Project ID: **60362**

Project Title: **Ion-Exchange Processes and Mechanisms in Glasses**

Lead Principal Investigator:

Dr. B. Peter McGrail
Staff Scientist IV
Pacific Northwest National Laboratory
MS K6-81
P. O. Box 999
Richland, Washington 99352
Telephone: 509-376-9193
e-mail: Pete.McGrail@pnl.gov

Co Principal Investigators:

Dr. David K. Shuh
Chemical Sciences
Lawrence Berkeley National Laboratory
MS 70A-1150
One Cyclotron Road
Berkeley California 94720
Telephone: 510-486-6937
e-mail: dkshuh@lbl.gov

Ion Exchange Processes and Mechanisms in Glasses

Pacific Northwest National Laboratory
June 1, 1999

Progress Report

Principal Investigator

Dr. B. P. McGrail
(509) 376-9193 (Phone)
(509) 376-2210 (Fax)
pete.mcgrail@pnl.gov
Pacific Northwest National Laboratory
PO Box 999, MSIN K6-81
Richland, WA 99352

Contributors and Collaborators

D. R. Baer (PNNL)
J. G. Darab (PNNL)
M. H. Engelhard (PNNL)
J. P. Icenhower (PNNL)
D. K. Shuh (LBNL)
S. Thevusathan (PNNL)

Research Objective

Recent performance assessment calculations [1] of a disposal system at Hanford, Washington for low activity waste glass show that a Na ion-exchange reaction can effectively increase the radionuclide release rate by over a factor of 1000 and so is a major factor that currently limits 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 Statement

This multidisciplinary research program involves two primary tasks to develop an understanding of the processes and mechanisms that control ion exchange, specifically Na ion exchange, in waste glass materials: 1) reaction mechanisms, and 2) glass structure correlations. The objective of the reaction mechanisms task is to identify specific ion-exchange mechanism(s) by using surface analytical techniques to probe the distribution of selected elements in the hydrated layers on glass surfaces. Differences in the uptake and distribution of selected isotopes will provide a signature characteristic of specific ion-exchange reactions. The objective of the glass structure task is to determine whether differences in key structural properties, such as the number of nonbridging oxygens (NBO), bonding of alkali to other elements in the glass, and alkali coordination, can be correlated with differences in measured rates of alkali exchange. The reaction mechanisms and glass structure tasks are discussed in detail in the following sections.

An overview of the proposed research plan is given in Figure 1. To simplify interpretation of the kinetics measurements and glass structure analyses, three series of simple glasses in the Na_2O-Al_2O_3-B_2O_3-SiO_2 family will be examined where the amounts of Na, Al, B, and Si are systematically varied along compositional joins. Selective substitutions of network modifiers such as CaO, ZrO_2, and La_2O_3, will also be made in the base glass to change the bonding coordination of Na^+ with network intermediate sites. Differences in the structural properties of these

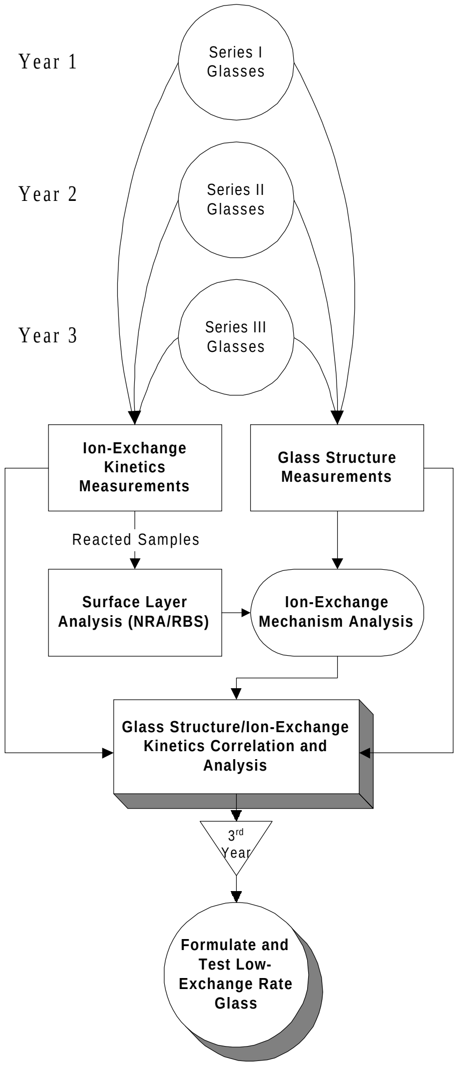

Figure 1. Research Plan Flow Chart

glasses will then be correlated with observed changes in the Na ion-exchange kinetics. It is the *combination* of the glass structure correlations with the identification of the ion-exchange reaction mechanism(s) that provides the underpinning scientific basis for formulation of glasses with lower rates of alkali ion exchange. This new understanding of ion-exchange processes and mechanisms will be evaluated at the conclusion of this research project in the formulation and testing of a low ion-exchange rate glass with a 25 wt% Na_2O loading.

