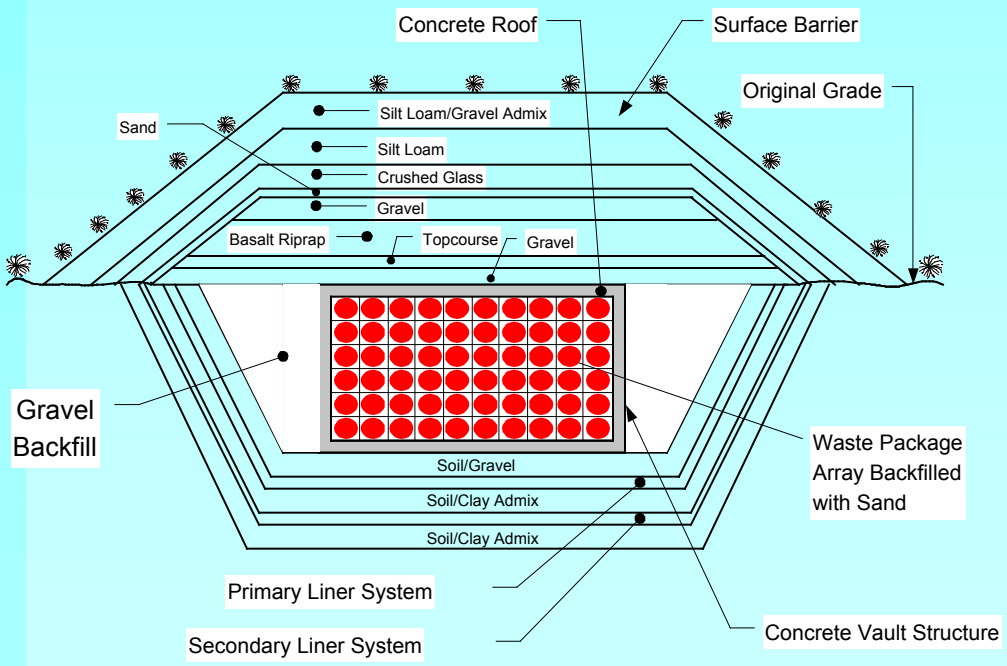
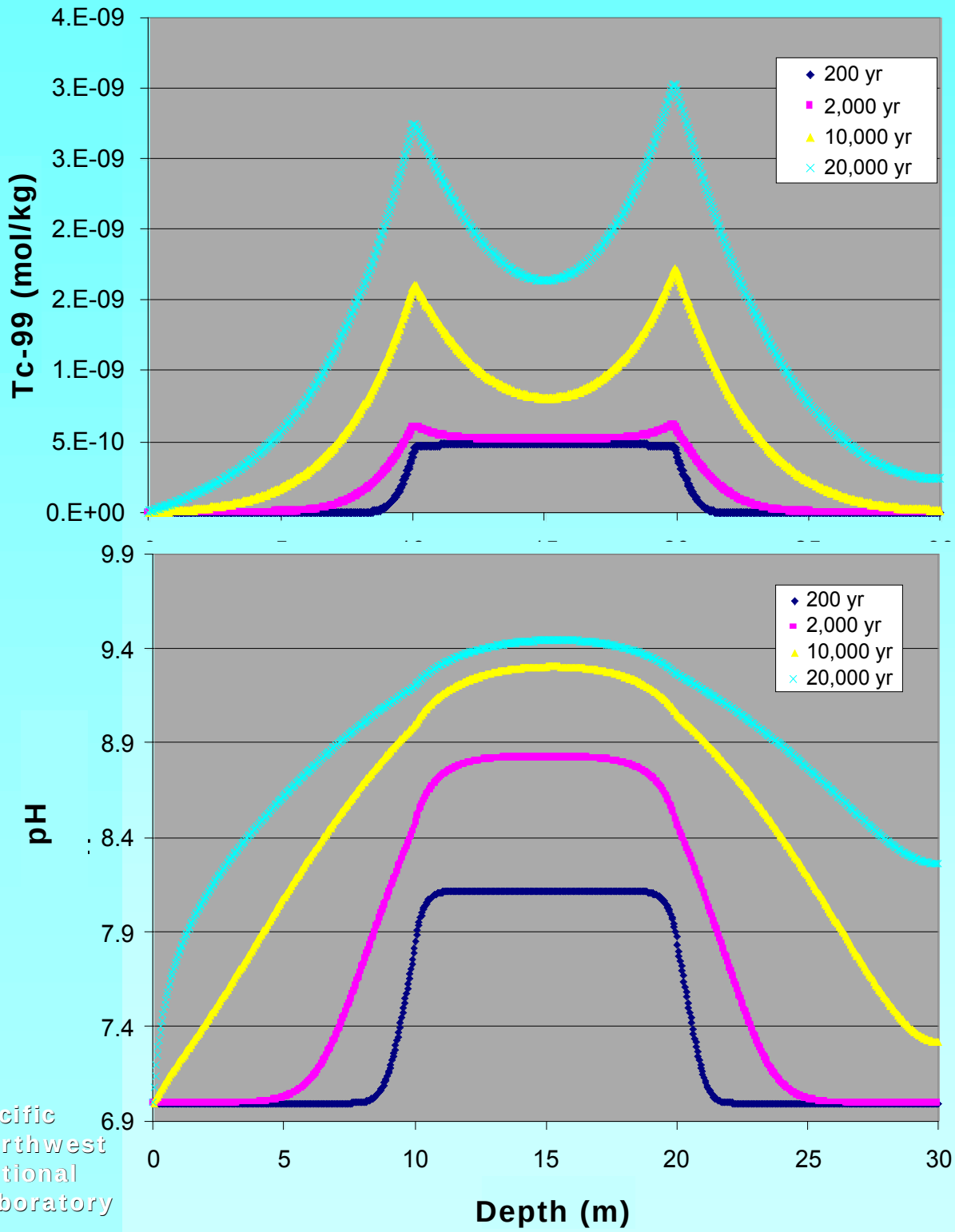
1. Nature of the Problem

