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EFFECTS OF RADIATION EXPOSURE ON SRL 131 COMPOSITION GLASS IN A STEAM ENVIRONMENT

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ABSTRACT

Monoliths of SRL 131 borosilicate glass were irradiated in a saturated air-steam environment, at temperatures of 150°C, to examine the effects of radiation on nuclear waste glass behavior. Half of the tests used actinide and Tc-99 doped glass and were exposed to an external ionizing gamma source, while the remaining glass samples were doped only with uranium and were reacted without any external radiation exposure. The effects of radiation exposure on glass alteration and secondary phase formation were determined by comparing the reaction rates and mineral paragenesis of the two sets of samples.

All glass samples readily reacted with the water that condensed on their surfaces, producing a smectite clay layer within the first three days of testing. Additional crystalline phases precipitated on the altered glass surface with increasing reaction times, including zeolites, smectite, calcium and sodium silicates, phosphates, evaporitic salts, and uranyl silicates. Similar phases were produced on both the nonirradiated and irradiated samples; however, the quantity of precipitates was increased and the rate of paragenetic sequence development was accelerated in the latter. After 56 days of testing, the smectite layer developed at an average rate of ~0.16 and 0.63 $\mu\text{m}/\text{day}$ for the nonirradiated and irradiated samples, respectively. These comparisons indicate that layer development is accelerated approximately four-fold due to the radiation exposure at high glass surface area/liquid volume (SA/V) conditions. This increase apparently occurs in response to the rapid concentration of radiolytic products, including nitric acid, in the thin films of water contacting the sample monoliths.

INTRODUCTION

Radiation may affect the long-term stability of nuclear waste glass in an unsaturated repository environment by (1) inducing solid-phase damage effects to the glass structure, thereby creating damage tracks and/or fractures that increase the effective surface area of the glass, and (2) interacting with air, water vapor, or liquid water to produce a variety of corrosive radiolytic products, including nitrogen and carboxylic acids, hydrogen peroxide, and radical species such as $\text{HO}_2^\bullet$ and O_2^- [1-8]. These radiolytic products may influence glass stability by altering the solution pH and Eh, or by complexing with released radionuclides and glass components.

Most studies of glass behavior in an irradiated environment have focused on conditions where the glass was completely immersed in a relatively large volume of water. In these liquid-water dominated tests, radiolysis was found to have a limited impact on glass stability because of the buffering capacity and/or diluting effects of the liquid medium [5, 7]. The present experiments are designed to examine what effect radiation will have on glass stability under test conditions that simulate an unsaturated geological environment. Under this scenario, concentrations of radiolytic products have been shown to increase rapidly in the limited quantities of water that condense as a thin film on the surfaces of solid materials [8]. This may result in the bicarbonate pH buffering capacity of the film of water being rapidly overwhelmed by the condensation of radiolytically produced nitric acid. The influx of nitric acid and the resultant pH decrease may affect glass alteration rates [9] and the stability of some secondary mineral phases.

EXPERIMENTAL

Experimental details were discussed in detail in previous publications [5, 6] and will only be briefly reviewed here. Glass disks were prepared from SRL 131 frit that was doped with

either U-238 (¹³¹U glass) or Tc-99 + Np-237 + U-238 + Pu-239 + Am-241 at levels approximating 23 μ Ci/g total activity (¹³¹A glass). The glass was cut into ~1 x 10 mm monoliths and ground to a 600-grit finish prior to testing. The ¹³¹U and ¹³¹A glasses were suspended via Teflon or Pt-Rh wire, respectively, inside 22 mL stainless steel reaction bombs. Deionized water was added to each vessel in an amount necessary to ensure vapor saturation of the air inside the vessel upon heating to test temperatures of 150°C, yet limited in quantity to prevent fluids from dripping from the glass samples. Test intervals ranged from 3 to 720 days for the nonirradiated samples and 7 to 56 days for the irradiated samples. These times allowed for comparisons of long-term nonirradiated glass reactions with short-term irradiated glass reactions. The ¹³¹A samples were exposed to an external gamma radiation dose of ~3500 rad/h, thereby subjecting these samples to an internal alpha-beta and external gamma source during testing. The ¹³¹U samples were reacted without any external radiation exposure.

The irradiated and nonirradiated sample results were compared to evaluate what influence the radiation and radiolytic products have on the stability of waste glass and its alteration phases. Sample 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 samples were examined using a variety of solid-phase analytical techniques, including optical microscopy, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), X-ray diffraction (XRD), and analytical electron microscopy (AEM). This combination of techniques proved diagnostic in identifying many of the mineral phases present on the sample surfaces.

