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Factors Influencing Chemical Durability of Nuclear Waste Glasses

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ABSTRACT

A short summary is given of our studies on the major factors that affect the chemical durability of nuclear waste glasses. These factors include glass composition, solution composition, SA/V (ratio of glass surface area to the volume of solution), radiation, and colloidal formation. These investigations have enabled us to gain a better understanding of the chemical durability of nuclear waste glasses and to accumulate a data base for modeling the long-term durability of waste glass, which will be used in the risk assessment of nuclear waste disposal. This knowledge gained also enhances our ability to formulate optimal waste glass compositions.

INTRODUCTION

The high-level nuclear waste stored in tanks at Savannah River, South Carolina, and West Valley, New York, will be immobilized as borosilicate glass and subsequently emplaced in a deep geologic repository. The contact of the buried glass with groundwater followed by passage of that groundwater through the repository is the most likely mechanism for the transport of radionuclides into the biosphere. The chemical durability of a nuclear waste glass in an aqueous solution or in a vapor atmosphere is important for the isolation of the radionuclides from the biosphere. The long half-lives of the fission products and actinides in high-level waste glasses require that the durability of nuclear waste glasses be up to 10^5 years. The chemical durability of a glass is usually defined as the ability to resist the alteration caused by aqueous solutions or other vapor reagents. It is measured by the dissolution rate (the rate of increase of the most mobile elements being dissolved from glass into solution) or by the alteration rate (such as rate of surface layer formation). This paper describes our efforts in the study of how the chemical durability of waste glass is influenced by glass composition, leachant composition, SA/V, radiation, and colloid formation.

EFFECT OF GLASS COMPOSITION

The most important factor in influencing the chemical durability of a waste glass is its composition. During the efforts to optimize the glass compositions for the vitrification of the liquid high-level nuclear waste stored at West Valley, an experimental study was carried out to determine the relationship between chemical durability and waste glass composition [1,2]. The glass designated as WV205 was used as a base glass composition. Various glass constituents such as SiO_2, Al_2O_3, Na_2O, K_2O, Li_2O, MgO, ZrO_2, TiO_2, Cr_2O_3, ZnO, NiO, CuO, La_2O_3, U_3O_8, and ThO_2 were added to the base glass to make about 50 different glass compositions. A modified MCC-3 leaching procedure [1] at SA/V of 2000 m^{-1} was used to evaluate the chemical durability of these glasses. The leach tests were carried out with deionized water (DIW) at 90°C for up to 180 days.

Our studies identified a sharply defined glass composition region (e.g., see Fig.1) where the glass durability is good and minimally depends on composition within the region [1,2]. However, adjoining this durable composition region is one where durability is a much steeper function of glass composition. A glass composition can be brought into the durable region by adding oxides such as SiO_2, Al_2O_3, and ZrO_2 or by removing alkali and boron oxides. When a glass is melted under reducing atmospheres (CO/CO_2), the oxidation states of some elements, primarily iron (12% in WV205), are reduced. The leachability of glasses in the durable region is insensitive to the oxidation state of the iron in glasses, while glasses outside the durable region exhibit a large increase in leachability if the glass is reduced [3, 4].

