some water loss.

Transmission spectra have been shown to provide quantitative information on both hydrogen speciation and concentration in glasses [5-9]. However, most hydrated layers are too thin to separate for transmission analysis. Diffuse reflectance has the advantage of requiring no sample preparation. Diffuse reflectance spectra have not previously been used for quantitative measurements because the path length through the sample is poorly constrained due to surface irregularities. Absolute measurements of the resulting absorption in diffuse reflectance are not used in this paper. However, in a single sample the light path is similar for all infrared and near-infrared wavelengths, leading to the possibility that in a single sample the relative peak heights of the absorptions shown in Figure 1 will be quantitatively maintained. Two tests of this were made. In the first (Fig. 2), the quantitative IR transmission spectrum of a separated 15 μm thick flake from a hydrated layer was compared to the diffuse reflectance spectrum of the same sample. The relative peak heights in

the infrared region were maintained within experimental error. Thus, diffuse reflectance may be used to determine water/hydroxyl ratios in hydrated layers.

In a second test of diffuse reflectance, natural hydrous obsidian samples previously studied [9] by transmission spectroscopy and hydrogen manometry were used. These samples, unlike the reacted nuclear waste glasses, contain water uniformly throughout the glass. They are the result of equilibrium hydration of silicate melts at high pressures [6,9,11]. Diffuse reflectance was able to reproduce the ratios of water to hydroxyl, as measured by the ratio of the 5200 cm^{-1} absorption to that at 4500 cm^{-1} (Figure 3). The scatter in the diffuse reflectance data is quite noticeable in comparison to the transmission data (both were run on the same machine). This scatter appears to be due to errors in baseline subtraction. Figure 4 shows a typical spectrum used for this test; the curvature of the background is due to instrumental factors (above 5000 cm^{-1}) and the tail of the very intense infrared absorption (below 5000 cm^{-1}). It is anticipated that the scatter may be eliminated by better baseline subtraction techniques, but we cannot rule out the possibility that there are small systematic differences in the relative intensities in diffuse reflectance and transmission work. Figure 3 indicates that errors of ±20% in the H_2O/OH ratio are to be expected.

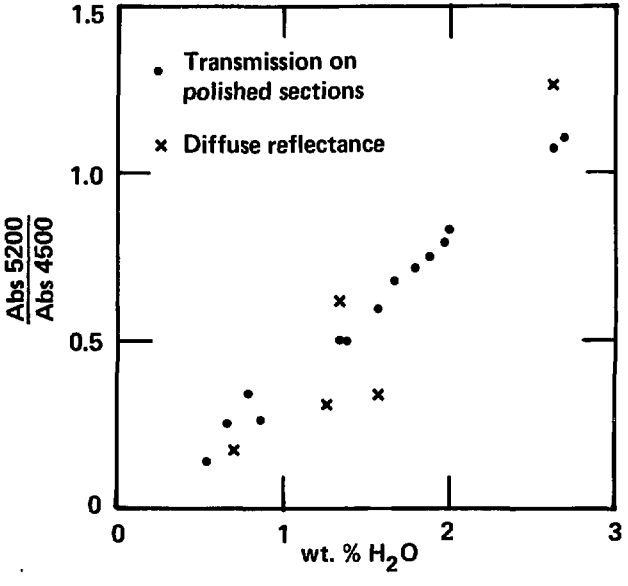

Figure 3. Comparison of peak ratios obtained from transmission spectroscopy [9] on natural hydrous obsidians, with that obtained from diffuse reflectance on samples from the same suite. Wt. % H_2O obtained by hydrogen manometry [9] is independent of both spectroscopic methods.

