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ABSTRACT

We analyzed the corroded surfaces of reference glasses developed for the Defense Waste Processing Facility (DWPF) to characterize their corrosion behavior. The corrosion mechanism of nuclear waste glasses must be known in order to provide source terms describing radionuclide release for performance assessment calculations. Different DWPF reference glasses were corroded under conditions that highlighted various aspects of the corrosion process and led to different extents of corrosion. The glasses corroded by similar mechanisms, and a phenomenological description of their corrosion behavior is presented here. The initial leaching of soluble glass components results in the formation of an amorphous gel layer on the glass surface. The gel layer is a transient phase that transforms into a layer of clay crystallites, which equilibrates with the solution as corrosion continues. The clay layer does not act as a barrier to either water penetration or glass dissolution, which continues beneath it, and may eventually separate from the glass. Solubility limits for glass components may be established by the eventual precipitation of secondary phases; thus, corrosion of the glass becomes controlled by the chemical equilibrium between the solution and the assemblage of secondary phases. In effect, the solution is an intermediate phase through which the glass transforms to an energetically more favorable assemblage of phases. Implications regarding the prediction of long-term glass corrosion behavior are discussed.

INTRODUCTION

High-level radioactive wastes stored at the Savannah River Site will be stabilized by vitrification at the Defense Waste Processing Facility (DWPF) for eventual disposal in a federal geological repository. The release of radionuclides from the repository over its service life must be predicted by coupling a description of the anticipated disposal environment with a model of waste glass corrosion and how it is affected by various environmental conditions. The release of radionuclides to transportable phases must also be known. Characterization of the advanced stages of glass corrosion is particularly important for modeling long-term performance. Argonne National Laboratory (ANL) has been testing high-level nuclear waste glasses for more than 15 years, to characterize their long-term corrosion behavior. We have gained valuable insight into the advanced stages of corrosion by conducting tests under conditions that accelerate glass corrosion and then analyzing the altered glass surfaces and leachate solutions to characterize the corrosion behavior and the disposition of radionuclides.

Glass is thermodynamically metastable and will, if provided with a pathway, transform into an assemblage of stable secondary phases. Water contact provides a pathway where glass can dissolve and more stable phases precipitate from the solution. The durability of a glass contacted by water is determined by the kinetic limitations of its dissolution and the nucleation and precipitation of secondary phases. Modeling the corrosion of high-level waste glasses over long periods requires, in part, characterization of the alteration phases.

Surface layers formed during glass corrosion in both laboratory and field tests have been studied for many years. However, the conditions under which the layers were generated have typically highlighted the early stages of corrosion and provide little insight into the phenomena controlling long-term corrosion. Because actual disposal conditions will differ significantly from the conditions of most laboratory tests, test results must be carefully interpreted as regards their relevance to glass corrosion behavior in anticipated service environments. For example, most laboratory tests are conducted with relatively large volumes of water and small glass surface areas, while repositories will be engineered to minimize the amount of water that contacts the waste glass. In addition, groundwater will accumulate slowly in a repository, whereas glass is contacted by a constant amount of water during most laboratory tests. An understanding of the glass corrosion mechanism and the effects of test parameters is required, to relate corrosion progress measured in laboratory tests to that under disposal conditions.

We analyzed alteration layers formed on several DWPF glasses, including SRL 211, SRL 131, SRL 165, SRL 200, SRL 202, and the Environmental Assessment (EA) glass. Corrosion tests employed a range of conditions to access different stages of the corrosion process and layer development. Static leach tests similar to the Materials Characterization Center-1 (MCC-1) test [1] and the Product Consistency Test (PCT) [2] were conducted in tuff groundwater or deionized water at glass surface area/solution volume (S/V) ratios from 10 to 20,000 m⁻¹, for reaction times ranging from a few days to five years. All MCC-1 and PCT-type tests were conducted at 90°C. Vapor hydration tests [3, 4] were also conducted at elevated temperatures for reaction times up to several years. The various test conditions (i.e., time, S/V, hydrothermal vs. vapor) generated samples with different extents of corrosion. The structure and chemical composition of the alteration layers formed on these glasses were characterized using scanning electron microscopy (SEM) with x-ray spectroscopy (EDS), transmission electron microscopy (TEM) with EDS and selected area electron diffraction (SAED), and x-ray diffraction (XRD). Descriptions of the laboratory tests and analyses were presented previously [e.g., 3-18]. These analyses provided a detailed description of the genesis and evolution of the alteration layers and insight into the glass corrosion path which will assist in relating test results with analytical models of glass corrosion behavior. A phenomenological description of layer formation and the overall glass corrosion mechanism is summarized in this paper. A more detailed description will be presented elsewhere.