Although these tests are designed to produce glass reactions expected in an unsaturated environment, they do not necessarily replicate reaction conditions expected for the potential high-level nuclear waste repository at Yucca Mountain, Nevada. This is principally due to test temperatures, pressures, and radiation dose rates exceeding those expected for actual waste glass exposure. The 150°C temperatures in these tests were used to accelerate glass reactions to reasonably short time frames, yet were low enough to avoid changing the underlying glass reaction mechanism [10,11]. Although waste glasses may initially be exposed to temperatures and gamma dose rates as high as those used in the tests, these conditions will persist for only a short time following geologic disposal. During that time, the integrity of the waste container will be maintained, thus preventing contact of the repository atmosphere with the glass. The waste containers are not expected to be breached until several hundred years or more have passed after the waste has been placed in the repository. At these later times, the radioactivity level of the waste will be significantly reduced, decreasing the temperature of the waste package to less than 100°C. The high test pressures (~5 atm) resulted from the confining pressure of the test vessel walls on the vapor pressure of water. Waste materials at Yucca Mountain will be exposed to pressures that are reflective of the local atmosphere. Previous studies have shown that pressures as high as 100 atm will have no effect on the rate of glass reactions [12].

RESULTS AND DISCUSSION

Upon exposure to the saturated air-steam environment, the surfaces of both the nonirradiated and irradiated samples rapidly developed a brown alteration layer and a cover of precipitates that formed as the solution contacting the glass became saturated with corrosion products. Further description of the alteration layer and surface precipitates is given below.

Layer Formation

Detailed AEM examinations of the alteration layers from the nonirradiated ¹³¹U glass revealed the presence of a thin (0.2 μ m), relatively coarse-grained outer clay layer containing individual platy particles that are oriented perpendicular to the original glass surface (Fig. 1). After five days of testing, this layer has doubled in some regions into two parallel layers with an aggregate thickness of 0.4 μ m, while in other regions a single layer still remains.

Lying between the coarse outer layer and the unaltered glass is an inner layer of fine-grained, randomly oriented clay (Fig. 1). This inner layer progressively thickens during the course of the tests by advancing along an alteration front into the glass. By contrast, the outer layer remains at a relatively constant thickness throughout the tests.

(a)

(b)

(c)

Fig. 1. Transmission electron images of ^{131}U glasses reacted for three days: (a) low magnification image showing outer oriented and inner random clay layers overlying unreacted glass, (b) high magnification image of outer oriented smectite clay with 12 Å lattice fringe spacing, and (c) high magnification image of inner random smectite clay with 12 Å lattice fringe spacing.

The inner random layer appears to crystallize in a nonuniform manner. For example, the reaction layer from the 56-day sample displays a crystallization sequence, where amorphous material has crystallized into fine-grained clays, which themselves have reformed into intermediate-sized clay particles. Numerous crystal nucleation sites lying between regions of amorphous material, along with cavities or microvugs rimmed by intermediate-sized clay grains, support this interpretation (Fig. 2). These latter features arise due to the higher density of the clay relative to its precursor glass and/or amorphous source material. Tests run for 91 and 180 days display a more uniform layer that is composed almost entirely of fine- to intermediate-sized clay particles. This homogenization signifies the near complete crystallization of this altered layer.

The composite clay sequence for the irradiated ^{131}A glass monoliths developed at a relatively constant rate of $\sim 0.63 \mu\text{m/day}$ throughout the entire 56 days of testing (Fig. 3). By contrast, reaction layer growth rates progressively decreased during alteration of the nonirradiated ^{131}U glasses. With these tests, cumulative rates were initially $0.52 \mu\text{m/day}$ after 7 days, $0.16 \mu\text{m/day}$ after 56 days, and a relatively constant $0.1 \mu\text{m/day}$ between 180 and 720 days of

Fig. 1a

Fig. 1b

20 nm

Fig. 1c

Fig. 2. High magnification transmission electron image of inner random smectite layer from ^{131}U glass reacted for 56 days, showing formation of intermediate-sized smectite crystals and microvugs.

Fig. 3. Alteration layer thicknesses measured from SEM examinations of 131A (SRL 131 glass doped with actinides + Tc-99) and 131U (SRL 131 glass doped with U-238). The 131A glass was exposed to an external gamma dose rate of ~ 3500 rad/h while the 131U glass was reacted without any external radiation. Brackets indicate layer thickness ± 1 s.d. for 20 cross-section measurements on each sample. Brackets have been omitted where the standard deviation is less than the height of the plotted symbol.

Fig. 2

reaction. A comparison of the 56-day results indicates that layer development was accelerated four-fold due to radiation exposure at high SAVV conditions. This increase was less than the 10- to 15-fold increase previously seen for SRL 202 glass reacted under similar test conditions [6].

Selected area diffraction (SAD) analyses obtained during AEM study indicate that the clay layers are composed of smectite-group clay minerals (Table I). The multiple qualitative SEM/EDS (not shown) and quantitative AEM/EDS (Table I) spectra suggest the presence of nontronite and/or ferroan saponite.

The inner random layer of the 131U glasses displays a residual enrichment of relatively insoluble elements, such as Ni (Fig. 4a) and Ti, relative to the outer layer. This feature, combined with the previously discussed random crystal orientation (Fig. 1), suggests that the inner layer formed *in situ* as a residual material that remained after the more soluble components had been leached from the glass. The perpendicular orientation of the outer layer relative to the original glass surface suggests that these clays precipitated directly from the film of water covering the sample surface.