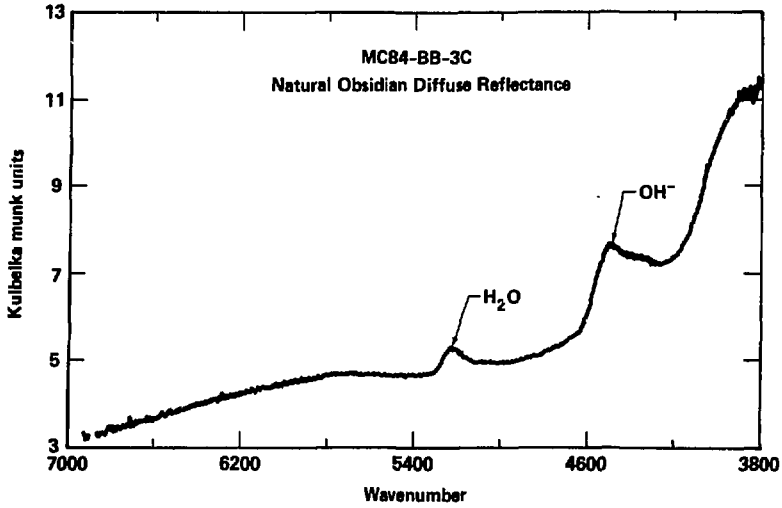

Figure 4. Diffuse reflectance spectrum of a natural hydrous obsidian sample containing 1.59% total H_2O, used in study [9]. One layer of 200-300 μm grains was used on a surface aluminized mirror, with the mirror as reference. Sample MC-BB-3C, [9].

RESULTS

SRL-131 glass. Two samples of hydrated SRL-131 glass were studied. The first was hydrated for 20 days at 202°C in a water vapor saturated atmosphere [12,13]. This resulted in a hydrated layer about 70 μm in thickness. This layer was studied in cross section, along with the adjoining (visibly unaltered) glass. The near-infrared spectrum obtained is shown in Figure 5. Molecular water (at 5200 cm^{-1}) is the dominant hydrogen species in this layer; hydroxyl is considerably less intense at 4350 cm^{-1}. The broader absorption seen in the ATM 1-C sample (Figure 1) for hydroxyl, from 4350-4500, indicates that hydroxyl environments are not identical in these leached glasses. Molar absorptivities (Beer-Lambert law absorptivities) are not highly variable in natural hydrous glasses [9]. Therefore we can use the molar absorptivity values (as H_2O) determined by Newman et al. [9] to estimate the quantities of water and hydroxyl in this layer. Their value of 1.61 (liters/mol-cm) yields 4.8 moles/liter molecular water from the 5200 cm^{-1} absorption; for hydroxyl their value of 1.73 (liters/mol(H_2O)-cm) yields 0.6 moles/liter water in the form hydroxyl (1.2 moles/liter of hydroxyl) from 4350 cm^{-1} absorption. The transition from the bulk glass to the hydrated layer is optically sharp in the visible region, and a similar result was seen in the infrared. No increase in water content is seen in the bulk glass (at a resolution of 35 μm) until the optically determined layer is reached. The water content of the unaltered glass could be determined from the absorption at 3500 cm^{-1}. Using Newman et al.'s [9] value for hydroxide absorptivity (100 liters/mol(H_2O)-cm) yields a hydroxyl content of 1.07×10^{-2} moles(H_2O)/liter.

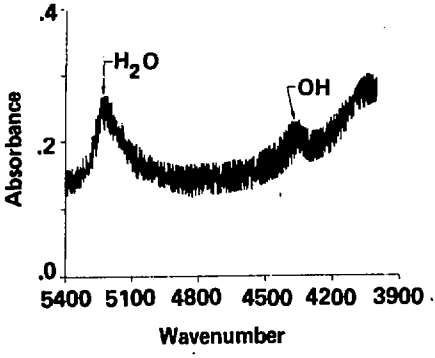

Figure 5. Transmission near-infrared spectrum of hydrated layer on SRL-131 glass formed by vapor hydration, 20 days at 202°C [12]. Layer observed in cross section at center of layer, using 35 μm aperture, sample 147 μm thick.

Infrared spectroscopic data only determine the number of absorbing species per unit volume. However, we can estimate the density of the hydrated layers to determine wt. % water. If the layer's density is 2.5 g/cc, the bulk glass contains less than 0.01 % H_2O, and the hydrated layer contains about 3.5% H_2O as molecular water, and 0.4 % H_2O as hydroxyl. The final result of vapor phase hydration was the addition of mostly molecular water to the glass.

A second SRL-131 sample that had been leached in deionized water under MCC-1 conditions (90°C S/V=0.1/cm) for 182 days [14] was examined by removing the hydrated layer with a razor blade. The layer flaked off easily. The transmission and diffuse reflectance mid-infrared spectra of this layer are shown in Figure 2. An area of about 3 mm^2 was examined in this measurement. This sample was too thin to determine water/hydroxyl ratios from the near infrared bands at 5200 and 4350 cm^{-1}. However, the 1600 cm^{-1} band may be used to determine water content, and the 3500 cm^{-1} band is proportional to the sum of water and hydroxyl. Again using Newman et al.'s values [9], the 1600 cm^{-1} intensity indicates 1.5 moles/liter molecular water, and the 3500 cm^{-1} band indicates a total water content of about 2.13 moles/liter as hydroxyl, taking into account the 1.5 moles/liter present as water determined from 1600 cm^{-1} absorption. The absorption intensity at 1600 cm^{-1} is a maximum value. There are typically minor absorptions from silicate overtones in this region [4,6] which may be contributing to the intensity in this region, but no accurate baseline is available because of the possibility that the silicate overtones are different in the hydrated glass and the anhydrous glass.

