Ion Exchange Processes and Mechanisms in Glasses

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Research Objective

Plans for immobilizing low-activity radioactive tank wastes at the Hanford Site call for vitrification followed by shallow subsurface disposal. Water percolating through the disposal system will eventually react with the vitrified waste, releasing the encapsulated radionuclides. Consequently, it is important to understand the glass corrosion mechanisms that ultimately control the radionuclide release rate. One important reaction involves the exchange of alkali ions in the glass with H^+ or H_3O^+ ions in water, which raises the pH in the disposal system and can enhance ^{99}Tc release rates by 100X or more. The objective of this work is to develop an understanding of the processes and mechanisms controlling alkali ion exchange and to correlate the kinetics of the ion-exchange reaction with glass structural properties. The fundamental understanding of the ion-exchange process developed under this study is targeted at developing lower ion-exchange rate glasses that would remain durable at higher alkali waste loading.

Research Progress and Implications

Sodium ion exchange and matrix dissolution rates were determined on Na_2O-Al_2O_3-SiO_2 (Series I), Na_2O-Al_2O_3-B_2O_3-SiO_2 (Series II), and several complex boroaluminosilicate glass compositions (Series III). The Series I glass compositions vary in Al_2O_3 content while keeping the ratio of $^{[Q3]}$Si to total Si approximately constant. This was done to monitor the effect of decreasing concentration of nonbridging oxygen (NBO) sites as the available Na^+ is used to form network repolymerizing AlO_2Na ($^{[4]}$Al) tetrahedral sites. These glasses were also doped with trace amounts of Mo (~0.1 mass% MoO_3), which was used as a tracer of matrix dissolution. In the Series II and III glasses, B was used to index matrix dissolution. The Series II glasses were formulated such that Al_2O_3 was swapped for B_2O_3, keeping the Na_2O and SiO_2 mol% constant. This was done to examine differences in Na ion-exchange rates as BO_2Na ($^{[4]}$B) tetrahedral sites are converted to AlO_2Na ($^{[4]}$Al) tetrahedral sites. The Series III glasses were selected as representative low-activity waste glasses based upon propriety glass formulation information received from British Nuclear Fuels Limited, Inc., although the Series III compositions themselves are not proprietary.

Glass-Water Reaction Experiments

Sodium ion-exchange rates were determined by a series of single-pass, flow-through (SPFT) experiments. Glass matrix dissolution was minimized in these experiments by pre-saturating the influent buffer solution with respect to amorphous silica. Experiments were conducted at 25°C and a constant pH of 8. The Series I glasses showed an increasing sodium ion exchange rate with decreasing Al_2O_3 content in the glass. Sodium release rates were ~100X faster than matrix dissolution, indicating the dominance of the alkali ion exchange reaction in silica-saturated solutions. In silica-saturated D_2O solutions, the Na ion exchange rate was ~30% slower than rates in H_2O. This is convincing evidence that the rate-limiting step in the ion exchange reaction involves the transfer of a proton and not other species such as H_3O^+ or H_2O. Ion exchange rates were found to increase with temperature with an activation energy of approximately 50 kJ/mol, which is 40% lower than typical activation energies (≈80 kJ/mol) for silicate glass matrix dissolution. This is consistent with the rate-limiting reaction for ion exchange involving rupture of a weaker O-H bond as compared with dissolution of the silicate matrix, which involves rupture of the stronger Si-O bond. SPFT experiments with Series III compositions also showed the strong influence that glass structure has on reactivity; sodium-exchange rates were found to decrease with an increasing ratio of network formers to network breakers in the glasses.

Glass Reaction Layer Analyses

Reaction layers in Series I glass compositions reacted with isotopically labeled $D_2{}^{18}O$ silica-saturated solutions were analyzed by nuclear reaction analysis (NRA). The magnitude of sodium depletion decreased with increasing Al_2O_3 content in the glasses. Sodium depletion profiles reveal at least three different regions in the reaction layer: 1) surface reaction zone, 2) mixed reaction-diffusion zone, and 3) inter-diffusion zone. Because of surface silanol condensation reactions, peak concentrations of ^{18}O and D occur at different depths. Accordingly, $^{18}O/D$ ratios vary with depth but reach near-constant values (between 1/2 to 1/3) in the inter-diffusion zone near the unreacted glass/gel layer interface. In general, the $^{18}O/D$ ratios are consistent with H_3O^+ as the principal diffusing hydrogen species.

NMR Studies

Magic angle spinning nuclear magnetic resonance (MAS-NMR) was performed on the Series I and Series II glasses at the EMSL User Facility at PNNL. The ^{29}Si chemical shift value became less negative as the Al_2O_3 content increased. This is consistent with the average chemical bond strength of the glass network increasing as Al_2O_3 is added. The ^{27}Al NMR spectra of all the Al_2O_3-containing glasses were nearly identical and were indicative of nearly all (>98%) of the aluminum being tetrahedrally coordinated. The ^{11}B NMR spectra of the Series II glasses were generally resolvable into overlapping narrow- and broad-line width components. The narrow component is due to tetrahedrally coordinated boron, $^{[4]}B$ (i.e., network forming sites). The broad component, on the other hand, is from boron coordinated to three equivalent oxygens to form trigonal planar complexes. Deconvolution of these two peaks and subsequent integration allowed for direct determination of the fraction of four-coordinate boron in the glasses.

XAS Studies

The local Na environment in Series I glass samples were analyzed at the Advanced Light Source (ALS) with x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS) techniques. Both the Na-O bond length and the Na-O peak width decrease with the increase of Al content in the glass. The decrease in Na–O peak width with increasing Al content suggests a decrease in coordination number and increased order around the Na atoms. This is reasonable because the increase of Al_2O_3 content increases the number of tetragonally coordinated Al atoms, which are more negatively charged compared with the Si-O tetrahedron. The more negatively charged AlO_2Na ($^{[4]}Al$) tetrahedra attract Na^+, thereby decreasing the average Na-O bond length and increasing the order (and possibly reducing coordination) around the sodium atoms. In summary, the EXAFS measurements show greater order and tighter bonding of sodium in the glass structure as Al_2O_3 is added. This is consistent with the lower rate of sodium ion exchange observed for these glasses.

Planned Activities

Complete glass-water reaction experiments will be performed with Series II glass. This will include investigating temperature effects on matrix dissolution and Na-release in both H_2O and D_2O. We will relate differences in Na-H exchange to structural changes determined by multiple techniques (NMR, XPS, XAS).

We will complete detailed investigations of Series III glass. We will elucidate the effects of systematic addition of La, Hf, and Zr on glass structure and Na ion exchange rates.

Information Access

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