CONF 921101--76

RECEIVED BY
MAIL ROOM

EFFECTS OF RADIATION EXPOSURE ON GLASS ALTERATION IN A STEAM ENVIRONMENT*

D. J. Wronkiewicz,¹ L. M. Wang,² J. K. Bates,¹ and B. S. Tani¹

¹Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439-4837.

²Dept. of Geology, University of New Mexico, Albuquerque, NM 87131.

ANL/CMT/CP--76240

DE93 006419

The submitted manuscript has been authored 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.

Submitted to
1992 Fall Materials Research Society Meeting
Scientific Basis for Nuclear Waste Management Symposium
Boston, MA
November 30-December 4, 1992

*Work supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under Contract W-31-109-ENG-38.

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.

INDEXED

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

EFFECTS OF RADIATION EXPOSURE ON GLASS ALTERATION IN A STEAM ENVIRONMENT

D. J. Wronkiewicz,* L. M. Wang,** J. K. Bates,* and B. S. Tani*

*Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439-4837.

**Dept. of Geology, University of New Mexico, Albuquerque, NM 87131.

ABSTRACT

Several Savannah River Plant (SRL) glass compositions were reacted in steam at temperatures of 150 to 200°C. Half of the tests utilized actinide-doped monoliths and were exposed to an external ionizing gamma source, while the remainder were doped only with U and reacted without gamma exposure. All glass samples readily reacted to form secondary mineral phases within the first week of testing. An *in situ* layer of smectite initially developed on nonirradiated SRL 202 glass test samples. After 21 days, a thin layer of illite was precipitated from solution onto the smectite layer. A number of alteration products including zeolite, Ca-silicate, and alkali or alkaline earth uranyl silicate phases were also distributed over most sample surfaces. In the irradiated SRL 202 glass tests, up to three layers enveloped rounded, and sometimes fractured, glass cores. After 35 to 56 days these remnant cores were replaced by a mottled or banded Fe- and Si-rich material. The formation of some secondary mineral phases also has been accelerated in the irradiated tests, and in some instances, the irradiated environment may have led to the precipitation of a different suite of minerals. The alteration layer(s) developed at rates of 2.3 and 32 $\mu\text{m}/\text{day}$ for the nonirradiated and irradiated SRL 202 glasses, respectively, indicating that layer development is accelerated by a factor of ~ 10 to 15X due to radiation exposure under the test conditions.

INTRODUCTION

Radiation may affect the long-term performance of waste glass in an unsaturated repository environment by inducing radiation damage to solid materials and by interacting with air, water vapor, or liquid water to produce a variety of radiolytic products, including nitrogen and carboxylic acids, hydrogen peroxide, and radical species such as $\text{HO}_2^\bullet$ and O_2^- [1-4]. The radiolytic products may influence glass stability by altering the solution pH, Eh, or by complexing with radionuclides and glass components. A summary review of radiation tests conducted with glass samples completely immersed in liquid water indicates that radiolysis has a minimal impact on glass reactivity [5 and references cited therein]. A single study of glass alteration in an irradiated vapor environment has identified the formation of deposits enriched in Mo and Ba, but direct comparisons between reactions in irradiated and nonirradiated environments were not made [6].

The present set of experiments examines the effects of radiation on glass reactions in a geologically unsaturated environment, such as that expected to exist at the potential Yucca Mountain Site, Nevada. In this type of environment, radiolytic product concentrations may rapidly increase in the limited quantities of water contacting the glass. Previous studies have demonstrated that nitric and organic acids are produced in both alpha and gamma irradiated air + water vapor systems [5]. In such a scenario, the pH buffering capacity of bicarbonate in the thin film of water contacting the sample may be rapidly overwhelmed by the condensation of radiolytically produced acids. The resultant pH decrease may accelerate glass alteration rates [7] and affect the stability of some secondary mineral phases.

EXPERIMENTAL

Sample disks were prepared by cutting ~1 x 10 mm wafers from SRL 131, SRL 165, and SRL 202 glass and polishing the disks to a 600-grit finish prior to testing. For the irradiated tests, the glass monoliths were doped with Tc-99, and actinides (Np-237, U-238, Pu-239, Am-241) at levels approximating 23 $\mu\text{Ci/g}$ total activity (designated 131A, 165A, 202A tests) [5]. Glass used in the nonirradiated tests were doped with only U-238 (designated 131U, 165U, 202U tests).

