

**Pacific Northwest
National Laboratory**

Operated by Battelle for the
U.S. Department of Energy

Radionuclide Incorporation in Secondary
Crystalline Minerals Resulting from
Chemical Weathering of Selected Waste
Glasses:
Progress Report: Task kd.5b

S. V. Mattigod
R. J. Serne
V. L. LeGore
K. E. Parker

R. D. Orr
D. E. McCready
J. S. Young

September 2003



Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RL01830



This document was printed on recycled paper.
(1/03)

**Radionuclide Incorporation in Secondary
Crystalline Minerals Resulting from Chemical
Weathering of Selected Waste Glasses:
Progress Report: Task kd.5b**

S. V. Mattigod	R. D. Orr
R. J. Serne	D. E. McCready
V. L. LeGore	J. S. Young
K. E. Parker	

September 2003

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

Experiments were conducted by Pacific Northwest National Laboratory¹ to evaluate potential incorporation of radionuclides in secondary mineral phases that form from weathering vitrified nuclear waste glasses. These experiments were conducted as part of the Immobilized Low-Activity Waste-Performance Assessment (ILAW-PA) to generate data on radionuclide mobilization and transport in a near-field environment of disposed vitrified wastes.

Static weathering of waste glass sample LAWBP1 conducted at 160 °C resulted in the formation of 60 -75%, zeolite P ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$). Other zeolite minerals such as analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, ~15 -30%) and cancrinite ($\text{Na}_6\text{Al}_6\text{Si}_6(\text{Na}_2\text{X})\text{O}_{24} \cdot 2\text{H}_2\text{O}$, ~10%) were also identified as products of weathering. Static weathering of LAWA44 glass at 160 °C resulted in the formation of about 65 wt% zeolite P and ~35% analcime. Reactions conducted at higher solution-to-solid ratios (2 and 3mL/g) produced analcime, a single crystalline product.,,

Dynamic weathering of LAWBP1 glass at 95 °C resulted in only trace quantities (<5%) of a “clay-like” crystalline mineral with a 9 Å spacing in a matrix of unaltered glass and gel. Similar tests conducted at 160 °C resulted in the formation of significant amounts of analcime. Crystalline minerals produced after 1 week of dynamic weathering at 160 °C consisted of approximately 80% analcime, 15% phillipsite, with 5% of a 9 Å clay mineral. A comparison of results of static and dynamic weathering of LAWBP1 glass showed that the weathering regime is a significant factor in the types of secondary mineral assemblages that form from waste glass.

During dynamic weathering of LAWBP1 glass at 95 °C, the mass fraction release rates for all major elements were relatively low (~4 x 10⁻⁵ to 2 x 10⁻³ /day) and constant during all reaction intervals, whereas at 160 °C the initial mass fraction release rates of ~3 x 10⁻⁵ to 5 x 10⁻² /day, declined with successive time intervals and at the end of the experiment appeared to be reaching a steady state that ranged from ~3 x 10⁻⁶ to 1 x 10⁻³ /day. Such decline in mass fraction release rates was probably due to longer diffusion paths created by an increasing thickness of hydrated gel layer or the decrease in pH.

The radionuclide-spiked Hanford Site groundwater (HGW) experiments indicated that ~16 - 18% of ¹²⁵I, ~7 - 13% of ⁷⁵Se, and ~5 - 12% of ⁹⁹Tc were sequestered in reaction products (the secondary crystalline phases and the hydrated gel layer) formed from weathering LAWBP1 glass. A similar degree of sequestration of ⁷⁵Se (~8 -14%) but noticeably lower degree of sequestration of ¹²⁵I activity (~12 – 13%) was observed when the spiked solution consisted of 1M NaOH. Experiments conducted using samples of LAWA44 waste glass reacted with radionuclide-spiked HGW resulted in sequestration of ~9 -16 % of ¹²⁵I, ~6 - 15% of ⁷⁵Se, and ~<1 - 6 of ⁹⁹Tc, and with radionuclide-spiked 1M NaOH solution resulted in sequestration of ~8 -11 % of ¹²⁵I, ~8 - 13% of ⁷⁵Se, respectively.