Research Progress

Project Status

This project was initiated in FY98 and is being performed cooperatively between PNNL and LBNL. Progress has primarily focused on three activities 1) developing and manufacturing the Series I glasses and formulating Series II glasses, 2) characterizing these glasses, and 3) conducting flow-through tests for measuring Na ion-exchange kinetics. A few scoping measurements of isotope distributions have also been completed using nuclear reaction analysis (NRA) and elemental depth profiles using Rutherford backscattering spectroscopy (RBS).

Technical Progress

Current plans for immobilizing low activity radioactive wastes includes vitrification followed by subsurface storage. All scenarios for waste disposal includes the provision that groundwater will eventually breach the outer containment and interact with the vitrified material. In many cases, high alkali loading in the glass is a concern because exchange of alkalis in the glass for hydrogen species in solution will cause a rise in solution pH with a concomitant rise in glass dissolution rates. Glass compositions that are vulnerable to alkali leaching may have significantly higher release rates of radioactive elements. Accordingly, our investigation is aimed at understanding the link between glass structure and alkali H-species exchange reactions. These studies will serve the dual purpose of providing decisive information for fashioning alkali leach-resistant glass compositions and probe fundamental glass structure-solution interactions.

The vitrification of low-activity waste (LAW) streams into durable glass waste forms will be limited by the ability of the glass to accommodate the sodium in the waste. In Na_2O-SiO_2 glasses, for example, the Na_2O enters the glass structure through the formation of and association with non-bridging oxygen (NBO) sites (e.g., $^{Q3}SiO_{2.5}Na$), making the glass more susceptible to chemical attack. Adding Al_2O_3, for example, to a Na_2O-SiO_2 glass formulation decreases the concentration of NBO sites through the formation of tetrahedrally coordinated AlO_2Na species.

Current models of glass interactions with aqueous solutions state that alkali H-species exchange occurs at small values of reaction progress. However, as we demonstrate below, this exchange process continues to occur at high values of reaction progress. This previously unrecognized behavior of glass-solution interactions is important to modeling long-term release rates of radioactive elements in vitrified waste.

Glass System Development

For our initial alkali leaching investigations, we have selected Na-Al-Si glass compositions designed to keep the fraction of metals in the glass that are network formers (f_M^N) constant at 0.50 while varying the distribution of Na^+ between association with ^{Q3}Si non-bridging oxygen sites (f_{Na}^{Q3}) and four-coordinated Al sites (f_{Na}^{Al}). Based on a 33.33Na_2O-66.67SiO_2 composition, which was given the nomenclature NaSiO-X, a total of five Na_2O-Al_2O_3-SiO_2 glasses were formulated with the concentration of Al_2O_3 ranging from 0 to 20 mol%. Each glass was also doped with 0.1 wt% MoO_3 for use as a tracer of glass matrix dissolution. The glasses were batched in 100+ gram quantities using Na_2CO_3, Al_2O_3 and SiO_2, melted at 1500°C for 1 hour in air, then quenched on a stainless steel plate. All melts except the NaSiO-20.0Al glass were visually homogeneous and readily pourable and yielded a clear, visibly homogenous glass. Table 1 summarizes the target composition of these glasses. The selected Series II set of glasses consist of a set of Na-B-Si and Na-Al-B-Si glasses shown in Table 1. Molybdenum was not added to these glasses because B provides an equivalent tracer element for glass matrix dissolution.

