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BY ACCELERATED LABORATORY TESTING METHODS

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REPRODUCTION OF NATURAL CORROSION BY ACCELERATED LABORATORY TESTING METHODS

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Various laboratory corrosion tests have been developed to study the behavior of glass waste forms under conditions similar to those expected in an engineered repository. The data generated by laboratory experiments are useful for understanding corrosion mechanisms and for developing chemical models to predict the long-term behavior of glass. However, it is challenging to demonstrate that these test methods produce results that can be directly related to projecting the behavior of glass waste forms over time periods of thousands of years. One method to build confidence in the applicability of the test methods is to study the natural processes that have been taking place over very long periods in environments similar to those of the repository [1].

In this paper, we discuss whether accelerated testing methods alter the fundamental mechanisms of glass corrosion by comparing the alteration patterns that occur in naturally altered glasses with those that occur in accelerated laboratory environments. This comparison is done by (1) describing the alteration of glasses reacted in nature over long periods of time and in accelerated laboratory environments and (2) establishing the reaction kinetics of naturally altered glass and laboratory reacted glass waste forms.

Vapor Hydration Tests on Tektite and Obsidian Glasses

We have performed vapor hydration tests on tektite and obsidian glasses between 75 and 230°C for up to 400 days. The mechanisms of glass corrosion are generally complex and strongly depend on reaction conditions [2]. In laboratory vapor hydration tests, however, reaction of water vapor with tektite and obsidian glasses is found to produce birefringent alteration layers, for which the growth kinetics can be simply expressed as a function of the square root of time for a given glass at a fixed temperature. These findings seem in agreement with findings from previous studies, in particular, those for naturally altered obsidians, for which a dating method has been developed based on measurements of the birefringent thickness in natural samples [3]. We also investigated various parameters that affect alteration of these glasses, and we find a strong correlation between the total water content of obsidian and the hydration rate and the activation energy of the reaction. Our studies indicate that the natural hydration of glasses can be quantitatively reproduced under accelerated laboratory conditions, when the reaction is dominated by a relatively simple process such as the molecular water diffusion.

Nine-Year Results from Testing Basaltic and Simulated Waste Glasses

We have performed vapor hydration tests on synthetic basaltic and simulated nuclear waste glasses at temperatures ranging from 70 to 250°C for periods of up to 9 years. Basaltic and waste glasses were found to react by similar processes. At temperatures higher than 150°C, glasses were altered progressively to various secondary phases within months, following this paragenetic sequence: unaltered glass → smectite → Na-chabazite → analcime + phillipsite → K-feldspar → illite → albite + tobermorite. This trend is found to be similar to both the horizontal mineral zonation formed during the surficial-temperature alteration of volcanic glass in saline-alkali lakes and the vertical stratification resulting from the percolation of water through hot volcanic materials [4].
Tests were also performed at temperatures below 100°C with synthetic basalt and simulated waste glasses. After 9 years of exposure to a saturated vapor environment, both glasses formed an amorphous hydrated gel plus small amounts of clay. This is similar to the initial reaction of these glasses at higher temperatures in short time periods. For comparison, we also conducted detailed microscopy analyses of natural basaltic glasses that had been subaerially weathered in Hawaii for the past 500 to 700 years at ambient temperature. We discovered that alteration layers formed in Hawaiian basalts (palagonite) were nearly identical to those formed in laboratory-reacted glasses in both microstructure and chemical composition.

Although the above studies seem to indicate the corrosion reaction in nature can be reproduced reasonably well under accelerated laboratory conditions without changing the underlying reaction mechanisms, it is still difficult to use data from natural samples to verify a kinetic expression developed based on laboratory experiments. This difficulty arises because the alteration layers formed on the natural glass surfaces were frequently found to have spalled from the base glass, and, as a consequence, the reaction rate, which is calculated from measurements of layer thickness could not be adequately established. There is also evidence that the corrosion of natural glasses may have been greatly affected by the local microenvironment (e.g., temperature, humidity, pH, etc.) of each individual glass. This result implies that the quantitative correlation between natural analogue and short-term laboratory results could be further hindered by a limited knowledge of the reaction conditions of natural samples.

REFERENCES


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