Remediation of 50,000,000 gal of high-level waste stored in single and double-shell tanks at Hanford will include vitrification of the separated low-activity waste stream to generate over 500,000 metric tons of low-activity waste glass for disposal on site.

The vitrified waste contains a fairly high Na content (20 mass% Na_2O or higher). Computer simulations of the disposal system containing this glass show that Na ion-exchange reactions significantly alter the pH of any water percolating through the system and, therefore, increase overall radionuclide release rates.

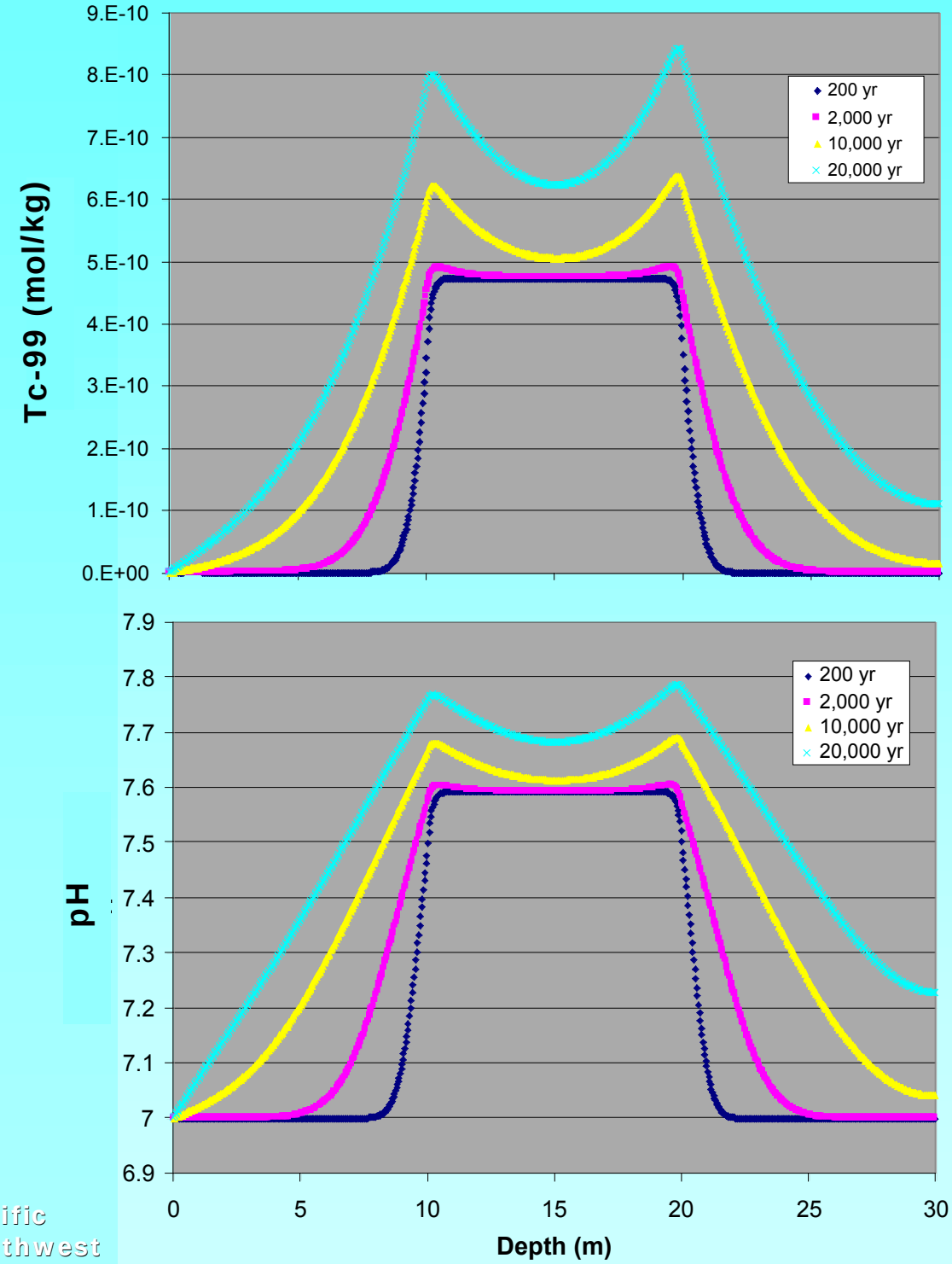


1a. Reactive Transport Simulations Using STORM
Including Na Ion Exchange Reaction