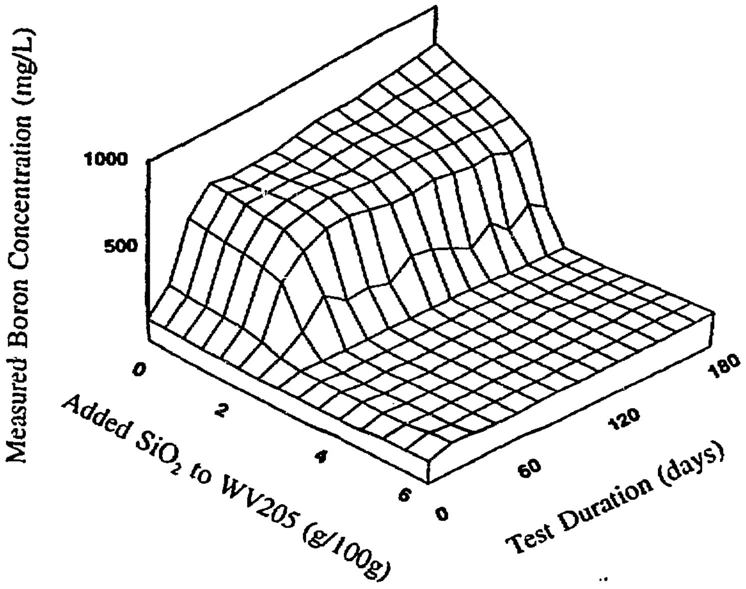

Fig. 1 Interpolated surface showing the dependence of chemical durability on glass composition vs. test duration in days. The chemical durability is shown as the boron concentration measured in a MCC3 type of test [2]. The glass composition is expressed as the # of grams of SiO_2 added to 100 grams of the base glass WV205. When 1.5 grams of SiO_2 was added to WV205 glass (52.77% in total mole percent), the durability remains almost the same as this of WV205. However, when additional 1 gram of SiO_2 was added (53.29% in total) the dissolution rate decreased by a factor of 10. Any addition of SiO_2 beyond 2.5 gram (53.29%) improves glass durability, but not nearly as effective of the first 2.5 gram addition. The region with equal or more than 2.5 grams of SiO_2 added is defined as the durable region in this manuscript. Similar composition-durability surface can be constructed for additions of Al_2O_3 and ZrO_2 [2].

To guide the glass-composition optimization efforts, an empirical model was developed [5]. It characterizes the chemical durability as a function of the Si, Al and Zr content in the glasses. Another model [6,7] was later developed to correlate glass durability with composition and the oxidation state of the glass constituents. This model is based on consideration of the bond strength between the cations and oxygens and the structural role of the cations in the glass. A modification of this model [8] has been successfully applied to the prediction of the temperature-dependent viscosity for more than 300 glasses. By considering the hydration energy of a complex aluminosilicate compound (such as low-albite) instead of simple silicates in a glass, it results in a good correlation between the measured glass durability and the hydration energy calculated according to glass composition [9]. These modeling efforts have improved our understanding of the composition effects and enhanced our ability to formulate waste glass compositions with good chemical durability and proper viscosity for processing. The glass composition affecting its chemical durability is mainly through its influence on the bond strength between the cations and oxygens of the glass constituents, and on its ability to hydrolyze in an aqueous environment.

EFFECT OF SOLUTION COMPOSITION

The chemical durability of a glass also strongly depends on the composition of the liquid phase in contact with the glass. Under IAEA (International Atomic Energy Agency) test conditions, WV205 waste glass leaches much less in a tuff groundwater than in DIW [10]. The addition of a salt to DIW substantially reduces the leachability of the glass [11]. This salt effect is dependent on the charge and size of the cations of the salts but is independent of ionic strength. This salt effect is interpreted by the shifting of kinetic ion exchange equilibrium [11]. The addition of Si or Al ions into DIW usually reduces the dissolution of the waste glass. This is due to (1) the reduced reaction affinity in Si and Al water, or (2) formation of protective layers on the glass surface [10]. The dissolution rate of WV205 in the groundwater is the lowest among the various leachants mentioned above. This is because the groundwater compounds the effects of addition of salt, Si, and Al ions, and has the buffering capacity needed to maintain the leachate at near neutral.