SRL-165 Glass. A suite of glass wafer samples used for static leach testing by Bazan and Rego [15] and similarly prepared unreacted samples were examined using diffuse reflectance. These samples were tested at temperatures of 90°C in DIW and J-13 water and S/V values ranging from 0.3 to 4/cm; the extent of reaction was not large (less than 8.5 g/m^2 after 56 days in DIW) [15]. Only hydroxyl is detectable in these samples. Surfaces of unreacted wafers that had been saw-cut or

polished in water showed absorption at 3500 cm^{-1}, while those that were prepared equivalently but using Buehler™ polishing oil showed no absorption. This indicates that initial hydration of the glass takes place during preparative procedures used for leach testing. The surface of one of these water-prepared wafers gave an absorption at 3500 cm^{-1} of 0.21 Kubelka-Munk units. After reaction for periods ranging from 14 days at SA/V=0.5/cm to 56 days at 0.3/cm, the absorbances ranged from 0.40 to 0.47 Kubelka Munk units. It appears that a significant amount of the total hydration occurred during sample preparation, and that the thickness of the hydrated layer changes only very slowly during leaching of this glass at elevated temperature. This confirms the small extent of reaction determined by normalized loss [15] and SEM examination of the surfaces [14]. Because we have not calibrated the absolute reflectance values as a function of water content, it is not possible to determine the amount of water that is present in these layers, but it is all in the form hydroxyl.

ATM-1c Glass. ATM-1c is a PNL 76-68 based glass that was originally designed as a reference glass for commercial high-level waste [16]. We studied both powder and wafer samples that were reacted in DIW and J-13 water [F. Bazan and J. Rego, unpublished]. An infrared spectrum of the powdered glass reacted in DIW was shown in Figure 1. In these powders, the total water content increased as a function of reaction time in DIW (Figure 6). Initially the added water was in the form hydroxyl (3 days at S/V=4/cm, DIW at 90°C). However, by 28 days, the water added to the glass, as determined from the absorptions in the Near Infrared (Figure 1), is predominantly molecular water with about 1/3 of the total occurring as hydroxyl. Similar results were found for reacted wafers, although these samples proved to be more difficult to study due to the relatively small surface area compared to the powders. In J-13 water (a silicate/carbonate ground water), however, there was no measurable addition of molecular water, and only a small (10%) increase in hydroxyl. This is in accord with the low reactivity of this glass in J-13 water.

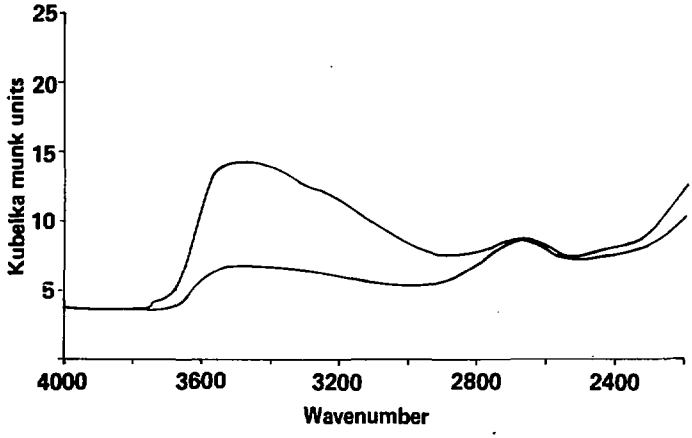

Figure 6. Diffuse reflectance spectra of two leached ATM-1c powders. Bottom ; 3 days, Top; 28 days. SA/V=4/cm, DIW at 90°C. Top is same sample as in Figure 1.

DISCUSSION

Previous Work

Previous studies of the hydration process of glass have proceeded along two paths of inquiry. The first has examined the process of hydration layer formation, and the concomitant loss of alkali elements in those layers. The second approach has emphasized the study of water in melts, and the hydrous glasses quenched from them. These two approaches have yielded fundamentally different interpretations of the nature of hydrated glass, which must now be reconciled.