¹ Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

Radionuclide re-mobilization (desorption) tests showed that at the end of three days, the released radionuclides reached steady-state activities in solution. Subsequent measurements extending up to 86 days showed no significant changes in solution activities. Such early release and relative constancy over an extended period indicated that these fractions of the activities were most likely associated with an easily soluble solid phase such as the hydrated gel. Calculations based on results of radionuclide sequestration and mobilization experiments indicated that ~55 – 80% and ~30 – 90% of the sequestered ^{125}I and about 60 – 70% and 30 – 90% of solid phase activities of ^{75}Se in the weathered LAWBP1 and LAWA44 glasses were sequestered in crystalline minerals such as zeolite P and analcime.

Weathering of stable isotope- and sodium aluminate-spiked waste glass samples LAWBP1 and LAWA44 with additives resulted in the formation of a cage-structured mineral, sodalite, as the dominant crystalline mineral. The quantities of Re and I sequestered in the sodalite structure were estimated to be ~9% and ~7%, respectively. These experiments demonstrated that radionuclide sequestration can be significantly enhanced by promoting the formation of cage-structured minerals such as sodalite from weathering glasses.

These results have important implications regarding radionuclide sequestration/mobilization aspects that are not currently accounted for in the ILAW performance assessment. Additional studies are required to confirm the results and to develop an improved understanding of the mechanisms of sequestration of radionuclides into the secondary and tertiary weathering products of the ILAW glass to help refine how contaminants are released from the near-field disposal region into the accessible environment. Of particular interest is to determine whether the contaminants remain sequestered in the glass weathering products for hundreds to thousands of years. If the sequestration can be shown to continue for long periods, another immobilization process can be added to the performance assessment analysis, and predicted risks should be lower than past predictions.

Acknowledgments

We thank Frederick Mann of CH2M Hill Hanford Group (CHG) for consistent support and encouragement. We also appreciate the editorial help from Rosalind Schrempf and word processing assistance of Kathy Neiderhiser. Part of the analytical work was performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

Contents

1.0	Introduction	1
1.1	Background	1
1.2	Scope and Objective.....	2
1.3	Document Outline	3
2.0	Materials and Methods	5
2.1	Glass Weathering Experiments	5
2.1.1	Static Weathering Experiments	5
2.1.2	Dynamic Weathering Experiments.....	6
2.2	Radionuclide Sequestration and Mobilization Experiments	7
2.2.1	Radionuclide Sequestration Experiments	7
2.2.2	Radionuclide Mobilization Experiments	8
2.3	Stable Isotope Sequestration Experiments	8
3.0	Results and Discussion	11
3.1	Glass Weathering Experiments	11
3.1.1	Static Weathering Experiments	11
3.1.2	Dynamic Weathering Experiments.....	12
3.2	Radionuclide Sequestration in Secondary Minerals	17
3.2.1	Radionuclide Sequestration Experiments	17
3.2.2	Radionuclide Mobilization Experiments	18
3.3	Stable Isotope Sequestration Experiments	21
4.0	Conclusions	29
5.0	References	32