Solution pH dominates the process of glass dissolution [12]. When the solution is buffered at low pH during WV205 testing, the dissolution process is dominated by ion exchange and lasts for long reaction times. Matrix dissolution dominates immediately when the solution is buffered at high pH. However, the choice of buffer materials also affects the dissolution rate of the glass [13]. The glass reaction rates of WV205 in organic buffers such as CHES [$C_6H_{11}NHCH_2CH_2SO_3H$], CAPS [$C_6H_{11}NH(CH_2)_3SO_3H$], TRIS [$(HOCH_2)_3CNH_2$], ethanolamine, and 4-methoxyphenol were a factor of three lower than those in inorganic buffers, such as borate and phosphate, at the same pH [13, 10]. This is explained by the ability of an organic buffer molecule to form a hydrophobic complex on the glass surface, which retards further attack by water and other hydrophilic molecules. The presence of metallic iron powders in solution also increases glass dissolution by forming iron-silicate precipitates [10]. In sum, the solution composition influences durability by changing the environment that is in contact with the glass. This changed environment affects the glass surface charge, the ability of the glass surface to form complexes with leachants, the degree of solution saturation, and the equilibria of chemical reactions.

EFFECT OF SA/V

In a chemical durability test, an amount of glass with a certain geometry (which defines the surface area of the glass) is immersed in a volume of leachant (or covered by layers of adsorbed water in the case of a vapor test), resulting in a value of the SA/V of the test. In a repository setting, a low SA/V scenario is associated with a large amount of groundwater in contact with the waste glass, while a high SA/V scenario is related to a very small amount of groundwater in contact with the glass. There is a strong desire to understand the SA/V effect on glass durability because the glass dissolution behavior is strongly influenced by SA/V [14,15]. This was demonstrated in tests of six nuclear waste glasses at SA/V of 10, 20, 200, 2000, 10,000, 20,000, and 40,000 m^{-1}, respectively for up to one year [14]. The solution pH at each SA/V was observed to increase to a constant value within a few days due to ion exchange reactions [15,16]. The constant pH value increased with higher SA/V. This constant pH value at a given SA/V also depended on glass composition, which reflects the amount and the nature of the ions available in the glass for the ion exchange reactions. The test results indicated [14,15] that SA/V effect is actually a manifestation of effects produced by solution pH and elemental concentration. The SA/V-induced pH effect influences the controlling step of glass dissolution, dominates the glass reaction rate, and plays a major role in the formation of the alteration products on the glass surface. The SA/V-induced elemental concentration also contributes to the overall glass reaction rate, determines when alteration products form if nucleation is not hindered, and affects the thickness of the glass-surface alteration layers. Understanding the fundamental nature of SA/V effect on glass reaction is one of the keys to the proper modeling of glass performance.

EFFECT OF RADIATION

Most investigations on nuclear waste glasses have been carried out using non-radioactive simulated nuclear waste glasses. However, the radioactive elements within actual high-level nuclear waste glasses will subject the glass itself to radiation exposure, although the chemical composition between the two glass types may be very similar. A few comparison studies between simulated and fully radioactive glasses at low SA/V and in relatively short test duration have concluded that the chemical durability, or leachability, for both types of glasses is similar [17]. In contrast, our recent long-term tests on SRL 200 nuclear waste glasses under high SA/V conditions reveal that fully radioactive SRL 200 may be 40 times more durable than simulated SRL 200 tested under identical conditions [17,18]. These results can be interpreted through an understanding of the radiation-induced pH decrease in the leachate of radioactive glasses and secondary phase formation [17,18]. The radiation of the fully radioactive glass induces the formation of nitric and other acids, resulting in a much lower pH in the leachates from the fully radioactive glass compared with the simulated glass. This lower pH retards the onset of increased glass reaction, while the simulated glass is reacted in a more alkaline environment, which accelerates glass reaction. The accelerated glass reaction produces high elemental concentrations in the leachate, which promotes the formation of secondary phases, which, in turn, increases reaction affinity [19].