Pacific Northwest National Laboratory

1b. Reactive Transport Simulations Using STORM
Excluding Na Ion-Exchange Reaction



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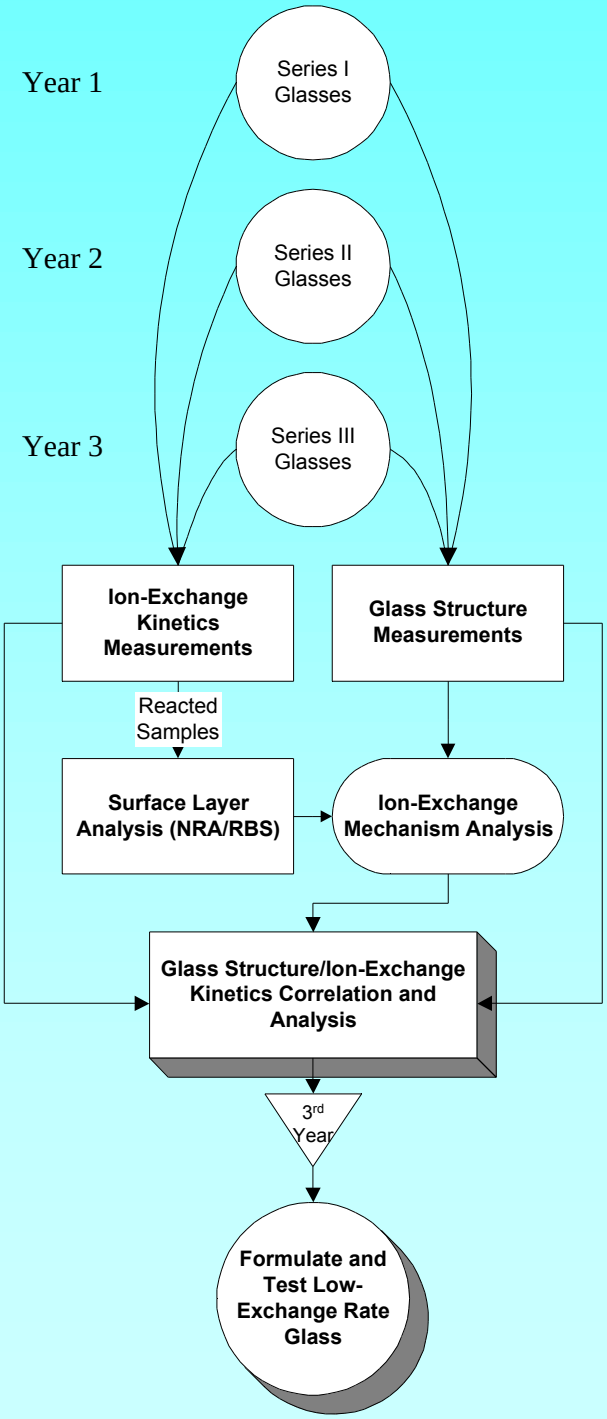
2. Research Objectives

- Develop fundamental scientific understanding of ion-exchange processes in silicate glasses
- Use fundamental knowledge to formulate and evaluate new glass compositions with lower Na exchange rates.

Overall Research Plan



3. Series 1 Glass Compositions

The objective of the glass formulation scheme used in this work was to allow for sufficient variation in the distribution of Na^+ in representative glasses (i.e., Na^+ distributed between ^{Q3}Si non-bridging oxygen and four-coordinated Al) to assess the affect of glass structure and chemistry, and in particular, the local environment of sodium, on the properties of the glass. After several test melts, a $33.33Na_2O$-$66.67SiO_2$ (composition in mol%) base glass composition was selected. This formulation contains the largest amount of Na_2O possible to theoretically maintain no more than one NBO per Si atom (i.e., all the Si occurs as ^{Q3}Si). A set of sodium aluminum silicate glasses was then 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 the $33.33Na_2O$-$66.67SiO_2$ 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%

4. Glass Structure Characterization by NMR

As the glass composition is systematically changed from that of NaSiO-X to that of NaSiO-15.0Al, a greater amount of the Na^+ is transferred from being associated with ^{Q3}Si sites to being associated with network forming Al sites. Samples of these glasses, as well as reference materials, were analyzed using ^{27}Al solid state NMR to indirectly confirm this distribution of Na^+. The results are summarized in the table above. Each of the glasses exhibited only a single, broad, asymmetric ^{27}Al NMR peak at 61±1 ppm, indicating that all of the Al in these four glasses is tetrahedrally coordinated, presumably by association with charge compensating Na^+ ions. Based on this presumption and the target concentration of Al_2O_3 and Na_2O in these glasses, the f_{Na}^{Al} values have been determined. Assuming that the remaining Na^+ is associated with ^{Q3}Si, the f_{Na}^{Q3} values have also been calculated.