Figures

1.	X-Ray Diffraction Data for Crystalline Secondary Phases Formed from Weathered LAWPB1 Glass	12
2.	X-Ray Diffraction Data for Crystalline Secondary Phases Formed from Weathered LAWA44 Glass	12
3.	XRD Data for Phases Formed from LAWPB1 Glass Weathered at 95 °C for 7 weeks.....	13
4.	XRD Data for Phases Formed from LAWPB1 Glass Weathered at 160 °C for 7 weeks.....	13
5.	Estimated Quantities of Crystalline Weathering Products	14
6.	Proton Activity (pH Values) in Contact Solutions as a Function of	15
7.	Cumulative and Rates of Elemental Mass Fraction Released During.....	16
8.	Radionuclide Activities in Solution as a Function of Time. Figures a, b, and c show the activities of ^{125}I , ^{75}Se , and ^{99}Tc in groundwater equilibrated with weathered radionuclide-laden LAWPB1 glass. Figures d, e, and f show the activities of ^{125}I , ^{75}Se , and ^{99}Tc in groundwater solutions equilibrated with weathered radionuclide-laden LAWA44 glass/secondary minerals. L-1 and H-1 indicate the low and high radionuclide spike levels used in weathering and sequestration experiments conducted in Hanford groundwater, and L-2 and H-2 indicate the low and high radionuclide spike levels in 1M NaOH solution used in weathering sequestration experiments.	19
9.	Time-Dependent pH Values of Hanford Groundwater Equilibrated with Weathered (in HGW and in 1M NaOH) and Radionuclide (LH - Low and High Spiked)- Sequestered LAWPB1 and LAWA44 Glasses.....	20
10.	XRD Data for Phases Formed from LAWPB1 Glass Weathered with Stable Isotope Spikes.....	22
11.	XRD Data for Phases Formed from LAWA44 Glass Weathered with Stable Isotope Spikes.....	22
12.	A Dense Mass of dodecatrapezohexoctahedral Sodalite Crystals.....	23
13.	Detailed Morphology of Sodalite Crystals Formed from.....	23
14.	A Large Cluster of Sodalite Crystals formed	24
15.	A Close-up View of Hexoctahedral Sodalite Crystals	24
16.	An Assemblage of Diploidal Sodalite Crystals Formed on the Gel-layer.....	25
17.	An Enlarged View of Diploidal Sodalite Crystals Formed from Re-Spiked Weathered LAWA44 Glass	25

18. A Magnified View of Intergrown Gyroidal Sodalite Crystals Formed	26
19. Intergrown Sodalite Crystals Formed from I-Spiked Weathered LAWA44 Glass	26

Tables

1. Chemical Composition of Waste Glasses.....	6
2. Chemical Composition of Uncontaminated Hanford Site Groundwater ^(a)	6
3. Estimated Quantities of Crystalline Weathering Products	11
4. Estimated Quantities of Crystalline Minerals Resulting from Static and Dynamic Weathering of LAWBP1 Glass ^(a)	14
5. Radionuclide Fractions Sequestered in Weathered LAWBP1 Glass	17
6. Radionuclide Fractions Sequestered in Weathered LAWBP1 Glass	18
7. Estimated Quantities of Crystalline Weathering Products from	21
8. Mechanisms of Radionuclide Incorporation in Zeolite Minerals.....	28

1.0 Introduction

A continuing performance assessment (PA) is evaluating the suitability of the unsaturated sediments at the Hanford Site for the long-term disposal of vitrified low-activity waste. This assessment consists of analyses that predict the transport of radionuclides and/or contaminants from a source to a receptor via pathways that are considered credible. Previous analyses for proposed disposal actions on the Hanford Site show that groundwater transport presents the greatest potential for long-term dose uptake by humans (Mann et al. 1998, 2001). Furthermore, these previous analyses have shown that the key risk drivers at the proposed disposal site include ^{99}Tc , ^{129}I , $^{233,235,238}\text{U}$, and to a lesser extent ^{237}Np and ^{79}Se .

1.1 Background

Currently, detailed data are lacking on the tendency of key radionuclides to be sequestered into secondary crystalline mineral structures formed when waste glasses weather in the subsurface environment. This lack of knowledge could adversely affect waste-disposal activities by increasing the uncertainty and requiring unrealistically conservative estimates to be used as inputs to dose calculations. That is, taking no credit for the ability of glass weathering products to continue to sequester potentially mobile contaminants leads to overly conservative performance assumptions and higher than probable dose projections.