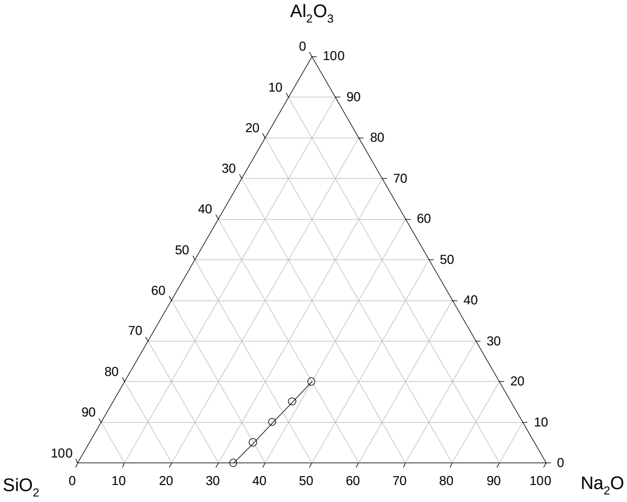

Figure 2. Ternary Diagram Illustrating Compositions of Series I Glasses

Table 1. Target compositions (in wt% oxide component), MAS-NMR ^{29}Si chemical shift values (δ), and normalized 7-day PCT mass loss of boron (NL_B) for the glasses studied in this work.

	Oxide Component					δ (ppm)	NL_B
Glass	SiO_2	B_2O_3	Al_2O_3	Na_2O	Other	^{29}Si [b]	(g/m^2)
Bas-1	74.0	6.0	-	20.0	-	-99±1	[c]
B-3	77.0	3.0	-	20.0	-	-99±1	[c]
B-16	64.0	16.0	-	20.0	-	-97±1	11.70
B-24	56.0	24.0	-	20.0	-	-94.5±0.5	12.13
Al-4	70.0	6.0	4.0	20.0	-	-96±1	6.908
Al-8	66.0	6.0	8.0	20.0	-	-95±1	1.267
Al-16	58.0	6.0	16.0	20.0	-	-92.0±0.5	0.145
Al-24	50.0	6.0	24.0	20.0	-	-90.3±0.5	0.151
NaSiO-X	65.9	-	-	34.1	-	-87±1	na
NaSiO-5Al	57.3	-	8.1	34.6	-	-86±1	na
NaSiO-10Al	49.3	-	15.7	35.0	-	-80±1	na
NaSiO-15Al	41.8	-	22.8	35.4	-	-78±1	na

[b] Chemical shift reported with respect to TMS (tetramethylsilane). [c] The Bas-1 and B-3 glasses completely dissolved during the test. na = not applicable.

NMR Characterization

Magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy is a sensitive technique for studying the structure and chemical environment of many of the nuclei contained in LAW glass (^{11}B, ^{27}Al, ^{29}Si, ^{31}P, etc.). We are building on our previous structural characterization work [2] to develop a model to predict the ^{29}Si MAS-NMR chemical shift value, δ, for a particular glass which we then use to describe the chemical nature of the glass network. By using δ as an indicator of the bonding characteristics within a glass network, we take into account the effects of primary bond strengths [2] as well as secondary effects, such as partial covalent bonding, which are not accounted for in other models. To date, we have focused on sodium borosilicate, sodium boro-aluminosilicate, and sodium aluminosilicate glasses as well as more complex simulated LAW glasses (see Table 1).

Room temperature ^{29}Si, ^{27}Al, and ^{11}B magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were obtained on a Varian VXR-300 spectrometer at 7.05 T using high-speed probes manufactured by Doty Scientific, Inc. Silicon nitride rotors (5 mm diameter) or sapphire rotors (7 mm diameter) with Vespel polymer end caps were used to spin the samples at 5 kHz. In addition to the long term corrosion studies, a product consistency test (PCT) was used to determine the leachability of the prepared glasses. Powdered glass samples were immersed in distilled/deionized water at 90°C for 7-days and the leachate analyzed chemically. Details are summarized elsewhere [2]. The relevant MAS-NMR and PCT results are given in Table 1.

For the Bas-1, B-, and Al- series glasses (see Table 1), there is a rudimentary relationship between the ^{29}Si chemical shift (δ) and the normalized release of boron (NL_B); for δ less than -99 ppm the glass completely dissolves during PCT evaluation, while relatively durable glasses give rise to δ values greater than about -92 ppm. Glasses with intermediate δ values are indicative of intermediate durability. We have discussed this relationship in more detail in a recent publication [3] and plan on testing this approach with the ion-exchange kinetics measurements obtained under this project. The first step in this approach, however, is measuring, or predicting, the ^{29}Si chemical shift value as a function of glass composition.

