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Aged Nuclear Explosive Melt Glass: Radiography and Scanning Electron Microscope Analyses Documenting Radionuclide Distribution and Glass Alteration

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Abstract

Assessment of the long-term performance of nuclear melt glass under saturated conditions provides insight into factors controlling radionuclide release into groundwater. Melt glass samples were collected from an underground nuclear detonation cavity at the Nevada Test Site that was in contact with groundwater for more than 10 years. The samples were made into thin sections and the distribution of alpha activity mapped using CR-39 plastic detectors. The melt glass is visually heterogeneous and the results of the alpha track radiography indicate that the highest alpha activity is associated with areas of dark colored glass. Analyses of the thin sections by alpha spectrometry show the prominent actinide species to be ^{238}Pu , ^{239}Pu and ^{241}Am . Scanning electron microprobe analysis of the bulk glass shows conspicuous alteration layers lining internal vesicle surfaces in the glass. X-ray diffraction patterns for the alteration phases are consistent with clay mineral compositions. Glass dissolution models indicate these layers are too thick to have formed at ambient temperatures over the 10 year period in which they remained in a saturated environment. This implies the alteration layers likely formed at temperatures higher than ambient during cooling of the cavity following the underground detonation. Mobilization of this clay alteration layer as colloidal particles in groundwater represents a potential source of actinide release into the environment.

Introduction

The possibility that radionuclides deposited during underground nuclear tests could be released into groundwater was recognized early in the testing program.¹ Most current risk assessment studies regarding radionuclide release into the environment focus on the viability of using synthetic borosilicate glass to contain nuclear waste.² These studies have spurred intense research and debate over the dissolution processes of both synthetic and naturally occurring glasses. Nuclear explosive melt glasses provide useful analogues for evaluating these processes, since they incorporate the majority of the refractory radionuclides, fission, and activation products produced in a nuclear detonation—including partitioning >98% of the actinide species (i.e., ^{235}U , ^{238}U , ^{237}Np , ^{239}Pu , ^{240}Pu).³ Melt glass produced from underground nuclear detonations at the Nevada Test Site (NTS) is presently less than 50 years old. However, this glass has the potential for releasing constituent radionuclides over periods in excess of 1000 years—a relatively short amount of time when compared to the long half-lives of some of these radionuclide species. Therefore, understanding the behavior of melt glass under saturated conditions is important to developing a credible conceptual model for radionuclide release, and for providing validation of current numerical predictions.

Melt glass is produced from three sources immediately following a nuclear explosion: 1) initial condensation of vapor (plasma) produced during the explosion, 2)

shock melting of the wall rock due to the high pressures and temperatures associated with the explosion, and 3) contact between the host rock and the melt at temperatures above the melting point of the rock.⁴ Glass initially lines the standing cavity before it accumulates at the bottom of the cavity area as a melt glass puddle. Glass from different sources gets variably mixed below the point of the detonation (working point) due to condensation, flow, and cavity collapse. The ability to trace the partitioning of actinides in the melt glass is important in the context of glass stability and radionuclide release.

The current study has two objectives: 1) design an alpha (α) track radiography application to spatially resolve the distribution of transuranic actinide elements in these samples, and 2) document glass-water surface alteration textures and chemistry.

Sample Description

Melt glass samples used in this study are from an underground nuclear test in the Yucca Flat region of the NTS. The nuclear test was fired below the pre-shot water table in a rhyolitic ash-flow tuff. The event was re-drilled more than ten years after the time of the explosion and a set of samples collected from the cavity region. The three centimeter-sized samples selected for analysis were collected below the water table in the vicinity of the melt glass puddle, at a vertical depth of approximately 50 m below the level of the working point. Table I is a list of the samples, sampling depths, and an abbreviated description.

TABLE I

Sample Number	Approximate Vertical Depth (m)	Description
#19/20	~ 660	Banded glass with light and dark laminae
#49	~ 660	Pink to gray highly vesiculated glass
#62	~ 645	Homogeneous black glass with vesicles

Alpha Track Radiography

Polished thin sections of standard 30 μm thickness were made from the glass samples. The thin sections were analyzed using conventional α -radiography techniques with varying exposure times.⁵ TASTRAK CR-39, a polycarbonate plastic α -track detector produced by Track Analysis Systems, Ltd. in Bristol, U.K., was used to record the tracks made by α -particles emitted from the melt glass samples. Exposure time varied from 6 hours to 21 days. The detector slides were then etched to enlarge the α -tracks recorded by the detector. For the purposes of this study, an etching time of 2 hours at 70° to 75° C in a 6.25N NaOH solution was sufficient to make the α -tracks clearly visible under low power magnification.