The hydrogen and alkali distribution in hydrated layers on glass was conclusively determined experimentally in a series of studies using depth profiling techniques [18,19,20]. These studies supported the interdiffusion theory of hydration, which has become known as the Doremus model [e.g. 20, 21]. In this theory, hydration proceeds through the exchange of hydrogen or hydronium ion from solution, for sodium (or other alkalis) in the glass. Experimental determination of smooth diffusion profiles for both participants strongly supports this mechanism. In many alkali-silicate glasses, hydrogen replaces alkalis at a ratio of three hydrogens to one alkali; however, other ratios as low as one are also found [20,21]. The depletion of sodium matches the increase in hydrogen as the layer forms, but the rate of hydration is found to be entirely dependent on hydrogen, which has a diffusion coefficient 3 orders of magnitude smaller than sodium [20] and controls the rate of interdiffusion.

The interdiffusion mechanism replaces sodium with a hydrogen ion species. However, it is also well known that glasses can contain molecular water ([5,6,7,8] and this work). In silicate melts, it has been conclusively demonstrated [6,11] that water, hydroxyl, and bridging oxygens exist in an equilibrium described by:

$$H_2O\text{molecular(melt)} + O^0\text{(melt)} = 2OH\text{(melt)} \qquad (1)$$

where O^0 refers to a bridging oxygen, and OH refers to an OH group attached to a silicate polymer. The equilibrium constant for this equilibrium is:

$$K = \frac{(a^m_{OH})^2}{(a^m_{H2O,mol})\,(a^m_O)} \qquad (2)$$

where a^m_{OH}, $a^m_{H2O,mol}$ and a^m_O refer respectively to the activities of hydroxyl groups, molecular water, and bridging oxygens in the melt. This equilibrium constant has been found to be equal to approximately 0.2 [6,9,11]. In a relatively siliceous melt (~40 to 80% SiO_2), the initial "water" added in hydration goes in as hydroxide. The amount of molecular water increases until it is equal to hydroxide at about 2 % (by wt.) in typical natural melts. At higher water concentrations, hydroxyl addition slows dramatically (as all bridging oxygen sites are used) and additional water enters in the form molecular water [11].

Although the study of hydrogen speciation in silicate melts has been largely conducted on glasses quenched from those melts, there have also been equivalent studies of water solubility in glasses below their softening point [5,7]. In these studies, identical behavior to that

described by equations (1) and (2) was observed. A notable study in this area was of the hydrogen speciation in colloidal silica gels as a function of heat treatment [8]. In this study, spectra which are nearly identical to those presented in this paper in both peak appearance and relative intensities were observed in pure silica gels, with initial water/hydroxyl ratios of about 2:1 decreasing as a function of temperature as the gels were gradually heated and dehydrated. Detailed assignments of spectral features to possible silica-water organizations are given. Although the equilibrium shown in (2) is not quantified in [8] for silica gel, the effects of the equilibrium are discussed in terms of structural changes in the gel. The very similar spectral characterization of silica gels, and hydrated glass layers, indicates they share some structural characteristics.

In summary, a number of excellent previous studies of the hydrated layers on alkali-silicate and nuclear waste glasses suggest that hydration occurs by alkali-hydrogen interdiffusion [1,3,18,19,20,21]. At the same time, studies of the actual speciation of hydrogen in hydrated glasses, including this study, have shown that molecular water is an important hydrogen species. This has not been previously demonstrated for nuclear waste glasses. The amount of molecular water increases relative to hydroxyl as a function of total water content in the SRL-131 and ATM 1-C glasses, and we infer that the absence of molecular water in the SRL-165 glasses is due to their limited extent of reaction, and hence hydration. There is experimental evidence that equations (1) and (2) apply to all hydrated glasses, and sound theoretical arguments may be made to that affect as well [11].

Properties of Hydrated Layers

We believe that the experimental evidence presented and discussed here is consistent with a mechanism whereby nuclear waste glasses, and possibly other alkali silicate glasses, hydrate by alkali-hydrogen interdiffusion. The hydrogen thus introduced into the very silica-rich outer layer then re-equilibrates, according to equations (1) and (2). Note that both these processes conserve charge within the hydrated layer. The actual diffusing species in the alkali-hydrogen interdiffusion has been suggested to be hydronium ion [20,21] based on a frequently observed ratio of 3 hydrogens added for each alkali removed. However, this ratio is also frequently violated ranging as low as 1:1 in previous work [21]. In reference [2] the ratio is approximately 2:1. In the SRL-131 glasses in this study, the ratio is about 0.7:1 (considering only Na and Li). Hydronium is not a common species in solids, and has only been identified as a stable species in crystalline hydrates of strong acids [4]. The spectroscopic evidence presented here may be adequately accounted for by a mixture of water and hydroxyl groups, in a very similar fashion to [5,6,7,8]. It is possible that hydronium is an intermediate species in the diffusion process, or that its spectroscopic manifestations are not distinct in this system. However, there is no direct evidence for its presence.