The resonance line shapes of the ^{27}Al MAS-NMR spectra obtained from the glasses studied here (not shown) are nearly identical for all the glasses and are indicative of predominantly (>98%) tetrahedral coordination to four oxygens [2], which we designate as Al^{iv}, presumably occurring as network forming units. For simplicity, we have assumed that 100% of the Al in these glasses occurs as Al^{iv} units. The environment of the boron in relevant glasses is a combination of both tetrahedrally (B^{iv}), and trigonally (B^{iii}) coordinated sites, the relative amounts of each depending on the composition of the glass [4]. MAS-NMR is very sensitive to the coordination symmetry of the B (spectra not shown), allowing for the quantitative determination of the relative amounts of B^{iv} and B^{iii} in these glasses [2,5].

The tetrahedrally coordinated Al^{iv} (chemically represented by AlO_2^-) and B^{iv} (BO_2^-) sites identified in these glasses need to be charge-compensated through association with alkali (Na^+) cations. Any excess Na^+ then most likely become associated with NBO sites such as ^{Q3}Si (e.g., $SiO_{2.5}Na$) and ^{Q2}Si (e.g., SiO_3Na_2). Based on the summary by Eckert [6] and the concentration of the sodium-gettering Al_2O_3/B_2O_3 components in the glasses examined in this work, the distribution of silicon species will occur predominantly between ${}^{Q4}Si$ and ${}^{Q3}Si$ with much less than 10% as ${}^{Q2}Si$ and close to zero ${}^{Q1}Si$. For simplicity, we have assumed that in the glasses discussed here, silicon occurs as ${}^{Q4}Si$ and ${}^{Q3}Si$ species only. The Na^+ in these glasses is thus distributed between the ${}^{Q3}Si$ NBO, B^{iv}, and Al^{iv} sites.

The glass composition and the distribution of structural units within a glass are important factors which dictate the ${}^{29}Si$ NMR chemical shift values. For example, as the relative Na_2O content in Na_2O-SiO_2 glasses is increased, the average ${}^{29}Si$ MAS-NMR chemical shift value, δ, becomes less negative as more ${}^{Q3}Si$ sites are generated at the expense of ${}^{Q4}Si$ sites [5-6]. Increasing the relative amount of Al_2O_3 in Al_2O_3-SiO_2 glass compositions causes δ for ${}^{29}Si$ to become less negative, due to changes in the electron density in the vicinity of the silicon.

Darab, et. al. [3] found that the overall ${}^{29}Si$ MAS-NMR chemical shift value for glasses typical of those studied here can be predicted ($r^2 = 0.9915$) using the following expression:

$$\delta = -111 + 51\, f_{Al}{}^{N} + 44\, f_{B4}{}^{N} + 22\, f_{Q3}{}^{N} \tag{1}$$

where

$$f_{Al}{}^{N} = [Al]/([Si] + [B] + [Al]) \tag{2}$$

$$f_{B4}{}^{N} = [B^{iv}]/([Si] + [B] + [Al]) \tag{3}$$

$$f_{Q3}{}^{N} = [{}^{Q3}Si]/([Si] + [B] + [Al]) \tag{4}$$

X-ray Absorption Spectroscopy Characterization

The modeling of the near-edge x-ray absorption fine structure (XAFS) spectra at the Na K-edge has been initiated using the FEFF7 computer code. A series of theoretical calculations of the Na K near-edge spectrum for the reference sodium compounds were performed and are shown in Figure 3 along with the smoothed near-edge spectrum of Glass #2, a specialty glass for Pu immobilization [7], for comparison. The Na K-edge XANES structure calculation were done using FEFF7 program and all energies were calibrated to Na K-edge at 1067 eV [8]. These results illustrate that there is a significant difference in the structures of sodium K-edge spectra for Na ions in different crystal environments. Qualitative interpretation of the spectra in Figure 3 suggests that the local structural environment of Na in Glass #2 resembles that found in Na_2O and Na_2SiO_3.

The theoretical calculations using the FEFF7 methodology form an essential component of the XAFS structural characterization program and will be used extensively throughout to maximize the information obtained from the experimental measurements. FEFF7 will continue to be used to model the Na K-edge spectra in the near-edge region and in the extended-XAFS region to extract structural parameters. Furthermore, FEFF7 simulations will be used to evaluate model compounds prior to experimentation to maximize the utility of beam time. For instance, theoretical calculations of Na K-edge from $Na_4Si_4O_9$ and well-characterized glasses ($Na_{0.17}Al_{0.03}Si_{0.23}O_{0.56}$ and $Na_{0.17}Al_{0.15}B_{0.04}Si_{0.09}O_{0.56}$) will be done to obtain an improved basis to interpret structural information from the experimental spectra. As the glass materials have a substantial component of disorder, a method to include this in the calculations beyond what is currently available is being examined.