Similarly, ^{29}Si solid state NMR spectra were obtained for each of these glasses. Only a single, relatively broad but symmetric ^{29}Si NMR peak was observed. The ^{29}Si NMR peak position systematically shifts from -87 ppm for the NaSiO-X glass to -78 ppm for the NaSiO-15.0Al glass (see Table above) due to the substitution of Al_2O_3 for SiO_2. This range of chemical shifts is typical of ^{Q3}Si.

4.1 Glass Structure Characterization by NMR

Composition, Theoretical Fractions of Sodium Associated with NBOs (f_{Na}^{Q3}) and Tetrahedrally Coordinated Al (f_{Na}^{Al}), and NMR Results Obtained for the Series I Glasses.

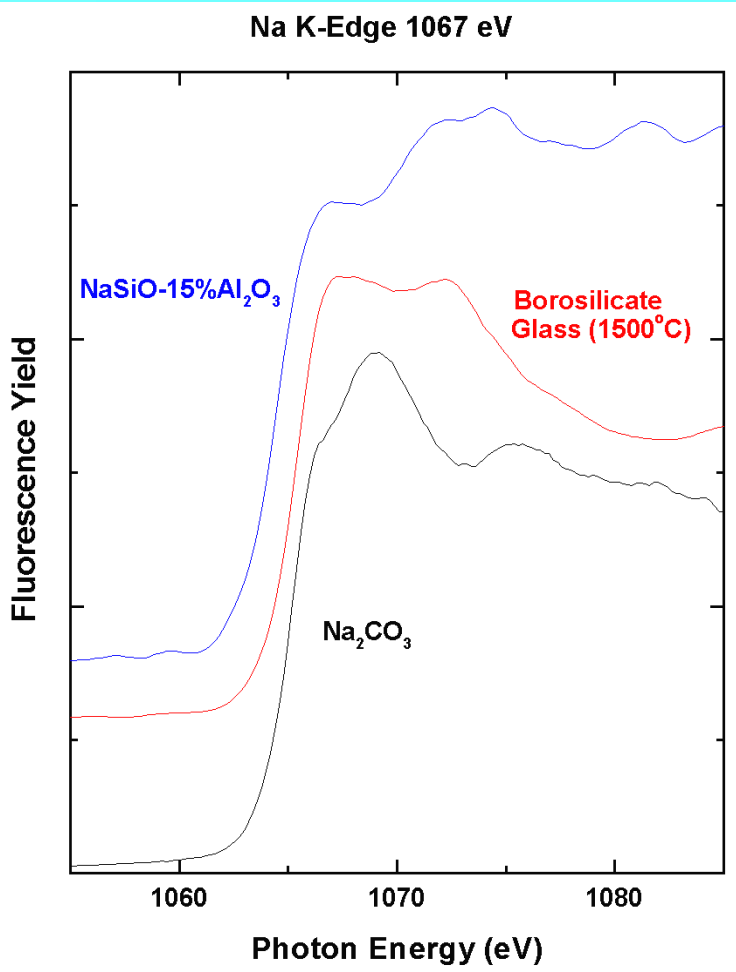
Sample	Composition (mol%)			f_{Na}^{Q3}	f_{Na}^{Al}	peak position (ppm)	
	Na_2O	Al_2O_3	SiO_2			$^{29}Si^a$	$^{27}Al^b$
NaSiO-X	33.33	-	66.67	1.00	-	-87±1	-
NaSiO-5.0Al	35.00	5.00	60.00	0.86	0.14	-86±1	+61±1
NaSiO-10.0Al	36.67	10.00	53.33	0.73	0.27	-81±1	+61±1
NaSiO-15.0Al	38.33	15.00	46.67	0.61	0.39	-78±1	+62±1
NaSiO-20.0Al[c]	40.00	20.00	40.00	0.50	0.50	-	-
α-Al_2O_3	-	100.00	-	-	-	-	+12±1

[a]Tetramethylsilane (TMS) was used as a ^{29}Si NMR reference. [b]$AlCl_3$ was used as a ^{27}Al NMR reference. [c]The NaSiO-20.0Al glass did not form a homogeneous melt and was thus not considered further. - indicates "not applicable."