If hydronium ion were the diffusing species, it could yield a hydroxyl group and molecular water in the hydrated layer, implying a constant ratio of hydroxyl to water of 1:1. However, it is likely that the equilibrium of eqs. (1) and (2) would cause the water to react to form hydroxyl at low concentrations, while at high concentrations hydroxyl would react to form water. If K=0.2 in eq. (2), the crossover would occur at the point where H_2O and OH^- are at the same concentration at equilibrium, or about 3 to 4% H_2O by wt. [11]. This

would result in a glass undergoing first hydrolysis, then condensation, of Si-O-Si linkages as a function of hydration. However, if all hydrogen is added as hydroxyl (i.e. the diffusing species is H^+), then the initial interdiffusion would result in a hydroxyl-rich layer, in which equilibrium according to (1) would be achieved by the reaction proceeding to the left, with precipitation of molecular water and a net condensation of the silicate framework. This condensation would occur for any value of the equilibrium constant K in eq. (2), because there is no water initially in the glass and all hydrogen would be added in the form of hydroxyl. For values of K similar to those observed in nature and in the high temperature (>300°C) hydration of alkali silicate glass, (around 0.2), the number of Si-O-Si linkages would increase substantially in this case. The exact number is equal to the number of water molecules, as presented in this paper (1.5 moles/liter in the MCC-1 leached SRL-131 glass).

We do not currently have enough evidence to establish the nature of the interdiffusing species. It is possible that the overall hydrogen stoichiometry is intermediate or variable. Detailed hydrogen profiling as in [2] must be combined with IR spectroscopy to attempt to resolve this; samples will be frozen after hydration to prevent loss of water. However, the low ratio of hydrogen added to alkali removed precludes H_3O^+ from being the dominant added species in the SRL glasses. The hydroxyl contents of the two SRL glasses are also nearly the same, despite the large difference in total water. This is predicted by the equilibration reaction (1); at high water contents, the hydroxyl content changes very slowly relative to H_2O [6,11]. We conclude that hydronium ion (H_3O^+) is not required to explain our results.

Since silicate glasses and melts may be induced to hydrate at high temperatures and pressures without loss of alkalis, i.e. by simple diffusion of water into the glass, it may be questioned whether that process occurs at a significant rate at the lower temperatures and pressures of interest here. This appears unlikely, due to the very low chemical diffusion coefficient for molecular water [20,21,22]. Even if initial hydration by simple diffusion occurs, hydration by interdiffusion would be 3 orders of magnitude more rapid. However, hydration in water vapor may not allow complete removal of alkalis, hindering interdiffusion and aiding simple diffusion. Also, simple diffusion may occur at a higher rate in glass already hydrated by interdiffusion.

The total water content (molecular and hydroxyl) of the nuclear waste glass layers in this study is not great, ranging up to 4% (by wt.) in the vapor-hydrated sample. This value is approximate since it is calibrated only against natural hydrous glasses. Comparison of natural and man-made hydrous glasses [6,9] suggests that molar absorptivities could vary by as much as 50%, yielding maximum values of 2-6% water by weight in our SRL-131 samples. A determination by weight loss in a similarly treated sample yielded about 7 % weight loss [14]. In reference [2], a nuclear profiling study of a hydrated layer in SRL-165 glass yielded a total hydrogen content approximately equal to twice the original alkali content of the glass (on a per atom basis), equivalent to about 11 wt % H_2O. (A total of about 6×10^{-3} moles/gram alkali, converted to half that number of moles H_2O per gram.) Thus it does not appear that hydrated layers on nuclear waste glass contain the large amounts of water associated with a gel (20% or greater), and their densities should only be slightly less than that of the original glass.

CONCLUSIONS

The hydrated outer layer of a leached nuclear waste glass contains substantial amounts of molecular water, up to several times as much water as hydroxyl. The amount of total water, and the ratio of water to hydroxyl, increases as a function of reaction time. This process is consistent with the alkali-interdiffusion concept of glass hydration, followed by which the introduced hydrogen re-equilibrates with the silicate framework.

