Environmental Management Science Program

Project ID Number 60362

Ion-Exchange Processes and Mechanisms in Glasses

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June 1, 1998

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Research Objective

Recent performance assessment calculations of a disposal system at the Hanford Site in Washington State for low-activity waste glass show that a sodium ion exchange reaction can effectively increase the radionuclide release rate by over a factor of 1000. The susceptibility of the glass to alkali ion exchange is thus a major factor limiting waste loading. However, low temperature ion exchange has not been thought to be important in recent analyses of waste glass durability. 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

This report summarizes eight months of work on this three-year project that is being performed cooperatively between Pacific Northwest National Laboratory and Lawrence Berkeley National Laboratory. A Series I set of glasses in the system Na_2O-Al_2O_3-SiO_2 was developed; the objective was to vary the distribution of Na^+ among Q3Si non-bridging oxygen (NBO) and four-coordinated Al sites. A base glass of $33.33Na_2O$-$66.67SiO_2$ (in mol%) was selected because this formulation contains the largest amount of Na_2O possible to theoretically maintain no more than one NBO per Si atom. Five Na_2O-Al_2O_3-SiO_2 glasses were formulated, with the concentration of Al_2O_3 ranging from 0 to 20 mol%.

Samples of these glasses, as well as reference materials, were analyzed using 27Al solid-state nuclear magnetic resonance (NMR). The results showed only a single, broad, asymmetric 27Al NMR peak at 61±1 ppm. A peak at this position indicates tetrahedrally coordinated Al rather than octahedrally coordinated Al, confirming that all of the Al in these glasses occurs as tetrahedrally coordinated network forming sites, presumably by association with charge-compensating Na^+ ions. Substituting Al_2O_3 for SiO_2 also shifts the ^{29}Si NMR peak position systematically as the Al_2O_3 content of the glass increases. This indicates that the Na^+ is transferred from being associated with Q3Si sites to being associated with network-forming Al sites, which will presumably affect the rate of Na^+ ion exchange.

Additional structural characterization of these glasses was carried out using a new experimental approach to obtain x-ray absorption fine structure (XAFS) data from the Na K-edge using the high photon energy capabilities of a spherical grating monochromator matched with an undulator source at the Advanced Light Source (ALS). To the best of our knowledge, these are the first studies to take advantage of these new opportunities. Smoothed Na XAFS spectra were collected at the ALS in fluorescence detection mode from the test glasses and a reference material. Differences were clearly observed in the near-edge region of the spectra. The data from the extended portion of the Na XAFS spectra are being processed and theoretically fit to determine whether they are of high enough quality to permit the extraction of the Na structural parameters. The results of these studies firmly substantiate that XAFS of glass constituents will provide the structural information component necessary to understand the role of Na in the ion exchange process and many other light element