The AEM/EDS compositional analyses indicate that both clay layers are highly depleted in Na and K, but enriched in Al, Mn, Ti, and Fe (Fig. 4b) relative to the unaltered glass. Nickel is depleted in the outer layer for the first 14 days and then enriched after 56 days, while it is enriched in the inner layer during all time periods tested (Fig. 4a). Magnesium is enriched in the outer layer and depleted in the inner layer, relative to the unaltered glass, for the first 14 days of testing (Fig. 4c). Thereafter, magnesium concentrations in the inner layer progressively increase until they approach the composition of both the glass and the outer layer. Calcium is generally depleted in both layers, relative to the unaltered glass, but does show some enrichment in the outer layer after 56 days of reaction (Fig. 4d).

Surface Precipitates

A variety of zeolite, smectite, calcium and sodium silicates, phosphate, evaporitic salts, and uranyl silicate phases were deposited on the sample surfaces of both the irradiated and nonirradiated SRL 131 glasses. The phases identified in this study agree well with those reported by Biwer et al. [13], who identified smectite, calcite, and analcime with SRL 131 composition glass reacted in both saturated and unsaturated air-steam tests at 75°C. With few exceptions, the types of phases present on the reacted glass surface are similar for both the 131U and 131A glasses (Figs. 5 and 6). The main differences are the greater abundance of secondary precipitates and the accelerated paragenetic sequence observed on the irradiated 131A glasses. An example of this accelerated sequence is evident in the development of analcime and tobermorite. This phase appears in the 131A reaction sequence as early as seven days, while they appear in the 131U sequence only after 56 days of reaction. Accelerated glass corrosion rates and the rapid saturation of the leachate with respect to secondary phases appear to be responsible for the more rapid advancement of the paragenetic sequence observed in the irradiated tests. There are also some differences observed in element pathways between the two sets of tests. For example, uranium is contained in sodium-weeksite, haiweeite, and soddyite in the 131U tests, while it occurs chiefly in potassium-weeksite and, to a lesser extent, haiweeite in the 131A tests.

Table I. Diffraction data obtained from inner clay layer of three-day 131U samples and JCPDS data for montmorillonite

3-day 131U d-spacings, Å	3-day 131U d-spacings, ±Å	JCPDS 29-1499, Å
4.53	0.12	4.45
		3.15
2.58	0.05	2.56
1.7	0.03	1.69
1.52	0.02	1.495
1.31	0.02	1.325

Fig. 4. Elemental reaction trends for selected glass components showing alteration layer compositions normalized to that of unaltered glass and plotted as a function of reaction time. Individual plots and normalized elemental weight percent in original glass are as follows: (a) Ni - 1.51%, (b) Fe - 15.41%, (c) Mg - 1.59%, and (d) Ca - 1.13%.

Samples were also scanned at electron accelerating voltages of 30 kV during SEM/EDS analysis to excite the more diagnostic inner electron shells of Tc and the transuranic elements Am, Pu, and Np. None of these elements was detected in the clay layer or any surface precipitates, despite the examination of an extensive suite of sample regions. This absence of discrete Tc-99 and transuranic-bearing phases suggests that these elements were being retained within the inner alteration layer at concentrations below SEM/EDS detectability, rather than dissolving and being reprecipitated on the sample surface. More sensitive techniques, such as autoradiography, may be employed in the future to identify the locations of these elements.

Fig. 5. Interpretive paragenetic sequence for major alteration phases observed on reacted SRL 131 glasses. Solid lines represent nonirradiated ^{131}U samples, and dotted lines represent tests with ^{131}A glass reacted while being exposed to an external gamma radiation source. Tests with ^{131}A glass were reacted a maximum of 56 days.

CONCLUSIONS

Comparative examinations of reaction sequences between gamma-irradiated ^{131}A and nonirradiated ^{131}U borosilicate glasses indicate the following:

- (1) After 56 days of testing, alteration layer thicknesses on the irradiated samples increased by approximately four-fold relative to the nonirradiated samples.
- (2) With the irradiated samples, the quantity of surface precipitates has increased and the paragenetic sequence of alteration phases has been accelerated relative to the nonirradiated samples.
- (3) Glass corrosion rates increased due to radiation exposure, probably as a result of the combined influence of water and atmospheric radiolytic products that are produced and/or condensed into the thin films of water contacting the surface of the glass.

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Fig. 6a

(a)

(b)

Fig. 6. SEM photomicrographs of SRL 131 glasses reacted for 35 days in a saturated vapor environment at 150°C. (a) Relatively sparse crystal growth on SRL 131U glass reacted without external radiation exposure, 100X. Scattered phases are mostly mounds of smectite clay. (b) Dense crystal growth on SRL 131A reacted under gamma radiation dose of ~3500 rad/h, 100X. Note advanced stage of alteration relative to the 131U glass sample and the dehydration and cracking of the clay layer. Scattered acicular phase is potassium-wecksite with salt covering, button-shaped phase to lower center is analcime, blocky "x" shaped crystals are phillipsite, and fine-grained crystals across entire clay surface are an unidentified Ca-Si phase. See Fig. 6a for scale bar.

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