Alpha activity was recorded by the TASTRAK detectors only for samples #62 and #19/20. The detectors for sample #62 have the highest density of α -tracks, even with an exposure time of only 6 hours. In fact, the α -tracks from sample #62 are so dense that the exact outline of the sample and the vesicles can be clearly seen on the detector—with or without magnification (Fig. 1). Sample #19/20 also emitted high enough activity levels for the TASTRAK detectors to record α -tracks, but only after 8 days of exposure. The high track density correlated with the dark glass laminae in sample #19/20. This darker

colored glass phase closely resembles sample #62. Even though some tracks can be seen in the lighter colored laminae of sample #19/20, they are very sparse. In general, the distribution of α -tracks is approximately uniform in the dark glass of both samples (#62 and #19/20). Sample #49 produced no α -tracks, even after 21 days of exposure—although it should be noted that this sample contained no dark melt glass.

Under magnification the α -tracks have two basic geometries, circular and teardrop-shaped. The teardrop-shaped tracks are due to α -particles traveling at an oblique angle to the surface of the thin section, while circular pits represent α -particles traveling approximately perpendicular to the surface of the thin section. The length of the teardrop correlates with the trajectory and energy of the α -particle as it enters the film.⁵

Radiochemistry

The glass samples were submitted for bulk analysis by gamma (γ) spectroscopy, and all three contained γ -emitting radionuclides. These include fission products (¹²⁵Sb, ¹³⁴Cs, ¹³⁷Cs, ¹⁵⁵Eu), activation products (²²Na, ⁶⁰Co, ¹⁵²Eu, ¹⁵⁴Eu) and residues of nuclear material fuels (²⁴¹Am).

Only one sample (#62) was submitted for plutonium assay by α -counting, but two separate thin sections cut from this sample were counted. The α -counting results from both thin sections produced two distinct peaks. A smaller peak, with an energy level of 5.157 MeV, is associated with the α -decay of ²³⁹Pu. A second peak has energy levels of 5.486 and 5.499 MeV that correlate with ²⁴¹Am and ²³⁸Pu α -decay, respectively. The presence of the Am, Eu, and Pu isotopes in these samples is consistent with predictions from condensation theory for refractory radionuclides.³

Activity ratios were calculated from the α -counting results for both thin sections of sample #62 using the equation:

$$\frac{I_A}{I_B} = \frac{A}{B-A} = \frac{(^{238}\text{Pu}+^{241}\text{Am})\text{dpm}}{(^{239}\text{Pu}+^{240}\text{Pu})\text{dpm}} \quad [1]$$

where I_A and I_B are the corrected peak heights for the radionuclide pairs ²³⁸Pu+²⁴¹Am and ²³⁹Pu+²⁴⁰Pu, and A and B are the total peak heights for ²³⁸Pu+²⁴¹Am and ²³⁹Pu+²⁴⁰Pu respectively. The activity ratios for two thin sections cut from different parts of the same sample vary by 1.5 times, implying a heterogeneous distribution of Pu isotopes within the sample.

It should be noted that these results represent only those α -particles being emitted from the very surface of each thin section, even though the α -activity is distributed through out the glass substrate. On an atomic scale, α -particles lose energy through ionization and elastic collisions with other atoms and molecules along the exit path.⁶ Therefore they are not recorded by either the counting or radiography detectors.

Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) Analyses

Bulk samples of the glass were examined under a field-emission scanning electron microscope equipped with an energy dispersive analyzer. A reaction rind is clearly

evident on the glass samples lining both exterior and freshly broken vesicle surfaces. This reaction rind is particularly well developed as vesicle coatings in samples #62 and #19/20 (Fig. 2a & 2b). Photomicrographs of the reaction layer show an abrupt transition between the unaltered glass and the reaction layer. In some vesicles, the alteration layer is entirely absent—or only incompletely developed. In other vesicles, the alteration completely encircles the void space. The reaction layers are composed of minerals $\leq 1 \mu\text{m}$ in size. The morphology and qualitative compositional data ($\sim\text{Si} > \text{Al} > \text{Mg} > \text{Ca} > \text{K} = \text{Fe}$) are consistent with the reaction layer being composed of clays. A single XRD analysis of this reaction layer was made by scraping a small quantity of the reaction layer from internal vesicles and sealing it into a quartz capillary tube and analyzing it using a Debye-Scherrer XRD powder camera. The results indicate that the secondary alteration layer is consistent with a layer silicate mineral, although exact identification of the clay species will require additional analyses.

Discussion

Detailed studies of nuclear melt glass provide new insights into the rate and mechanism of glass corrosion, the formation of alteration layers, and how these alteration layers affect the release of radionuclides into the groundwater.⁷ For example, Kersting et al.⁸ documented the migration of plutonium on colloidal particles at the NTS. The secondary mineral phases contained in the observed alteration layer may be a potential source of groundwater contamination if they separate from the matrix to form colloidal-sized particles. The length of time this glass remains below the level of the standing water table, combined with the rate of glass alteration, is integral in understanding the rate at which radionuclides are released into the environment.

For this study, α -track radiography was used for pinpointing areas of actinide activity in nuclear melt glasses. Specifically, the α -track results indicate that the highest levels of activity are concentrated in the dark colored melt glass fractions. The dark color of the glass may be due to radiation damage, or may reflect the chemical composition of the glass. Whether specific areas of high α -activity are the result of compositional changes in the glass chemistry needs to be addressed. It is noteworthy that within the dark glass, the actinides are not preferentially associated with textural features. In addition, α -counting results show that the α -activity is primarily due to plutonium isotopes (^{238}Pu , ^{239}Pu). Even though the α -activity appears to be homogeneously distributed through out the dark melt glass, the variation in the activity ratios indicate that the distribution of Pu isotopes may vary within the dark colored melt glass. To our knowledge, this is the first time that spatial variations in plutonium activity have been documented in nuclear melt glass.

SEM analyses of the melt glass samples show that secondary alteration minerals have formed on the surfaces of vesicles (Fig. 2a & 2b) in these samples. Previous studies have shown that exposure of glass to aqueous solutions results in the *in situ* formation of a secondary phase—typically a thin clay layer on the glass surface.⁹⁻¹² For example, naturally occurring basaltic glass in contact with both fresh and seawater are known to form smectite and illite layers.^{13, 14} The presence of smectite and illite on exposed surfaces of silicate glasses in contact with water is also predicted on the basis of thermodynamic reaction modeling.¹⁵ However, this is the first time that *in situ* formation of a secondary

alteration layer is documented in nuclear melt glasses. Preliminary XRD data indicating clay mineral compositions is consistent with the aforementioned studies.

Whereas many studies show that long-term interaction with aqueous solutions results in glass corrosion, understanding of the corrosion mechanism remains unresolved.¹⁶ Currently, the most commonly accepted mechanism for corrosion of glass is alteration and dissolution through hydration of the surface, where physical conditions, surface area, solution chemistry, and glass chemistry all have an influence on the rate of dissolution. For example, the rate of dissolution of amorphous silica is strongly controlled by both temperature and pH with dissolution processes slowing to minimum between pH of ~6.5 to 8.5, depending on the solution temperature.^{16, 17} Overall, dissolution rates increase dramatically with increasing temperature and pH values greater than ~7.¹⁸

For groundwaters at the NTS, which have an average pH ~8, and an average temperature of ~30°C,¹⁹ the dissolution rate of nuclear melt glass can be calculated using the glass dissolution model outlined by Bourcier et al.²⁰ Using an average SiO₂ content of 75 wt % (typical for rhyolitic glass) from electron microprobe analyses of these samples, the calculated glass dissolution rate would be approximately 10⁻⁴ g/m² /day at 30°C. This calculated rate is consistent with recent flow-through leaching studies of nuclear melt glass at 25°C and near-neutral pH.²¹ Note that the model predicts an exponential increase in dissolution rates with temperature, the rate increasing to ~10⁻¹ g/m² /day at 100°C.