PHENOMENOLOGICAL DESCRIPTION OF THE REACTION PROCESS

The glass structure comprises a three-dimensional network of silica units in a tetrahedral coordination. Depending on their charge and coordination, other components may be incorporated into and maintain the silicate network structure or may terminate it. Monovalent and divalent cations may couple with trivalent components, such as aluminum and boron, to continue the network, or may bond to silica and thereby terminate the network. Terminal groups are typically more easily hydrated than groups incorporated into the silicate network and therefore decrease the durability of the glass. Other glass-forming components, such as boron and phosphorous, may form separate phases within the silicate glass. How a component is incorporated into the glass structure will strongly influence its behavior during corrosion [19].

Contact of waste glasses by groundwater during disposal will result in corrosion of the glass and dissolution of soluble glass components. Selective leaching of glass components occurs because of differences in solubility between individual components, or in the rates of the specific reactions that release them. Alkali metals and boron are typically leached from the glass at a high rate, while the release of silicon is slow; thus, the glass surface is altered as components released faster than silicon are depleted from the outer surface, while components released slower than silicon accumulate. The preferential release of soluble components and the retention of insoluble components changes the composition and structure of the glass surface. The chemically and physically altered region is referred to as an alteration layer. The evolution of this layer occurs in four stages, illustrated below in photomicrographs of cross-sectioned layers of corroded DWPF glasses.

1. Formation of gel layer.

The leaching of alkali metals and boron from the glass and the incorporation of water results in a partial break-down of the network structure in the near surface region, forming a water-saturated (gel) layer. The gel layer is not precipitated from (or in equilibrium with) the bulk solution and continually dissolves as the silicate network is hydrolyzed. (Hydrolysis of the network likely occurs throughout the volume of the gel.) Fresh gel forms at the gel/glass interface as water diffuses into the glass and alkali metals and boron are released from the glass and diffuse through the gel and into solution. The region at the glass/gel interface where water, alkali metal, and boron concentration gradients exist is sometimes referred to as the transition zone [17]. Insoluble components released from the glass in the transition zone may become distributed throughout the gel phase. Formation of the gel layer occurs under conditions that promote the leaching of soluble components, thus, gels are most commonly observed in tests that maintain dilute solutions (e.g., at S/V less than about 400 m^{-1} , at low temperatures and under dynamic conditions). **Figure 1** shows a gel layer formed in a MCC-1 test with SRL 165 glass. Layers with a similar appearance have been observed on SRL 131 glass reacted in deionized water at 10 m^{-1} for four years at 40°C .

Because the gel layer forms as the result of differences in the solubilities of different glass components, disposition of radionuclides during gel formation will be controlled by their solubilities. Highly soluble Tc and moderately soluble U and Np are released to solution as the gel layer forms, while sparingly soluble Pu and Am remain in the gel layer, either bonded to the residual glass network or as insoluble secondary phases.

2. Transformation of gel layer into clay layer.

The gel layer is a transient phase that, for gels formed on DWPF glasses, has a composition similar to smectite clays. The gel layer eventually transforms into a clay layer. Analyses of many samples showed that crystals nucleate within the layer and not at the surface. For example, clay crystals are seen to nucleate within the gel layer formed on SRL 165 glass after about 28 days, as shown in **Fig. 2**. The solution within the gel layer is probably different than that of the bulk solution, and equilibrates with the clay.

The outer part of the layer (near the layer/solution interface) is usually observed to crystallize before the inner part (near the layer/glass interface). This may be due to the chemistry of the solution within the gel layer or to effects of the hydrated silicate network structure upon transforming into clay crystallites. The crystals continue to grow out into the solution without steric inhibition as the leachate solution provides material for crystal growth. Dissolved components not incorporated into the clay structure may form separate phases within or on top of the layer. For example, **Fig. 3** shows an amorphous uranium-bearing phase in the center of the layer on SRL 202 glass reacted at 340 m^{-1} for 360 days.

Clay formed on DWPF glasses under all S/V conditions tested. The time required for clay formation decreased with increasing S/V. For example, clays typically form on DWPF glasses after about 91 days in tests at 10 m^{-1} , within 14 days in tests at about 340 m^{-1} , and within 3 days in tests at 2000 and $20,000\text{ m}^{-1}$. The earlier formation at higher S/V is probably due to the faster increase in the concentrations of glass components and the higher pH values attained in these tests.