Irradiated and nonirradiated samples were suspended via Pt-Rh and Teflon wires, respectively, inside 22 mL stainless steel reaction vessels (Figure 1). Enough deionized water was added to saturate the air inside the heated vessel, but not cause solution runoff from the suspended sample. The actinide + Tc-99 doped samples were also exposed to an external gamma dose rate of ~3500 rad/hr., thereby subjecting these samples to an internal alpha-beta and external gamma source. This dose rate was chosen as an upper bounding condition and is used to evaluate whether the potential exists for radiation to affect glass reactions. Cumulative gamma exposures for the 56 day tests were $\sim 5 \times 10^6$ rads.

A comparison between the alteration patterns of irradiated vs. nonirradiated samples is used in this study to evaluate the influence of radiation on the stability of glass. An abbreviated experimental matrix for the tests appears in Table I. The elevated temperatures used in these tests (150 to 200°C) exceed those that may be expected for glass waste in an actual repository. These high temperatures were used to accelerate glass reactions based on the premise that the glass reaction mechanism in water vapor remains unchanged within the range of 70 to 240°C [8].

Investigations focused on measuring the thickness of the alteration layer and identifying the sequence of secondary precipitates that developed on the glass surface. The altered sample surfaces were examined using a variety of analytical techniques including optical microscopy, scanning electron microscopy /energy dispersive spectroscopy (SEM/EDS), X-ray diffraction (XRD), and analytical electron

Figure 1. Experimental apparatus used to test glass samples in vapor

Table I
Experimental Matrix. All tests were run in duplicate.

Glass Type*	Temperature (°C)	Test Length (days)	Dose Rate (rad/hr)
202U	200	7, 14, 21, 35, 56	None
165U	200	7, 14, 21, 35, 56	None
131U	150	3, 5, 7, 14, 21, 35, 56, 91, 182	None
202A	200	7, 14, 21, 35, 56	3500
165A	200	7, 14, 21, 35, 56	3500
131A	150	7, 14, 21, 35, 56	3500

*Based on SRL 202, SRL 165, and SRL 131 glass. "U" denotes U-238 doped, and "A" denotes Tc-99, Np-237, U-238, Pu-239, and Am-241 doped glass.

microscopy (AEM). This combination of techniques was diagnostic in identifying many of the mineral phases present on the nonirradiated test samples. Examinations of actinide + Tc-99 doped samples were limited to optical and SEM/EDS analysis. Phase identification for these samples was based partly on knowledge gained during previous examinations of nonirradiated samples.

RESULTS AND DISCUSSION

Both the nonirradiated and irradiated samples rapidly developed an *in situ* alteration layer and a ubiquitous cover of precipitates that formed as the solution contacting the glass became saturated with leached components.

Layer Formation

The irradiated 202A monoliths had completely reacted through their 0.7 to 0.9 mm thicknesses within the first 14 days of testing, suggesting a maximum localized glass reaction rate of 32 $\mu\text{m}/\text{day}$ (Figure 2). The alteration layer progressed nonuniformly into these samples with rapidly developed alteration fronts occurring along preferential zones (fractures?) that completely enveloped rounded and apparently unaltered glass cores. In some regions the remnant cores remained intact, while in others they were highly fractured, but otherwise appeared unaltered during optical examination. It is not known for certain whether the fracturing is related to release of thermal stresses incorporated during sample casting, due to stresses induced by water diffusion into the glass, or a result of radiation damage to the glass. Radiation damage is the least plausible explanation because damage zones would be expected to be uniformly distributed throughout the samples and the $\sim 10^6$ rads of cumulative dose these samples received is two to three orders of magnitude less than that suggested to cause structural damage [9,10]. Therefore, either sample casting or water diffusion related stresses appear to be responsible for glass fracturing.