It is an interesting observation that PNL 76-68 glasses hydrate more slowly, and yet are less durable, than SRL-131 and 165 glasses [13,14]. The nature of the hydrated layer on the SRL glasses may be partly responsible for this difference. Because of the necessary condensation of the silicate framework at high water contents regardless of the actual diffusing species, H^+ or H_3O^+, the hydrated layer on a waste glass may be more resistant to dissolution rather than less resistant, as has been commonly assumed.

ACKNOWLEDGMENTS

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REFERENCES

1. J.E. Mendel, (compiler) Final Report of the Defense High Level Leaching Mechanisms Program, Pacific Northwest Laboratory, Report PNL 5157 (1984).
2. D.L. Phinney, F.J. Ryerson, V.M. Oversby, W.A. Lanford, R.D. Aines, and J.K. Bates, Integrated testing of the SRL waste form. This volume.
3. T.A. Abrajano and J.K. Bates, Transport and Reaction Kinetics at the Gel: Glass Transition Zone: Results of Repository-Oriented Experiments. This volume.
4. R.D. Aines and G.R. Rossman, Water in minerals? A peak in the infrared. Journal of Geophysical Research 89, 4059-4071, (1984).
5. R.F. Bartholomew, B.L. Butler, H.L. Hoover, C.K. Wu, Infrared spectra of a water-containing glass. Journal of the American Ceramic Society 63, 481-485.
6. E. Stolper, Water in silicate glasses: an infrared spectroscopic study. Contributions to Mineralogy and Petrology 81, 1-17 (1982).
7. D.R. Wolters and H. Verweij, The incorporation of water in silicate glasses. Physics and Chemistry of Glasses 22, 55-61 (1981).
8. D.L. Wood, E.M. Rabinovich, D.W. Johnson, Jr., J.B. MacChesney, E.M. Vogel, Preparation of high-silica glasses from colloidal gels: III, Infrared spectrophotometric studies. Journal of the American Ceramic Society, 66, 693-699 (1983).
9. S. Newman, E.M. Stolper, S. Epstein, Measurement of water in rhyolitic glasses: Calibration of an infrared spectroscopic technique. American Mineralogist, 71, 1527-1541 (1986).
10. R.N. Clark and T.L. Roush, Reflectance spectroscopy: Quantitative analysis for remote sensing applications. Journal of Geophysical Research 89, 6329-6340, (1984).

11. E. Stolper, The speciation of water in silicate melts. Geochemica et Cosmochemica Acta 46, 2609-2620.
12. J.K. Bates, L.J. Jardine, M.J. Steindler, The Hydration Process of Nuclear Waste Glass: An Interim Report. Argonne National Laboratory, Report ANL-82-11 (1982).
13. F.E. Diebold and J.K. Bates, Glass-water vapor interaction. American Ceramic Society, Proceedings, 1986, in press.
14. J.K. Bates, unpublished.
15. F. Bazan, and J. Rego, Parametric Testing of a DWPF Glass. Lawrence Livermore National Laboratory, Report, UCRL 53606.
16. J.W. Wald, Fabrication and Characterization of MCC Approved Testing Material - ATM-1 Glass. Pacific Northwest Laboratory, Battelle Memorial Institute, Report PNL-5577-1, (1985).
17. J.M. Delany, Reaction of Topopah Spring Tuff with J-13 Water: A Geochemical Modeling Approach Using the EQ3/6 Reaction Path Code. Lawrence Livermore National Laboratory, Report UCRL-53631, (1985).
18. I.S.T. Tsong, C.A. Houser, S.S.C. Tong, Depth profiles of interdiffusing species in hydrated glasses. Physics and Chemistry of Glasses 21, 197-198, (1980).
19. C.A. Houser, J.S. Herman, I.S.T. Tsong, W.B. White, W.A. Lanford, Sodium-hydrogen interdiffusion in sodium silicate glasses. Journal of Non-Crystalline Solids 41, 89-98 (1980).
20. W.A. Lanford, K. Davis, P. Lamarche, R. Groleau, R.H. Doremus, Hydration of soda-lime glass. Journal of Non-Crystalline Solids 33, 249-266 (1979).
21. R.H. Doremus, Diffusion-controlled reaction of water with glass. Journal of Non-Crystalline Solids 55, 143-147 (1983).
22. M. Nogami, and M. Tomazawa, Diffusion of water in high silica glasses at low temperature. Physics and Chemistry of Glasses 25, 82-85 (1984).

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