EFFECT OF COLLOID FORMATION

Another important factor of chemical durability of a waste glass is its ability to generate colloid, because colloids are a potential vehicle for the transport of radionuclides [20]. Glass dissolution contributes to colloid formation through increasing ion concentrations in groundwater, which causes nucleation of colloids; releasing radionuclides that adsorb onto existing groundwater colloids; and spalling of the surface layers of the reacted glasses [20,21]. Three types of colloids which are associated with radionuclides have been identified: real colloids, which are formed by solubility-limited hydrolysis and polymerization of radionuclides from glass; pseudocolloids, which are formed by adsorption of radionuclides onto existing groundwater colloids; and primary colloids, which are formed from the fragments of alteration layers that spall from glass [20]. The major radioactivity in the leachate under the test conditions was identified as caused by the primary colloids [20]. The colloids in the leachate of waste glasses are mainly silicon-rich particles, such as smectites and uranium silicates [20,21]. When salt concentration is high, the colloidal suspensions agglomerate. However, the agglomerated particles can be resuspended if the salt concentration is lowered by dilution with groundwater. The colloids agglomerate quickly after the leachate is cooled to room temperature. Most of the colloids settle out of solution within a few days at ambient temperature. The isoelectric point (zero charge) is at a pH of approximately 1.0. Between pH 1 and 10.5, the colloids are negatively charged and will therefore deposit readily on positively charged surfaces. The average particle size is largest at the isoelectric point and is smallest around pH 6. This information is important to assess the ability of the colloids generated in glass reaction with groundwater to transport radionuclides.

UNDERSTANDING GLASS DISSOLUTION BEHAVIOR

An assessment of the long-term durability of nuclear waste glasses for up to 10^5 years is needed because of the long half-lives of the fission products and actinides in the high-level waste glasses. This assessment can only be achieved through an understanding of the fundamental mechanisms of glass alteration and dissolution under repository-relevant conditions and through modeling [22]. Glass is a metastable phase and may eventually transform into more stable phases. Vapor tests and high SA/V tests are used to accelerate glass reactions, and they provide valuable information about the evolution of the glass leachate and the paragenetic sequence of secondary mineral assemblages that form on the glass surface[23].

The observed difference of dissolution behavior between simulated non-radioactive and fully radioactive glasses can be better explained if the controlling glass reaction step is accounted for [24,25]. Waste glass WV205 has been leached in both deuterated water and ordinary water. The observed isotope effects, as measured by the ratio of glass dissolution rate in H_2O over that in D_2O, reveal information about the fundamental processes of glass dissolution [26]. A small isotope effect was observed when WV205 glass was leached at low SA/V ($< 200\ m^{-1}$) for a short period of time. This effect is consistent with diffusion of H_3O^+ or D_3O^+ as the controlling process. However, a large isotope effect (of up to 3.6) was observed when WV205 was tested at high SA/V ($\geq 2000\ m^{-1}$). This effect has been attributed to a primary kinetic isotope effect, indicative of the involvement of the breakage of a bond to hydrogen in the rate-determining step of the glass reaction [26].

CONCLUSION

Our investigations have revealed that the chemical durability of waste glasses is a complex function of many factors. The glass composition contributes to the durability through its influence on the bond strength between the cations and oxygens and on its ability to hydrolyze in an aqueous environment. The solution composition changes the environment that is in contact with a glass, thereby affecting the glass surface charge, the ability of the glass surface to form complexes with leachants, the extent of solution saturation, and equilibria of chemical reactions. The SA/V influences glass dissolution through fundamental parameters such as solution pH and elemental concentrations. The radiation effect posed by the fully radioactive glass is mainly through the effect on generating acidic environment and lowering solution pH in the case of SRL 200 glasses studied. Finally, the colloid formation is another avenue for the release of actinides from the glass. Understanding the dissolution process is the key to predicting the long-term chemical durability of high-level nuclear waste glasses.

Our studies have enabled us to develop a better understanding of chemical durability of waste glasses and to accumulate a data base for long-term durability modeling of waste glass behavior in risk assessment of nuclear waste disposal. This knowledge enhances our ability to develop better composition formulations for waste glasses. These studies on the chemical durability of nuclear waste glass are continuing.

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