5. Glass Structure Investigation

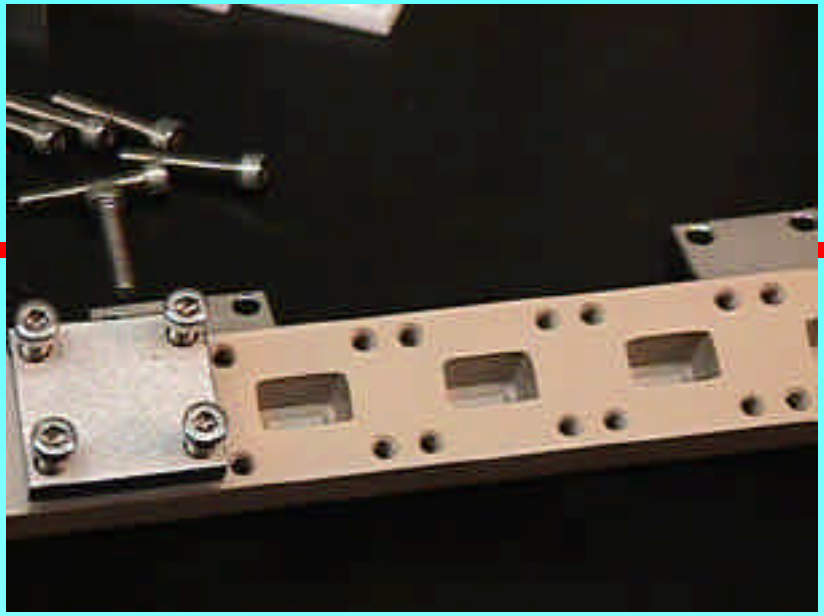
A new experimental approach to obtain x-ray absorption fine structure (XAFS) data from the Na K-edge has been explored utilizing the high photon energy capabilities of a spherical grating monochromator (SGM) matched with an undulator source of the ALS. To the best of our knowledge, these are the first studies to take advantage of these new opportunities. All previous studies have employed double crystal monochromators to perform Na XAFS. The Figure to the right shows smoothed Na XAFS spectra collected at the ALS in fluorescence detection mode from the test glasses and a reference material. Differences in the near edge region of the spectra are obvious. The data from the extended portion of the Na XAFS spectra are currently being processed and theoretically fit. This will determine if the data obtained from this experimental approach is of high enough quality to permit the extraction of the Na structural parameters.

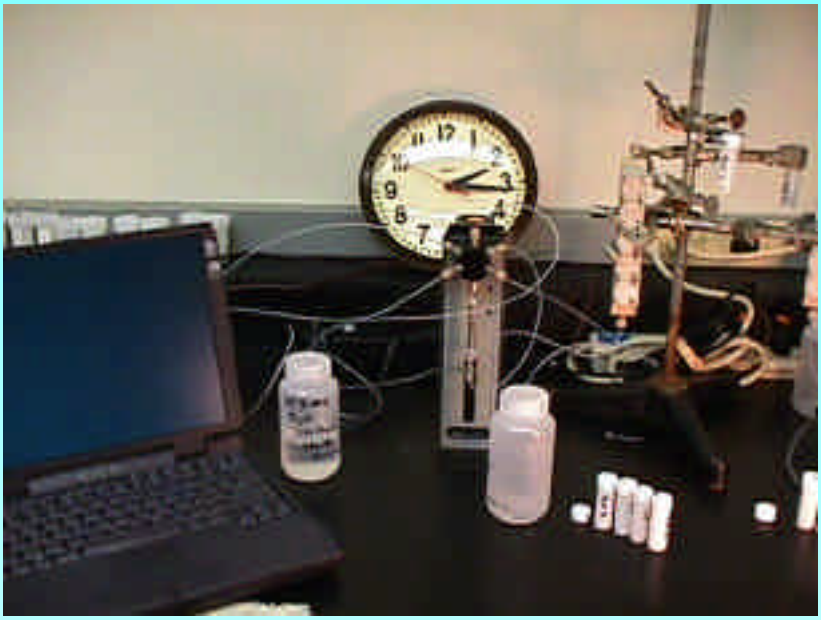
Using XAFS


Na K-Edge 1067 eV
NaSiO-15%Al2O3
Borosilicate
Glass (1500°C)
Na2CO3
Fluorescence Yield
1060
1070
1080
Photon Energy (eV)

6. Ion-Exchange Kinetics

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. To accomplish this, a flow-through experimental design was selected. However, numerous design challenges had to be overcome because 1) glass coupons must be used to provide samples for surface layer depth profiling, 2) several coupons must be exposed to the leachant solution simultaneously to provide a time sequence set of samples for analysis, and 3) fluid volumes need to be minimized because D_2O^{18} will be used in some tests and it is expensive. The flow-through reactor design we developed to meet these challenges is shown to the right . It employs a single pass flow through column made of polyetheretherketone (PEEK) and contains five compartments or “cells” to hold individual glass coupons of approximately 1.0-cm x 1.0-cm x 0.3-cm in size. Each cell is independently accessible by removing its stainless steel cover and Teflon seal. The column is orientated vertically with the direction of influent flow moving up through the column. For tests run at elevated temperature, the column is shrouded in a thermally controlled blanket and heated with a Kapton heater. Influent is delivered to the system using a programmable syringe pump.