3. Equilibration between solution and clay layer.

As the reaction continues, the amorphous inner layer eventually crystallizes and separates from the underlying glass. This is shown in **Figs. 3 and 4**. The layer has a twinned appearance where clay laths perpendicular to the surface radiate into solution and in towards the glass. No amorphous or crystalline material remains attached to the glass surface beneath the layer, though some amorphous secondary phases may remain at the center of the layer. After the clay layer forms and separates from the glass, reaction continues beneath it at the exposed glass surface. Corrosion of the glass is nearly stoichiometric, and only a thin sodium-depleted layer (about 50 nm) is ever detected at the glass surface. Glass components are released into the solution between the glass and the layer.

Soluble components diffuse through the layer into the bulk solution. Other components are incorporated into the clay layer or other secondary phases.

Species released into solution prior to clay formation may also become incorporated into the clay or other phases which form on the glass surface. For example, magnesium is depleted in the gel layers, while levels of calcium in the gel remain close to those in the glass [13]. Magnesium is then removed from solution and incorporated into the clay as the layer crystallizes, replacing calcium, which is excluded from the clay as it forms and incorporated into other phases [5]. Analyses show that the magnesium concentration in the solution decreases as the layer crystallizes.

Radionuclides that dissolve as the gel is formed (e.g., Tc, Np, and U) will not be affected by the crystallization of the layer. Residual Pu and Am may be incorporated into the clay or into secondary phases within the clay. Spallation of the clay has been observed to generate colloids containing Pu and Am [20].

4. Precipitation of secondary phases from solution and accelerated corrosion.

As the glass dissolves, the leachate solution attains a composition conducive to mineral formation but may remain super-saturated for long periods because of slow nucleation and precipitation of the minerals. The eventual formation of these phases will reduce the solution concentrations of several glass components and may increase their release rates from the glass. The formation of secondary mineral phases does not change the corrosion mechanism, it simply increases the rate at which particular glass components dissolve and, consequently, the rate at which the clay layer is formed. The (outer) clay layer formed prior to secondary phase formation affects the growth of clay crystallites formed after secondary phase formation (the inner layer). The crystallites formed after secondary phase formation are smaller and more randomly oriented than those formed earlier.

Figure 5 shows the thick clay layer formed after secondary phases precipitated from solution. (Precipitation from the bulk solution is inferred from the observation that the phases form a layer of sediment on top of the glass.) The thickness of the outer layer does not increase significantly after secondary phases are formed. Thus, glass corrosion leads primarily to growth of the inner layer of fine-grained clay crystallites. The observation that the outer layer is unaffected by the increased corrosion rate, and that the new clay is formed beneath it, verifies that the clay is formed by transformation of the leached glass rather than precipitation from the bulk solution. That is, the inner clay is not formed by a dissolution/precipitation mechanism involving the bulk solution. Analyses of the inner and outer layers by TEM/EDS and SAED show the inner and outer clays to have the same structure and similar compositions, the main difference being that the outer layer has more magnesium and less calcium than the inner layer. This implies that exchange of calcium in the inner layer with magnesium from the leachate is slowed by mass transfer within the layer itself. The release of boron from the glass is not affected by the presence of the layer.

Further reaction progress is dominated by the maturation of the assemblage of secondary phases from kinetically favored to thermodynamically favored phases (Oswald ripening). Evidence of this is seen in tests performed in water vapor where the paragenesis of the assemblage of secondary phases can be followed using samples reacted from several days to a year [21]. The evolution of the secondary phase assemblage to more stable phases is accelerated by the high temperatures used in these tests, although the stabilities of the minerals formed are probably only weakly temperature dependent.

The release and disposition of glass components is shown schematically in **Fig. 5**. Boron is almost entirely released into solution, though small amounts of boron may be retained in the layer. Most of the silicon released from the glass is incorporated into the clay layer, though some is released into solution. Sparingly soluble components such as aluminum and iron are mostly incorporated into the layer. The clays are generally solid solutions of various end-member clays, and their compositions reflect the compositions of the glasses from which they form. Glasses with high iron contents typically form clays similar to nontronite, while magnesium-rich glasses form clays similar to saponite or montmorillonite, etc. Clay formation is also strongly affected by the solution pH. Components having low solubilities in the leachate solution and not incorporated into the clay layer form other secondary phases. Isolated aluminum-, calcium-, and uranium-bearing phases are commonly observed on corroded samples.