The initial experimental Na XAFS investigations have shown that Beamline 8.0 at the Advanced Light Source (ALS) is the best beamline to make these measurements on prior to the commissioning of the new Beamline 6 facility designed for 1-2 keV science. Efforts to collect Na XAFS on Beamline 9.3.2 have been slowed by the availability of the high-energy monochromator diffraction grating, which has been sent out for repair. An Independent Investigator Program proposal was submitted to the ALS to obtain the beam time necessary on Beamline 8.0 to collect the XAFS from the glass materials [9]. The experimental equipment to make the measurements on Beamline 8.0 has been assembled and tested during the most recent beam run at the ALS on Beamline 7.0.

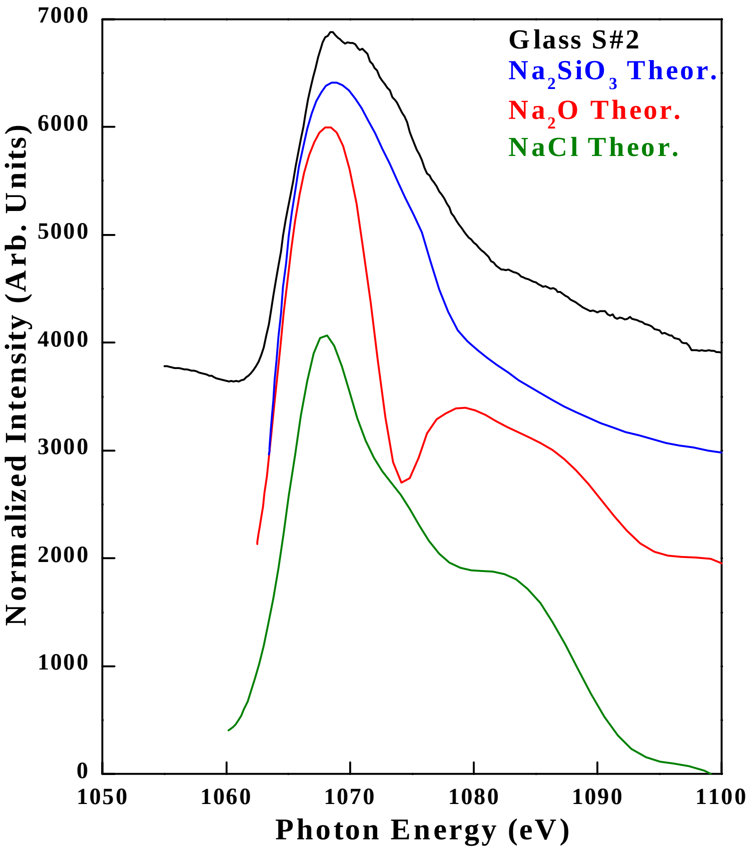

Figure 3. NEXAFS spectrum of Glass #2 (smoothed) and results of theoretical calculations of the Na K-edge for reference sodium compounds. The traces are from top to bottom; the experimental spectrum of Glass #2 and the simulated edges from the Na reference materials Na_2SiO_3, Na_2O, and NaCl, respectively. Intensities are normalized to the intensity of the main peak of the Na XAFS and the spectra are aligned to 1067 eV. A linear background also has been subtracted from the experimental near edge spectrum.

Ion-Exchange Kinetics

An accurate measurement of the rate of Na ion exchange from the test glasses is one of the key challenges on this project. The experiments must be performed under controlled conditions of constant pH, temperature and solution composition. The kinetics of Na-Al-Si glass dissolution and ion exchange were determined with a unique single-pass flow-through (SPFT) system. Glass coupons (up to five) were placed into columns fashioned from polyetheretherketone containing five individual cells. The cells are interconnected by a narrow tunnel that passes from the bottom to the top of the column, allowing solutions to flow from the reservoir, past each glass coupon, and out of the column to the sample collection vial. In this manner, the solution reacts with the samples and individual coupons can be removed from the column for analysis of reaction layers without disrupting the other coupons (see Figure 4).