After 35 days the remnant glass cores in the 202A tests were completely replaced by a mottled or banded textured, microcrystalline, Si- and Fe-rich material (Figure 3a). This complete transformation of the glass prior to 35 days indicates a minimum glass alteration rate of 19 $\mu\text{m}/\text{day}$. Up to three additional layers enveloped this Si-Fe core, with some of the layers also displaying a banded texture. The layer

Figure 2
Average alteration layer thicknesses for 202A and 202U glasses. The 202A glass was exposed to an external gamma dose rate of ~3500 rads/hr while the 202U glass was reacted without any external radiation. Brackets indicate layer measurements ± 1 s.d. for 20 cross-section measurements on each 202U glass sample. 202A trend is interpreted from the complete alteration of the glass disks within the first 35 days of testing.

immediately overlying the Si-Fe core appeared as a brownish gel that was lighter in color at its base and displayed numerous dissolution pits at its surface. The composition of this layer is consistent with the presence of nontronite and saponite clays. Overlying this brown layer is a thin sheet of white, fine-grained, anemone shaped, Ca-Si crystals. This thin Ca-Si layer was, in turn, overlain by a heterogeneous mixture of crystalline material that was intergrown to an extent where it behaved as a cohesive layer. A number of individual crystalline phases were identified in this layer, including tobermorite, adularia, haiweeite, Na-U-silicates, and fine-grained material with a morphology and composition consistent with smectite or mixed layer smectite/illite clay.

The 202U samples (reacted without external radiation) developed a ~130 μm alteration layer only after 56 days of reaction (Figure 2). Two individual layers were identified on 202U glasses. An *in situ* layer of smectite was detected on the surfaces of all 202U samples terminated prior to 21 days of testing. This layer was depleted in Na and K, but enriched in Mg, Ti, Fe, and Ca relative to the unaltered glass. Major d-spacings measured from selected area electron diffraction patterns (Figure 4) indicate the presence of smectite, while compositional analyses are consistent with nontronite and/or ferroan saponite clays. After 35 days, the smectite was blanketed with a layer of high-albedo clay material (Figure 3b). Compositional and XRD analyses identified this material as illite. Small amounts of illite were also detected on the support wires for these samples indicating that this phase precipitated from solution in contact with the glass surface.

Optical surveys of SRL 131 and SRL 165 glasses also indicate that the irradiated samples are more extensively altered than their nonirradiated counterparts. The 165A glasses also display localized mounds of altered material that suggest internal voids may have developed during testing. More detailed examinations of these samples will be performed in the future.

Surface Precipitates

Alteration patterns for both the irradiated and nonirradiated SRL 202 glasses were characterized by the formation of a variety of zeolite, clay, Ca-Si, and alkali or alkaline earth uranyl silicate phases. More rapid glass alteration rates are observed in the irradiated vapor-rich environment as evidenced by the greater abundance of

Figure 3. SEM photomicrographs of SRL 202 glasses reacted for 35 days at 200°C. Horizontal white bars on photos a and c due to electronic distortion. (a) Secondary electron image (SE) of auto-fractured 202A glass showing banded textured Si-Fe core (200X); (b) backscattered electron image (BSE) of polished cross section of 202U glass showing (from bottom to top) unaltered glass, smectite layer, illite layer, and precipitate cover (1000X); (c) BSE image of 202A glass surface displaying large stellar weeksite, large trapezohedron and dimpled analcime (deposits on Pt-Rh wire running from lower right to upper left), and bright BSE images of fine-grained Na weeksite (50X); and (d) SE image of 202U glass surface with large dimpled analcime, fine-grained adularia buttons, Ca-Si rosettes, and Si-K-Ca-S-Al-Na needles (100X).

Figure 4. Transmission electron images of porous smectite layer from 202U glasses reacted for 14 days in a saturated vapor environment at 200°C. (a) Low magnification image with selected area diffraction pattern to upper right, (b and c) high resolution electron micrograph images showing lattice fringe spacings in smectite layer.

secondary precipitates on the sample surfaces (Figure 3c and d). A comparison of the paragenetic sequences for both test types indicates that secondary mineral formation has also been accelerated in the irradiated tests relative to the nonirradiated tests (Figure 5). For example, analcime, weeksite, and adularia were detected on earlier tests of the 202A relative to the 202U glasses. Transient phases such as herschelite and phillipsite, that formed early in the 202U tests, were not detected at all on the 202A samples, although it is possible that these phases first precipitated and then dissolved prior to the collection of the first samples at seven days. Faster leach rates and rapid saturation of the leachant with respect to secondary phases appears to have caused the accelerated paragenetic sequence observed in the irradiated tests. A number of secondary precipitates were also only detected on the 202A samples, the two most notable being Na weeksite and haiweeite.

