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SIMULATION OF NATURAL CORROSION BY VAPOR HYDRATION TEST: SEVEN-YEAR RESULTS

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ABSTRACT

We have investigated the alteration behavior of synthetic basalt and SRL 165 borosilicate waste glasses that had been reacted in water vapor at 70°C for time periods up to seven years. The nature and extent of corrosion of glasses have been determined by characterizing the reacted glass surface with optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive x-ray spectroscopy (EDS). Alteration in 70°C laboratory tests was compared to that which occurs at 150-200°C and also with Hawaiian basaltic glasses of 480 to 750 year old subaerially altered in nature. Synthetic basalt and waste glasses, both containing about 50 wt % SiO_2 , were found to react with water vapor to form an amorphous hydrated gel that contained small amounts of clay, nearly identical to palagonite layers formed on naturally altered basaltic glass. This result implies that the corrosion reaction in nature can be simulated with a vapor hydration test. These tests also provide a means for measuring the corrosion kinetics, which are difficult to determine by studying natural samples because alteration layers have often spalled off the samples and we have only limited knowledge of the conditions under which alteration occurred.

INTRODUCTION

Various laboratory tests have been developed to study corrosion behavior and to establish chemical models with which to calculate the long-term behavior of glass. In particular, the vapor hydration test developed at Argonne National Laboratory accelerates the glass corrosion process by combining the effects of high surface-area-to-volume ratios (S/V) and high temperatures [1]. However, it is challenging to demonstrate that the vapor hydration test method produces results that can be directly related to the behavior of glass waste forms over time periods of thousands of years. One method to build confidence in the applicability of this test method is to study the corrosion of natural materials that has taken place in natural environments over very long periods [2]. Basalt glass has been chosen for such a comparison study because its silica content is similar to that of a typical waste glass. If it can be demonstrated that the long-term alteration of a glass by natural processes can be simulated in laboratory experiments, then the same test can be used to study the long-term corrosion behavior of waste glasses. Such a natural analogue study will provide confidence that the kinetic models that have been developed based on short-term experiments can be applied to calculate the long-term corrosion of waste glass. In this paper, we compare alteration patterns that occur in naturally altered basalt glasses with those that occur in vapor hydration tests conducted at 70°C.

EXPERIMENTAL

The composition of the synthetic basalt used in the laboratory tests was modeled after a Hawaiian alkali basalt glass (52 wt% SiO_2 , 1.7 wt% TiO_2 , 12.7 wt% Al_2O_3 , 12.7 wt% Fe_2O_3 , 0.2 wt% MnO_2 , 6.2 wt% MgO , 10.7 wt% CaO , 3.8 wt% Na_2O , and 0.6 wt% K_2O) [3]. The glass was made by melting appropriate amounts of reagent-grade oxides and carbonates at 1600°C, quenching and homogenizing the resulting frit, remelting, and annealing the final product at 550°C for about two hours. Tests were also conducted with a reference nuclear waste glass from Savannah River Laboratory (SRL) 165 black frit for comparison. The SRL 165 glass contains 55.7 wt% SiO_2 , 4.3 wt% Al_2O_3 , 12.0 wt% Fe_2O_3 , 2.9 wt% MnO_2 , 0.6 wt% MgO , 1.5 wt% CaO , 10.5 wt% Na_2O , and 0.6 wt% K_2O [3]. Test samples were prepared as wafers approximately 1 cm in diameter and 1 mm thick. Each face of the sample was polished with 600-grit carborundum paper, followed by a final finish with diamond pastes of 6 to 1 μm with silicon oil as

a lubricant. Each sample was thoroughly cleaned and suspended with a Teflon thread from a type 304L stainless steel support bar in the test vessel. Samples were reacted in vapor of 100% relative humidity at 70°C for time periods up to seven years. The details of vapor hydration tests have been described elsewhere [1]. At the end of a test, each sample was examined with optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive x-ray spectroscopy (EDS) to observe the alteration layer and characterize its chemical composition. The details for preparing glass samples for SEM and AEM observation have been described previously [1,3,6]. The crystallinity of precipitates in the alteration layer was also determined with selected area electron diffraction, and crystalline phases were identified by matching the measured composition and diffraction patterns with the reference materials.

For comparison studies, ten samples of volcanic basaltic glass received from two archaeological sites at Oahu, Hawaii, were examined. These samples were located 5 to 85 cm below the ground level in generally wet and cool environments, although the exact humidity and temperature values are not known. The ages of the samples range from 480 to 720 ± 80 years B.P. (Before Present), according to radiocarbon dating of the occupation layer of charcoal [4]. The glasses have been altered by meteoric water and a humid atmosphere in nature. The Hawaiian basalt glasses were analyzed with optical microscopy, SEM, TEM, and EDS.

RESULTS AND DISCUSSION

Natural Weathering of Hawaiian Basalt Glass

All the Hawaiian glass samples examined in our study, regardless of age, exhibit surface alteration with similar features. These features include a brown-colored palagonite layer at the surface (Fig. 1a) and a high density of etching pits in areas from which the palagonite has spalled off the sample (Fig. 1b). The palagonite layers were often not continuous on surfaces (which allowed for the observation of etching pits underneath), and its coverage of the glass surface differed significantly from sample to sample. The spallation of the palagonite layer may have serious implications in determining the kinetics of corrosion on these samples, because the reaction rates are calculated based on the measurement of the thickness of palagonite layers formed on the glass surface [1]. Examination of cross sections shows that the palagonite layers are predominantly amorphous, with various precipitates of (Fe,Ti)-oxides distributed in the layer (see Fig. 2a). Analysis of the amorphous palagonite with EDS shows depletion of Na, Mg, and Ca and enrichment of Fe, Ti, and Al compared to the unreacted glass (see Fig. 2b).