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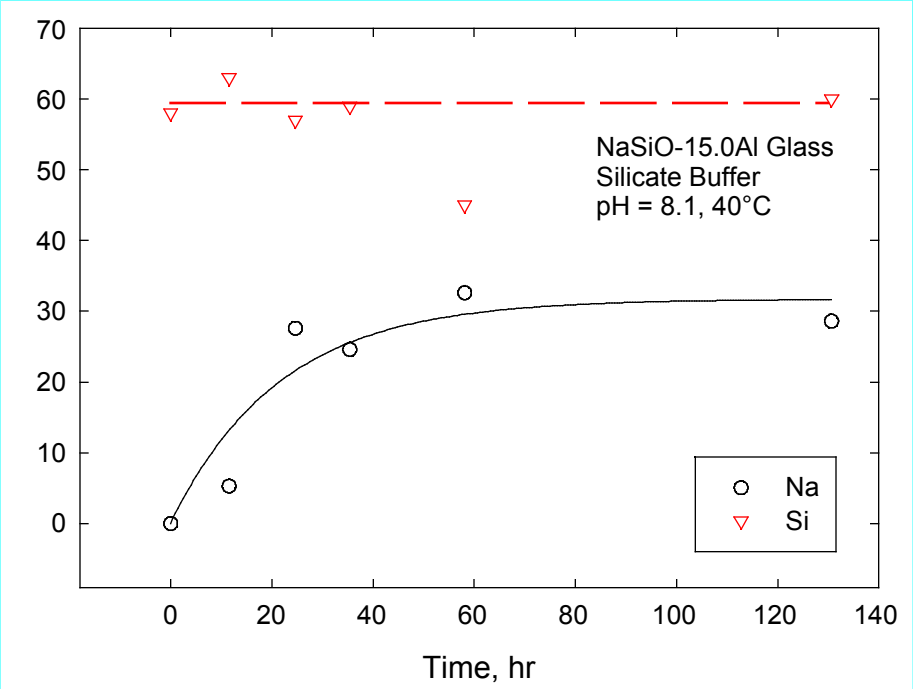
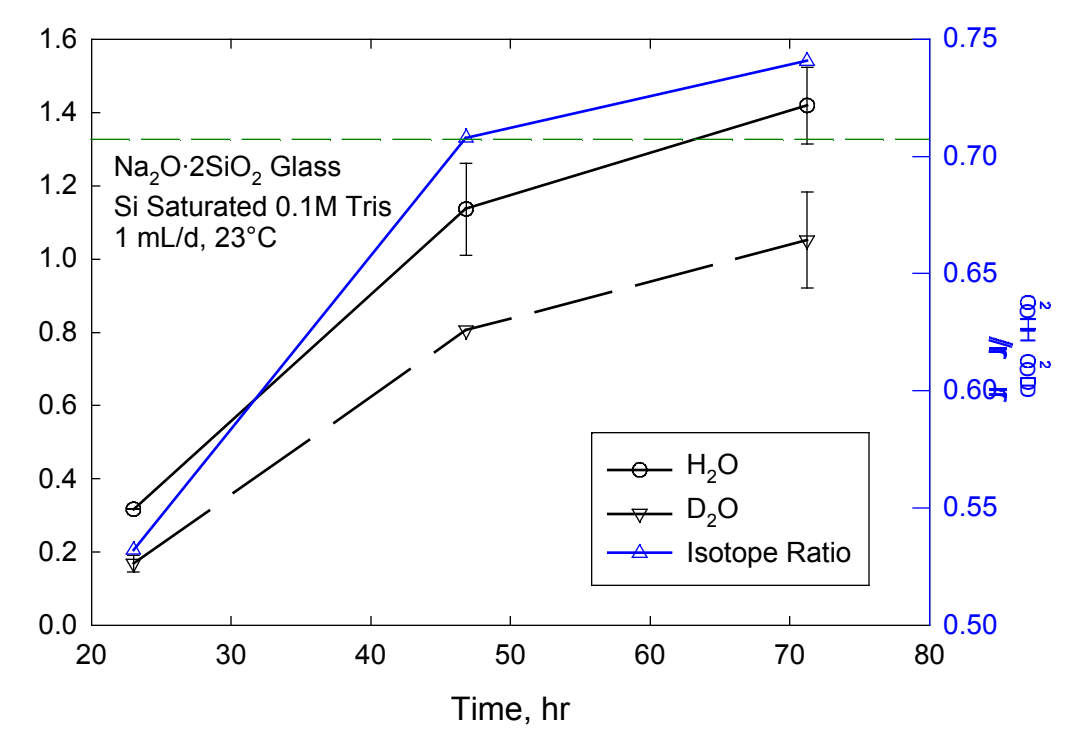
7a. Early Analytical Results



Measured Na concentrations, after subtracting out background Na levels in the buffer, and Si concentrations are plotted above for the 15 mol% Al glass. The Si concentrations remained approximately constant, as expected for the saturated buffer solution. The Na concentrations approach a steady-state concentration, which is the goal of the flow-through test design, of about 31.7 ±4.7 mg/L. This corresponds to a Na release rate of $2.4 \times 10^{-8} \pm 3.5 \times 10^{-9}$ mol Na/m_·s. The Na release rate for this simple glass is about 3 orders of magnitude faster than the long-term ion-exchange rate we have measured in static tests on typical low-activity waste glasses at this same temperature. However, the static tests were conducted in deionized water where the pH rises 2 to 3 units higher than in these tests. Ion-exchange rates are expected to be a strong function of pH so rates in the pH 8 flow-through experiments are expected to be higher.