IMPLICATIONS REGARDING LONG-TERM GLASS PERFORMANCE

It is important to recognize that (1) test conditions strongly influence the extent of glass corrosion observed, (2) to understand the corrosion mechanism, several different test conditions must be used to characterize different corrosion stages, and (3) laboratory tests may provide insight into the corrosion mechanism, but test conditions will differ significantly from the disposal environment. For example, even though the PCT is widely used to compare the performance of waste glasses, the corrosion conditions in the test are irrelevant to the disposal site and neither the test solution nor the altered glass simulate corrosion under disposal conditions. However, the results of the PCT test do provide valuable information regarding the corrosion mechanism. Once the corrosion mechanism is characterized, the effects of environmental conditions on glass corrosion can be predicted.

Alteration layers formed during the glass reaction provide insight into which aspects of the long-term glass behavior need to be incorporated into computer models. Important observations are that clay formation does not affect the glass corrosion rate and the leachate solution has free access to the glass surface after the layer has crystallized. Continued glass corrosion occurs beneath the layer. Thus, the layer composition does not represent that of the dissolving glass. While the solution and secondary phases approach equilibrium, the solution can not reach equilibrium with the glass, so glass corrosion will continue until it has been entirely converted to secondary phases. Perturbations in the solution chemistry due to the presence of other materials and other interactions will affect both the assemblage of secondary phases that form and the glass corrosion rate.

SUMMARY

Glasses relevant to DWPF corrode by first forming a gel layer at the solution interface due to the leaching of alkali metals and boron and the incorporation of water. Dealkalization causes an increase in the solution pH that promotes hydrolysis of bonds forming the silicate network. The gel layer is transient and is transformed into a clay layer, which equilibrates with the solution. Formation of the clay layer does not significantly affect the glass corrosion rate, but the clay does incorporate many insoluble glass components, including some radionuclides. The clay layer separates from the glass and the glass beneath the layer continues to dissolve, typically at a low rate. Clays that spall from the surface may form radionuclide-bearing colloids. Secondary phases precipitate from the solution as it becomes concentrated in glass components. Changes in the solution chemistry (primarily the silicic acid concentration and the pH) as secondary phases form will increase the rates at which the glass dissolves and clays are formed. An understanding of how the precipitation of secondary phases affects the glass corrosion rate is a key to predicting the durability of waste glasses in a repository.

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Amorphous Layer

Unreacted Glass

← Figure 1. Layer Formed on SRL 165 Glass after 14 days at 90°C and 30 m⁻¹

100 nm ==

Amorphous Layer

Unreacted Glass



→ Figure 2. Layer Formed on SRL 165 Glass after 28 days at 90°C and 30 m⁻¹

100 nm ==



Amorphous U-bearing phase

Crystalline Layer

Unreacted Glass

← Figure 3. Layer Formed on SRL 202 Glass after 360 days at 90°C and 340 m⁻¹

100 nm ==

Crystallized Outer Layer

Crystallized Inner Layer

Unreacted Glass



→ Figure 4. Layer Formed on SRL 202 Glass after 182 days at 90°C and 20,000 m⁻¹

100 nm ==

Figure 5. Clay Layer After Secondary Phase Formation and Schematic Representation of the Disposition of Glass Components as the Glass Dissolves. The layer formed on SRL 202 glass after 364 days at 90°C and 20,000 m⁻¹ is shown. The arrows above the photomicrograph show the disposition of key glass components after they are released from the glass. The bold type indicates where each element usually accumulates. Highly soluble components such as B are released almost completely into solution. Most Si and Al is retained in the clay layers. The outer layer equilibrates with the bulk solution. Alkali metals are primarily released into solution, but small amounts may be incorporated into the clay. Moderately soluble components such as Mg and Ca are distributed throughout the clay layers and may participate in ion exchange reactions between the bulk solution and clays in the outer layer. Magnesium usually becomes more concentrated in the outer layer. Other components have similar concentrations in the inner and outer layers. Sparingly soluble components such as Fe, Mn, Ni, and Ti are incorporated into the clay as it forms. Disposition of radionuclides is affected by their solubilities: soluble radionuclides such as Cs, Tc, are dissolved, moderately soluble radionuclides such as U and Np are partially retained in the layer, sparingly soluble radionuclides such as Pu and Am are retained in the layer. Components present in excess of their solubilities in the solution and in the clay form other secondary phases in the solution or in the alteration layer.