Solutions were made up by adding THAM (tris hydroxymethyl aminomethane) to deionized water to bring the concentration up to 0.01 or 0.05 M. Ultra pure nitric acid was then added to the solution to bring the solution pH to the desired value (8 or 9). We found that the maximum buffering capacity of this weak buffer solution is at pH values of 8. We additionally added silicon to the solution (2.3×10^{-3} M) in the form of amorphous silica. The solutions were heated to 90°C to facilitate the dissolution of silica into solution. The high concentrations of Si in solution correspond to oversaturated conditions, which simulates high reaction progress and minimizes glass matrix dissolution. In summary, the solutions are designed to maintain a uniform pH and to fix the reaction affinity at a constant high level, conditions that are lacking in previous investigations.

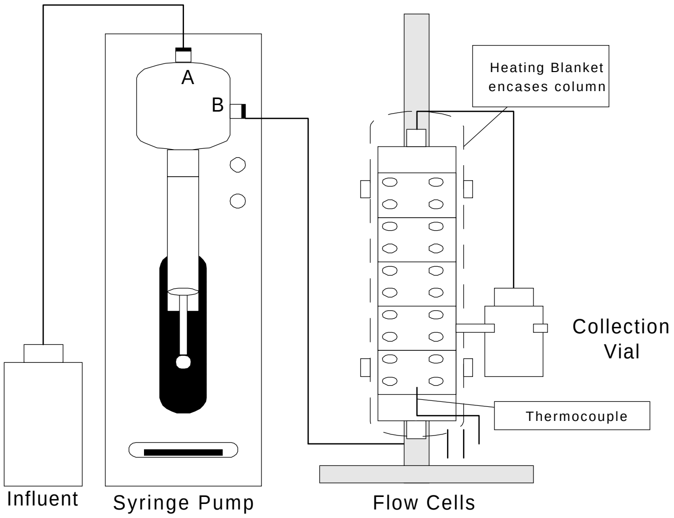

Figure 4. Schematic of Multichamber Flow-Through Column for Ion-Exchange Kinetics Tests

Flow-through rates varied depending on the glass composition. To maintain constant pH, even when the solutions are buffered, we found that flow-through rates of 20 ml/day were necessary for the 5 mol% Al_2O_3 glass. In contrast, flow-through rates of 1 to 3 ml/day were adequate for the 10 and 15 mol% Al_2O_3 glasses. Relatively low flow-through rates, such as those used in these experiments, are necessary to yield concentrations of elements in solution high enough to be detected during chemical analysis (ICP-MS). Typical run durations varied from 6 hours to 28 days, depending on the information sought. Short run times (6 to 72 hours) were necessary to detect differences in sodium depletion profiles as a function of time with Rutherford Backscattering Spectroscopy (RBS). In contrast, longer duration experiments are necessary to establish steady-state dissolution rates, as explained in the next section. All experiments have been conducted at room temperature.

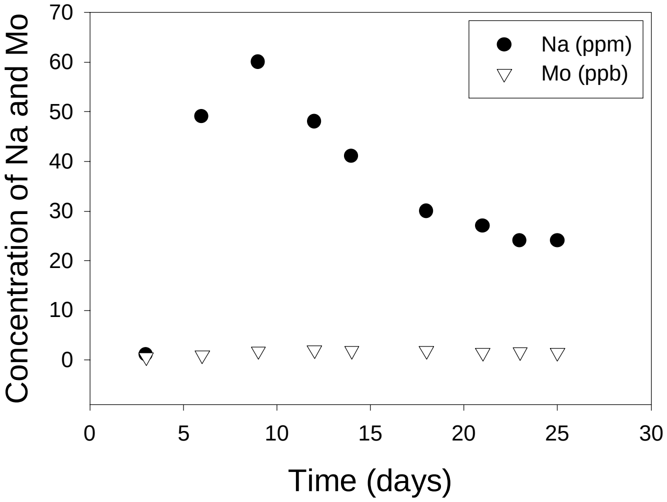

Figure 5. Concentrations of Na and Mo vs. time for 10 mole% Al_2O_3 glass, T = 15°C, pH = 8