Electrons at 30 kV accelerating voltage were also utilized during SEM/EDS analysis to excite the L shell electrons of the transuranic elements. Transuranic elements were not detected in any of the secondary phases, suggesting that the transuranics were retained at concentrations below detectability within the *in situ* alteration layers. More sensitive autoradiography techniques will be employed in future studies to better characterize the distribution of transuranics within altered glass profiles.

Optical examinations of irradiated 165A glasses displayed a relatively simple mineralogical sequence with the precipitation of analcime, weeksite, adularia, and the unidentified Ca-Si rosette phase. The mineralogical sequence developed on the 165U glasses was similar to that of the 165A samples, except that tobermorite and calcite were identified on the former. Optical examinations of irradiated 131A glasses were characterized by the development of weeksite, herschelite, phillipsite, analcime, and several unidentified phases. Secondary phases on the 131U glasses include herschelite, analcime, calcite, weeksite, phillipsite, and a number of unidentified phases.

CONCLUSIONS

A comparison of alteration patterns for glass samples exposed to irradiated and nonirradiated water vapor environments, at temperatures of 150 to 200°C, indicates that radiolytic products, including nitrogen acids have led to enhanced rates of glass alteration. The irradiation environment has also accelerated the formation of some secondary minerals, while in other instances has led to the precipitation of a different suite of phases. Alteration layer development also appeared to progress along preferential fractures and pits with the irradiated tests while in the nonirradiated tests alteration fronts were more planar. A comparison of the rate of alteration layer development between the two tests indicates that layer development may be accelerated by a factor of ~10 to 15X due to radiation exposure at high glass surface area /liquid volume conditions.

ACKNOWLEDGMENTS

Work supported by the U.S. Department of Energy, Office of Environmental Restoration and Waste Management, under Contract W-31-109-ENG-38. This manuscript has been improved through reviews by N. E. Bibler, W. L. Ebert, W. Lutze, and J. J. Mazer.

Figure 5. Interpretive paragenetic sequence identified for SRL 202 glasses. Solid lines represent 202U samples while dotted lines represent 202A samples exposed to an external gamma irradiation field.

REFERENCES

1. W. G. Burns, A. E. Hughes, J. A. C. Marples, R. S. Nelson, and A. M. Stoneham, *J. Nucl. Mater.* **107**, 245 (1982).
2. A. Barkatt, A. Barkatt, and W. Sousanpour, *Nucl. Tech.* **60**, 218 (1983).
3. W. J. Weber and F. P. Roberts, *Nucl. Tech.* **60**, 178 (1983).
4. D. T. Reed and R. A. Van Konynenburg, *Mat. Res. Soc. Symp. Proc.* **112**, 393-404 (1987).
5. D. J. Wronkiewicz, J. E. Young, and J. K. Bates, *Mat. Res. Soc. Symp. Proc.* **212**, 99-106 (1991).
6. H. Yokayama, H. P. Hermansson, H. Christensen, I. K. Bjorner, and L. Werme, *Mat. Res. Soc. Symp. Proc.* **44**, 601-608 (1985).
7. G. L. McVay, W. J. Weber, and L. R. Pederson, *Nucl. and Chem. Waste Mgmt.* **2**, 103 (1981).
8. T. A. Abrajano, Jr., J. K. Bates, and J. J. Mazer, *J. Non-Cryst. Sol.* **108**, 269 (1989).
9. S. Sato, H. Furuya, K. Asakura, K. Ohta, and T. Tamai, *Nucl. Instru. Meth. in Phys. Res. B1*, 534 (1984).
10. D. G. Howitt, H. W. Chan, J. F. DeNatale, and J. P. Heuer, *J. Am. Ceram. Soc.* **74**, 1145 (1991).

END

**DATE
FILMED**

5 / 14 / 93