For these altered melt glass samples, it is unknown when the observed alteration layer formed. Knowing the temperature at which the alteration layer formed can help elucidate whether this layer formed soon after the detonation during the hydrothermal conditions in the cavity, or over the 10-year period that these samples existed in a saturated environment. Using the model of Bourcier et al.,²⁰ and making a set of assumptions, we can speculate on the temperature required to produce the observed alteration layer. The assumptions are: 1) that the system is chemically and hydrologically open, 2) that the thickness of the alteration layer represents the amount of glass that has reacted, 3) that the alteration layer consists of clays having an average density of 2.5 g/cm³, and 4) that the dissolution rates are constant and can be used to estimate the rate of secondary mineral formation. From the SEM analyses, the average thickness of the alteration layer is determined to be ~5µm, with a range of ~3 to 7µm. For a 1m² surface area of glass that is in open communication with the groundwater, this corresponds to an alteration layer volume of 5x10⁻⁶ m³ with a mass of 12.5 g. Using the glass dissolution model of Bourcier et al.,²⁰ the mean groundwater temperature required to react 12.5 g of glass in 10 years is ~62°C. These temperatures and masses are reasonable considering that the model predicts that at 30°C, 0.5 g/m² of glass would be dissolved, while at 100°C, 263 g/m² of glass would be dissolved in groundwater over a 10 year period. For the same time period, similar calculations show that a clay alteration layer formed in 30°C groundwater would have an average thickness of 0.2 µm. The implication is that the mean temperature of reaction producing the alteration layers in these samples was probably greater than ambient conditions for NTS groundwater.

Most clays begin to de-water and become unstable at temperatures over 100°C. If the clay species observed are illite and smectite, smectite group minerals are typically stable at temperatures less than 140°C while illite can remain stable to temperatures of 400°C.²² Therefore, alteration layers could theoretically begin to form as temperatures within the cavity cooled below 400°C. Hence, the observed clay alteration layers may

have formed shortly after the nuclear detonation, when fluid-glass reaction rates were enhanced by elevated temperatures. At ambient temperatures, the alteration layers are likely to continue forming at a reduced rate.

Conclusions

We have applied an α -track radiography technique for analyzing nuclear melt glasses where the α -tracks produced in a CR-39 detector spatially resolve areas of high actinide activity in nuclear melt glass samples. Our results indicate that the α -activity is greatest in the darker colored melt glass, and that the α -track density in the melt glass samples appears to be homogeneous in the dark glass and not associated with specific textural features.

For the first time the *in situ* degradation and alteration of nuclear melt glasses is documented. Calculations indicate that this secondary alteration layer probably formed at temperatures higher than ambient for the NTS, but $< 400^{\circ}\text{C}$. At ambient temperatures, glass alteration is expected to continue, albeit at a much slower rate. This rate can be approximately determined from previous studies of glass dissolution kinetics.

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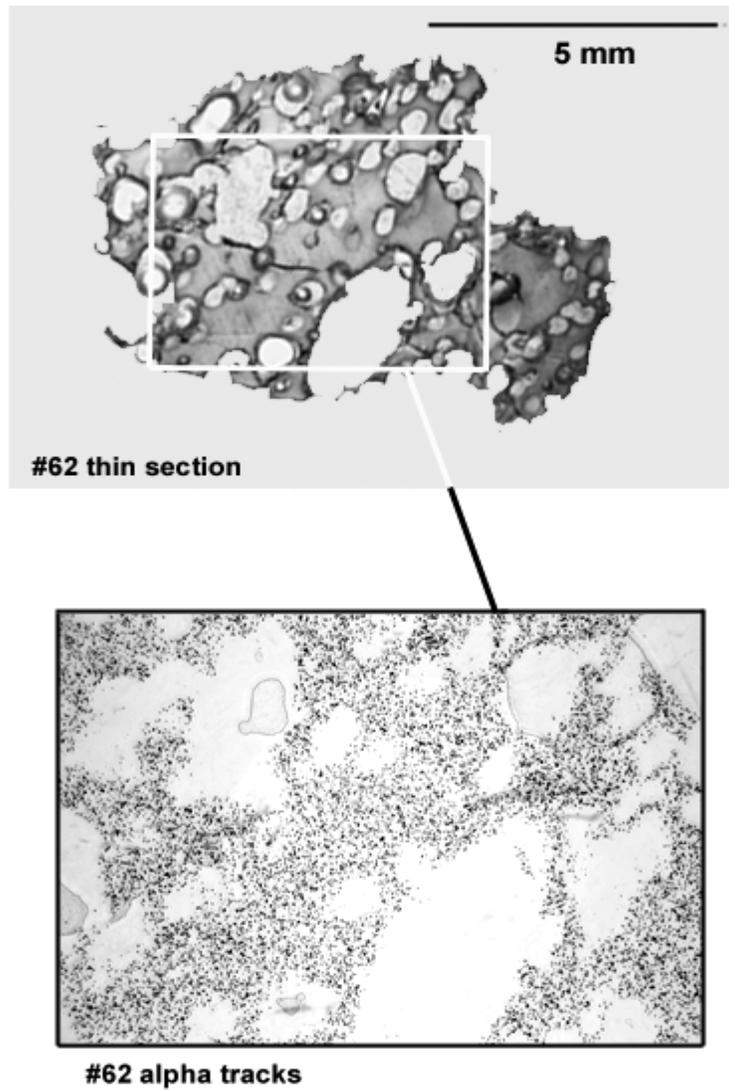