A typical concentration (Na and Mo) profile versus time in an experiment with low flow-through rates is illustrated in Figure 5, in this case, 2 ml/day. The concentrations of Na and Mo at steady-state conditions were then used to calculate normalized release rates, as shown in Figure 5. For each glass composition, the apparent dissolution rates based on Na and Mo differ by a factor of ~100. These disparities in apparent dissolution rates indicate that two distinctly different glass-solution reactions are operating. Sodium concentrations in solution are due to two distinctly different processes: (1) dissolution of the glass into aqueous components; and, (2) exchange of Na^+ in glass with H_3O^+ (or H^+) in solution. In contrast, the presence of Mo(VI) in solution is probably due solely to dissolution of the glass framework. Calculations suggest that the proportion of Na$^+$ to Mo(VI) in solution is much greater (80 to 120X) than the proportion of these cations in glass, indicating that the alkali for hydronium exchange is operating even when the solution is supersaturated with respect to amorphous silica (i.e., affinity term maximized). Therefore, a major postulate of this investigation appears to have been confirmed; alkali exchange is an important mechanism of glass/solution reactions even when reaction progress in high.

The number of Na atoms in the leached layer were determined by comparing the RBS spectra for the reacted to that of non-reacted (‘blank’) coupons. Spectra were collected by accelerating 2.04 MeV He ions at the target coupons. The accumulated charge was 60 μC and the scattering angle 170 degrees. Hydrogen-uptake profiles in the leached layer were determined by nuclear reaction analysis (NRA) by comparing spectra between reacted and non-reacted (‘blank’) samples. The analyses were performed using ^{19}F ions with energies between 6.4 to 9.0 MeV. A typical RBS spectra plot is illustrated in Figure 7 for a leached and a non-reacted (‘blank’) coupon. This illustration plots channel vs. counts, which is roughly equivalent to plotting energy vs. concentration. The number of counts in this illustration has been normalized to the number of Si atoms so the two spectra can be compared. Several features of the spectra should be noted, beginning with the sharp rise in the number of counts from the left of the diagram (towards low ‘channels’ or energy). This feature represents the Si edge, and the Na edge is evident in the ‘blank’ coupon spectra further to the right of the diagram. The smaller number of counts in the energy region corresponding to Na in

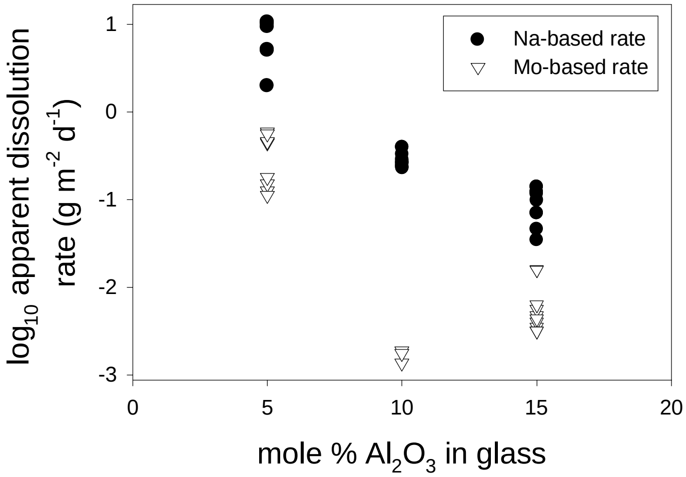

Figure 6. Plot of apparent dissolution rates vs. Al-content of glass T = 15°C, pH = 8-9

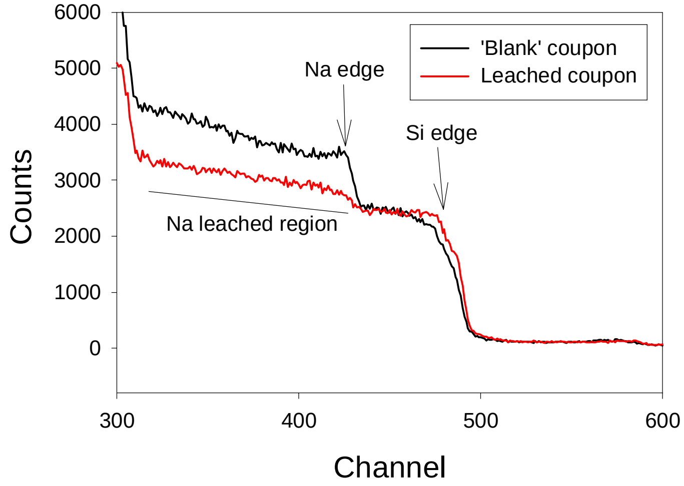

Figure 7. RBS spectra illustrating channel (= energy) vs. counts for glass coupons, normalized to Si atoms