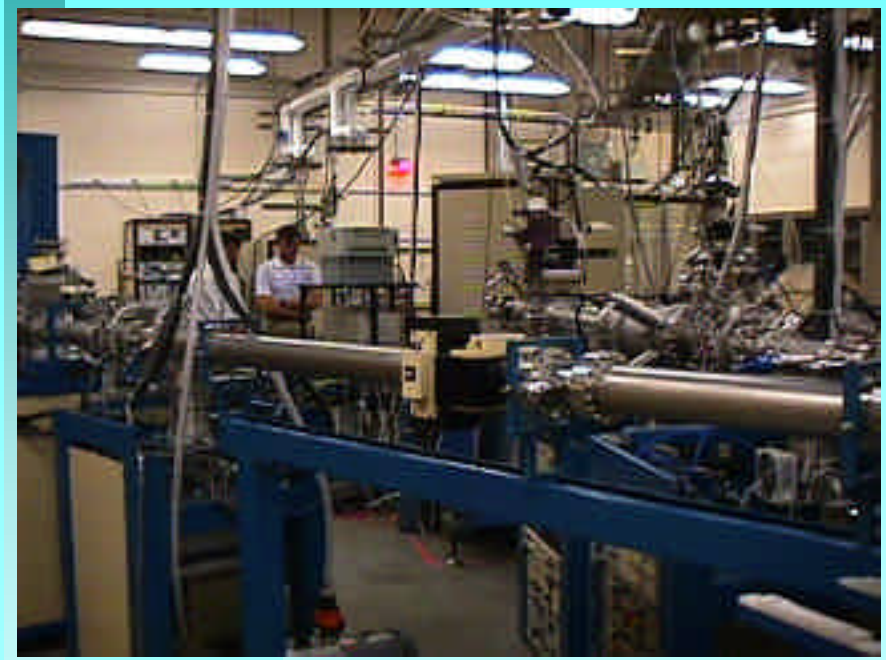
7b. Early Analytical Results

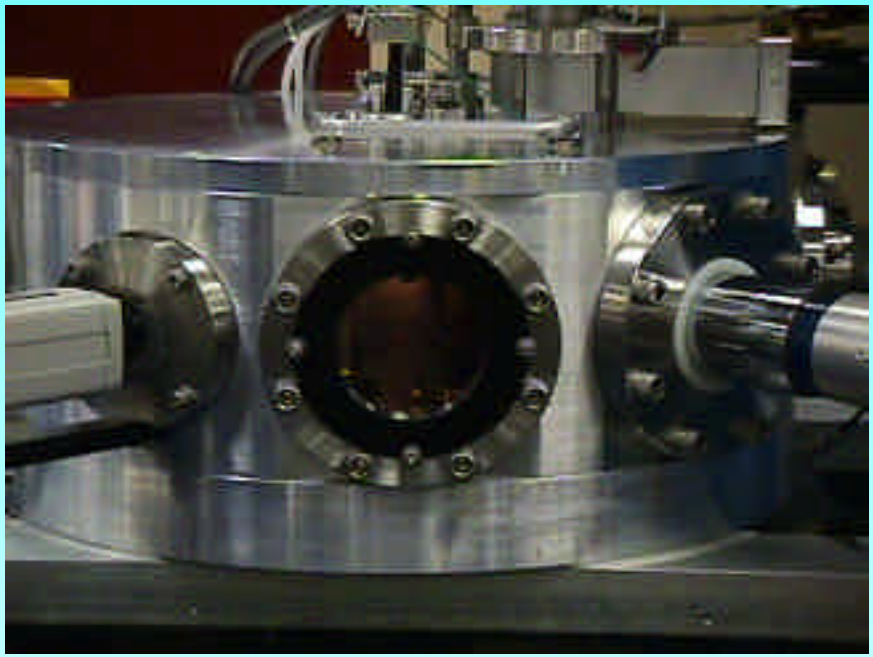


This figure shows the measured Na release rate from the sodium disilicate glass in both H_2O and D_2O. A significant isotope effect is observed. The data in blue show the ratio of the rates in D_2O and H_2O. The ratio approaches a value between 0.70 and 0.75, which is equivalent to the ratio of the square root of the rest masses of the deuterium and hydrogen ions $[(m_H/m_D)^{1/2} = (1/2)^{1/2} = 0.71]$ involved in the formation of Si-OH versus
Si-OD bonds.

8a. Nuclear Reaction Analysis

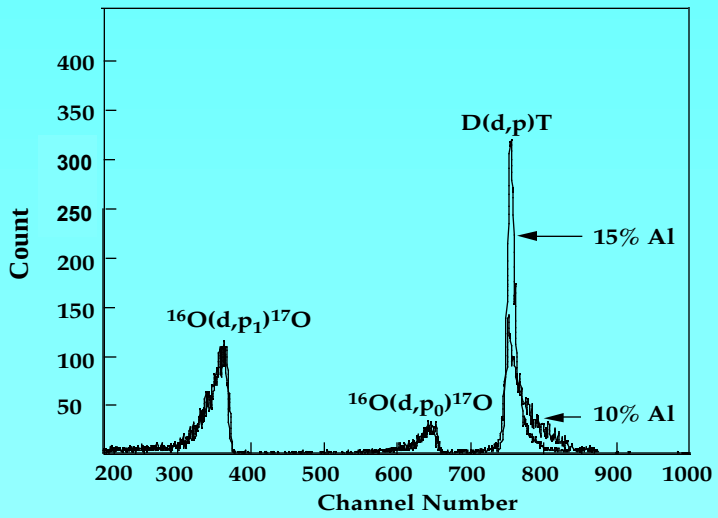
Tandem electrostatic accelerator at the Ion Beam Materials Analysis Laboratory within EMSL