Fig. 1. (a) Optical image of the palagonite at the surface with evidence of spallation (see arrows) and (b) SEM image of etching pits in areas where the palagonite spalled.

(a)

(b)

Fig. 2. (a) SEM cross-sectional view of palagonite layer and (b) EDS spectra comparing the glass and palagonite layer. The spectrum was acquired with an ultrathin EDS detector attached to the SEM.

Examination of the palagonite with AEM provides additional information at higher resolution. At high magnification, it can be seen that palagonite is composed of aggregates of small particles (about 10 nm) together with some clay particles (see Fig. 3). The clay was identified with electron diffraction and EDS to be Fe-rich smectite. The presence of nanometer-sized colloids is consistent with a dissolution/precipitation mechanism, by which glass is first dissolved into solution and then insoluble materials precipitate onto the glass surface to form palagonite. The existence of etching pits at the glass surface seems to indicate a dominant dissolution process of glass during its reaction with water. The formation of a crystalline clay phase could result from precipitation from solution or *in situ* conversion of the amorphous phase over time, with dissolution occurring at the layer/glass interface.

Laboratory Hydration of Synthetic Basalt Glass

Tests were performed with synthetic basalt at 70°C in saturated water vapor for up to seven years. A hydrated layer of about 0.5 μm thick was found to have formed on the surface, similar to the palagonite formed on the naturally altered basalt. Examination of the layer at high magnification with TEM shows an amorphous phase plus small amount of clay (Fig. 4a), a feature characteristic of naturally altered basalt. Analysis of the alteration layer with EDS shows depletion of Ca and enrichment of Fe and Ti, compared to the unreacted glass core (Fig. 4b), similar to that observed on naturally altered Hawaiian basalts. The exact location of Ca is unclear at this stage. It is possible that Ca may diffuse to the surface, dissolve and accumulate in a thin layer of water, and then precipitate as Ca-rich phases or be flushed away when in contact with water during the sample preparation. The above results indicate that nearly identical alteration layers are produced in both laboratory-reacted and naturally-occurring basalt glasses and, therefore, the long-term alteration by natural processes can be simulated in laboratory vapor hydration tests.

We also compared alteration at 70°C to that observed during previous tests conducted at 150-240°C [3]. The alteration layer formed at 70°C is similar to the layer formed during the initial reaction at higher temperatures (120-240°C) in short time periods (several days), which exhibits an amorphous microstructure that contains some smectite clays. This suggests that the corrosion of basalt glass may be further accelerated at higher temperatures without altering the fundamental reaction processes, since increasing the reaction temperature resulted in higher reaction rates.

Fig. 3. Transmission electron microscope image of alteration layer of Hawaiian basalt glass weathered for 700 years. The layer consists mainly of nanometer-sized amorphous particles and clay crystals (see arrows).

The fact that the corrosion products in nature can be simulated under accelerated laboratory conditions suggests that the glass reacts by similar reaction processes. Alternatively, the dominant corrosion process under a specific reaction condition can be inferred through the study of the reaction kinetics and may depend on reaction conditions. The kinetic expression for glass corrosion can be developed based on measurements of layer thickness, and the reaction kinetics of basalt glass hydrated in vapor hydration tests have been reported as both diffusion controlled and a linear function of time [1, 5]. However, it is difficult to use data from natural samples to verify a kinetic expression based on laboratory experiments. Because the alteration layers spalled from the base glass during wet/dry cycling and we only have limited knowledge of the reaction environment, the reaction kinetics cannot be established for naturally subaerially altered basalt samples.

Laboratory Hydration of SRL 165 Waste Glass

Vapor hydration tests were also performed with SRL 165 waste glass at 70°C in saturated water vapor for seven years. These tests produced a hydrated gel-like alteration layer, which consisted of an amorphous phase plus small amount of clay (Fig. 5a). This microstructure is nearly identical to those observed in the basalt glass reacted under the same conditions (see Fig. 4) or subaerially altered in nature (see Fig. 3). The alteration layer is enriched in Mn, Ni, Al, and Cl and depleted in Ca in comparison with the unreacted glass core (Fig. 5b). The alteration of SRL 165 at 70°C is also found to be similar to the initial reaction of this glass in tests conducted at

(a)

(b)

Fig. 4. Analyses with TEM and EDS of synthetic basalt reacted at 70°C in 100% RH for 7 years: (a) TEM image of alteration layer and (b) EDS spectra comparing the glass and amorphous layer (peaks located at energies lower than Al, such as O, Na and Mg, were not detected by the Be-coated Si EDS detector attached to TEM).

Fig. 5. Analyses with TEM and EDS of SRL 165 waste glass reacted at 70°C in 100% RH for 7 years: (a) TEM image of alteration layer and (b) EDS spectra comparing the glass and amorphous layer.

higher temperatures (120-240°C) in short time periods (7 to 91 days) [3, 6, 7]. At later stages of reaction at high temperatures, other alteration phases precipitate at the surface [1, 3]. The similarity of alteration products between SRL 165 waste glass and basalt glass suggests that both glasses initially corrode by the same reaction processes, at least under vapor hydration test conditions at low temperatures.

CONCLUSIONS

We have examined the alteration products formed on basalt and waste glasses reacted at 70°C in water vapor for up to seven years and compared the laboratory corrosion to subaerial alteration of 450- to 700- year old Hawaiian basalt. By characterizing the alteration products formed in laboratory tests and in nature, we have shown that the long-term subaerial alteration by natural processes can be simulated in vapor hydration tests. We have also shown that the same reaction products form in vapor hydration tests with a waste glass. These findings provide confidence in the application of this test method for studying the long-term corrosion of waste glass.

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