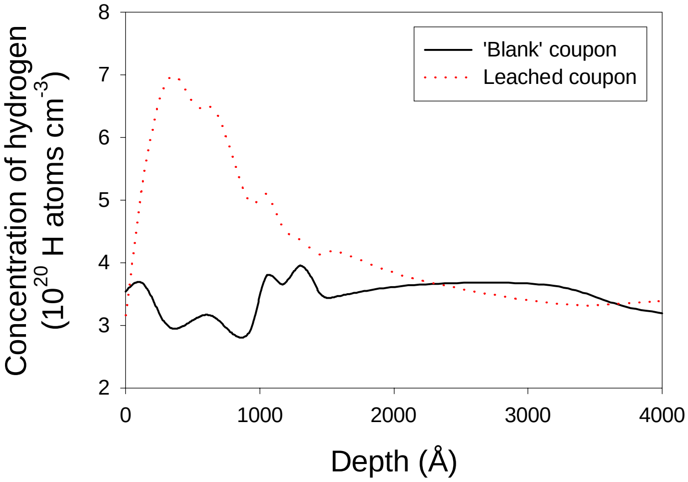

Figure 8. Plot of depth vs. hydrogen concentration for leached and unleached coupons based upon fluorine RBS spectra

the leached compared with the ‘blank’ coupon represents sodium loss from the glass. The approximate depth of Na depletion is estimated to be between 2000 and 3000 Å. The depth of Na depletion roughly corresponds to the depth of hydrogen uptake, as illustrated in Figure 8. Comparing leached and ‘blank’ glass coupons, Figure 8 shows that hydrogen concentrations are relatively enriched in a region approximately 500 to 1000 Å.

Future Research Directions

Dissolution experiments using D_2O and $D_2{}^{18}O$ have been initiated but the results are not available for this report. Measurement of D and ^{18}O uptake in the glass coupons will provide crucial information on the exact mechanism of alkali H-species exchange. Additional experiments will be carried out to establish the temperature dependence of alkali exchange and matrix dissolution. We expect that the activation energy of ion exchange will be much lower than matrix dissolution, underscoring the importance of alkali exchange at the lower temperatures (10 to 20°C) that will prevail in a disposal vault.

References

1. Mann, F. M., R. P. Puigh II, C. R. Eiholzer, Y. Chen, N. W. Kline, A. H. Lu, B. P. McGrail, and P. D. Rittmann. 1998. *Hanford Immobilized Low-Activity Tank Waste Performance Assessment*. DOE/RL-97-69, Rev. 0, Project Hanford Management Contractor, Richland, Washington.
2. Darab, J. G., X. Feng, J. C. Linehan, P. A. Smith, and I. Roth. 1997. “Composition-Structure Relationships in Model Hanford Low-Level Waste Glasses.” *Ceram. Trans.* **72**:103-110.
3. Darab, J. G., J. C. Linehan, and B. P. McGrail. 1999. *Mat. Res. Soc. Symp Proc.* in press.
4. Yun, Y. H. and P. J. Bray. 1978. *J. Non-Cryst. Solids* **27**:363.
5. Kirkpatrick, R.J. 1988. In *Spectroscopic Methods in Mineralogy and Geology*, ed. F.C. Hawthorne (Mineralogical Soc. of America, Washington, D.C.), pp. 341-403.
6. Eckert, H. 1992. *Progress in NMR Spectroscopy* **24**:159.
7. Darab, J. G. et al. 1997. “Redox of Pu and Ce in Vitrified Waste.” In Plutonium Futures - The Science Conference, Los Alamos National Laboratory, Albuquerque, New Mexico.
8. Ankudinov, K. L., S. I. Zabinsky, J. J. Rehr, and R. C. Albers, “Ab Initio Multiple-Scattering X-Ray Absorption Fine Structure and X-Ray Absorption Near Edge Structure Code," (Copyright 1992, 1993, 1994, 1996) University of Washington, Seattle, Washington.
9. ALS Independent Investigator Proposal (ALS-00177): K. E. Ivanov, P. Liu, D. K. Shuh, B. P. McGrail, J. G. Darab, and D. Baer, “Investigation of Sodium Structure in Waste Form Glasses by Na K-Edge X-ray Absorption Fine Structure, Submitted December, 1 1998.