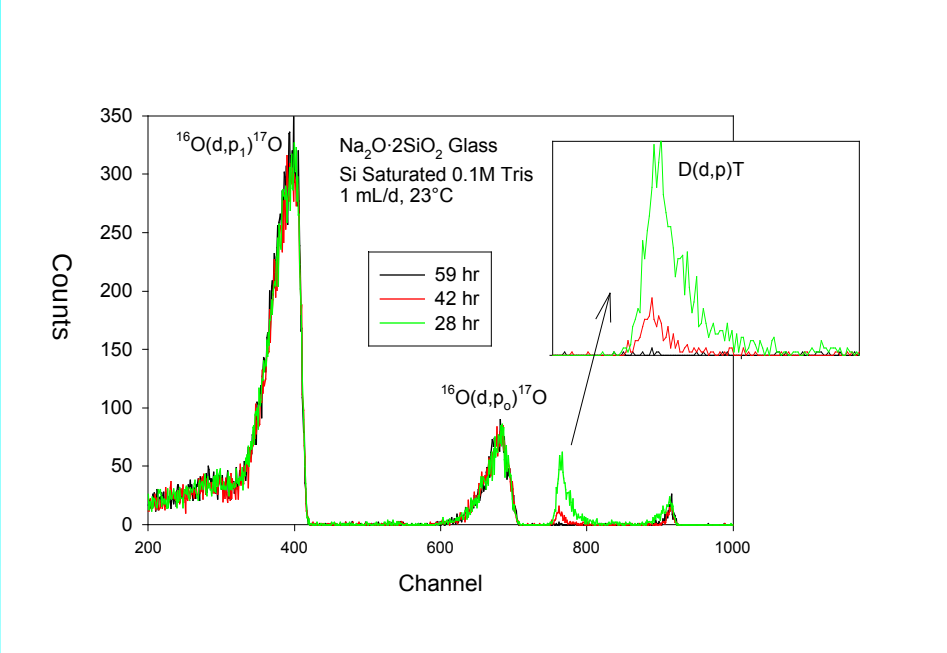
Isotope specific surface spectroscopies were used to characterize distribution of labeled water species in the hydrated glass surface layers. These measurements are made using a Van de Graaff accelerator (see below) and nuclear reactions D(d,p) ^{3}He, ^{18}O (p, α) ^{15}N for deuterium and oxygen analysis.

8b. Nuclear Reaction Analysis



The NaSiO-10Al and NaSiO-15Al glasses were exposed to 30 ml of water made up from 10 ml of ($D_2{}^{18}O$ - 97.46 atom% ^{18}O and 76.4% D) and 20 ml of ($D_2{}^{16}O$ 99% D). Samples of these glasses were exposed for 220 hours at 50° C under static conditions. The figure above shows D(d,p) ^3He nuclear reaction data with peaks for deuterium and oxygen. The changes in amplitude and width of the deuterium peak relate to the concentration and depth of the deuterium penetration into the glass. For the deuterium measurement, the surface appears at the lower kinetic energy side of the peak while the higher energy proton comes from deeper into the material. Both glasses showed considerable amount of deuterium uptake. The amplitude of the deuterium signal indicates the amount of deuterium adsorbed near the surface, while the tail indicates the amount of penetration into the material. Although the surface intensity for the 15 mol% Al glass is about 4X that of the 10 mol% Al glass, the D decreases quickly with depth into the glass. For the 10 mol% Al glass, there is much less D at the surface, but there is considerable penetration. These results are consistent with the expected differences in durability of these glasses.

8c. Nuclear Reaction Analysis



The figure above shows the results from the flow-through testing (see Part 7) with a $Na_2O{\cdot}2SiO_2$ glass. Contrary to expectations, the D uptake decreases with increasing reaction time. However, pH control was lost during the flow-through test with the pH increasing from the starting value of approximately 8.0 to a final value of 11.7. Because the silicate buffer was far from saturation with respect to SiO_2(am) at the higher pH, extensive dissolution of the layers formed at earlier times occurred, thus leading to the lower observed deuterium uptake with increasing reaction time.

Conclusion and Planned Work

The Series I set of glass compositions has been formulated, manufactured, and structural characterization is underway by NMR and XAFS. A multicell flow-through chamber has been designed, built, and tested for measurements of ion-exchange kinetics. Preliminary results show that the flow-through system and isotope specific spectroscopies will provide the data needed to develop a fundamental understanding of the ion-exchange processes in these glasses.

The observed variation of the ^{29}Si NMR chemical shift value with respect to glass composition is likely due to variation in the electronic interactions within the glass network, an indicator of the bonding characteristics within the network. An experimental beam run has also been scheduled at the ALS to collect XAFS data in fluorescence detection mode at the Na K-edge. The results of these Na investigations, the theoretical simulations, and the quality of the structural parameters obtained will determine the approach used for characterizing Na environments for the duration of this project. The Na structural information derived from the XAFS and NMR will be used to eventually correlate the structural properties of these glasses with their corresponding Na^+ ion-exchange kinetics.