Figure 1: Top: thin section photograph of sample #62. Uncrossed polars. Vesicles are ~ 3 mm in maximum dimension. Secondary reaction layers have developed on the rims of some of the vesicles. Bottom: photograph of a TASTRAK detector from sample #62. Note that there is no α -radiation from within the vesicles, making the outline of the glass visible.

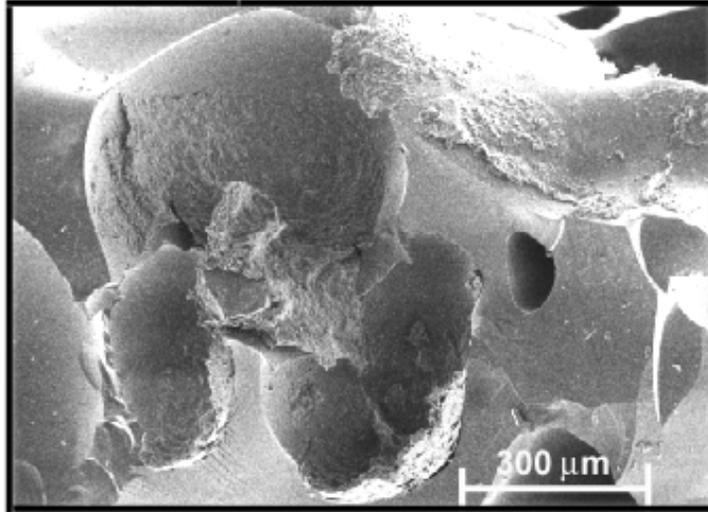


Figure 2a: Sample #62

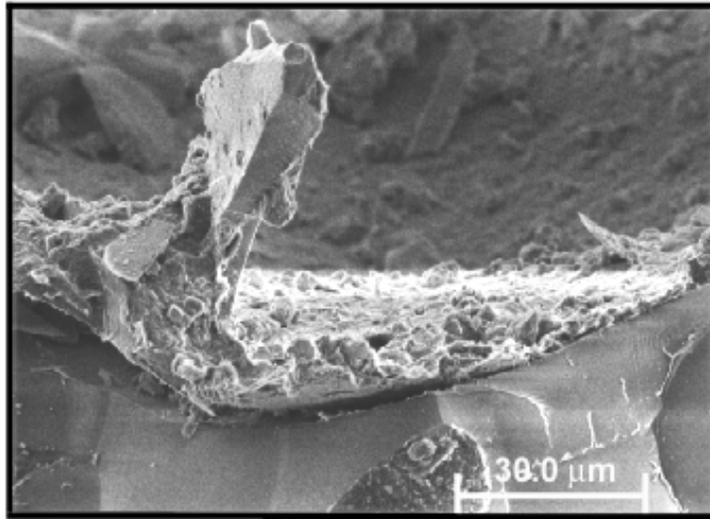


Figure 2b: Sample #19/20

Figure 2: SEM photomicrographs of glass samples. Shown are 2a) alteration layers lining vesicles from sample #62, and 2b) a clearly defined alteration layer lining a vesicle in the dark glass from sample #19/20.