It is expected that the leachate from the glass waste forms disposed in the immobilized low-activity waste (ILAW) facility will have high ionic strengths (high concentrations of dissolved constituents) and will be alkaline (high pH) in nature (Mann et al. 1998). Based on predictions using the STORM glass leaching code (Mann et al. 2001), current ILAW PA predictions show a steady state pH condition of 9.8 throughout the near-field and most of the impacted vadose zone proximate to the burial trenches. In the early weathering stage inside the glass-dominated portion of the burial facility, pH values can exceed 9.8. Under such alkaline conditions, several complex geochemical reactions are known to occur in glass waste forms, neighboring engineered structures, and surrounding sediments that include dissolution of several carbonate and silicate minerals, precipitation of secondary and tertiary mineral phases, radionuclide adsorption onto minerals (primary, secondary, and tertiary), and sequestration of radionuclides into secondary and tertiary mineral phases. Several studies of waste and volcanic glasses and grouts have shown that formation of zeolitic and smectitic secondary crystalline minerals as a product of chemical weathering is a very common phenomena (Collella et al. 1978; Holler and Wirsching 1978; Van Iseghem et al. 1985; Van Iseghem and Grambow 1988; Haaker et al. 1985; Lutze et al. 1988; Caurel et al. 1988; McGrail et al. 1997a, 1997b, 1998; Ebert and Tam 1997; Luo et al. 1997; Fortner et al. 1997, Mattigod et al., 1998; 2002a). Extensive reviews by Barrer (1982) and Newman and Brown (1987) of literature on isomorphous substitution in zeolites and smectites suggest that radionuclides in waste forms could, upon chemical weathering, be sequestered in these secondary crystalline mineral structures. Because zeolites and smectites have significantly

lower solubilities than glass waste forms, the aqueous-phase activities (concentrations) of isomorphically substituted radionuclides would be significantly decreased.

Experiments conducted previously on chemical weathering of two different waste glasses (SRL202 and LD6) indicated that secondary crystalline minerals such as phillipsite and nontronite sequestered radionuclides of interest, namely, ^{79}Se , ^{99}Tc , ^{129}I , and $^{233,235,238}\text{U}$ (Mattigod et al. 1998). Additional weathering studies (Mattigod et al. 2002a) conducted with LD6 glass and another sodium borosilicate glass (LAWA33) resulted in the formation of secondary crystalline minerals such as analcime, herschelite phillipsite, and paragonite. Herschelite appeared to be a metastable fast-forming mineral that crystallized rapidly during the initial weathering phase of LAWA33 glass, converting subsequently to a more stable mineral, analcime. Weathering of LAWA33 glass samples spiked with stable isotopes [I, Se(IV), Se(VI), and Re] produced the same suite of crystalline minerals that were observed in unspiked samples. In spiked samples, however, the rate of alteration of herschelite to analcime was noticeably slower as compared to the unspiked samples. The oxidation states of Se in spikes did not seem to have any influence on the rates or products of chemical weathering of LAWA33 glass. Analcime was also identified as the dominant crystalline product in samples spiked with stable isotopes [I, Se(IV), Se(VI), and Re].

These data have important implications regarding the radionuclide mobilization aspects of the ILAW PA. Therefore, additional studies were conducted to elucidate and refine certain aspects of such sequestration phenomenon.

1.2 Scope and Objective

The objective of this study was to determine the degree of sequestration of key radionuclides (^{129}I , ^{79}Se , and ^{99}Tc) in secondary crystalline minerals that form as products of chemical weathering of specific glass compositions such as LAWBP1 and LAWA44 that will be used to stabilize Hanford tank wastes. This study consisted of four sets of experiments. An initial set of cold (no radionuclides) experiments with no stable isotopes of potential contaminants was used, and the objectives were to identify and characterize the type of secondary minerals that form from chemical weathering of waste glass samples of differing composition in contact with uncontaminated Hanford Site groundwater (HGW). In this first set of cold tests, two types of experiments were conducted. The first type of experiment consisted of static tests in which glasses were reacted with HGW in a closed system for a specified time period (~6 weeks). The second type, dynamic experiments, involved replacing the HGW at weekly intervals with fresh HGW, saving the reacted contact solution, and subsampling the reacted glass (i.e., removing a portion of the reacting glass at each sampling time). This weekly cycle of reaction and sampling extended over a total period of ~6 weeks.

A second set of experiments (with radionuclides and stable isotopes) was conducted to assess the degree and range of incorporation of key radionuclides in secondary mineral phases and to establish that these radionuclides are part of the secondary mineral structures. The second set of

experiments was static weathering tests with a 6- week reaction time at 160 °C. A third set of experiments was conducted to assess the potential release of radionuclides that were sequestered in secondary crystalline minerals during the second set of tests. The radionuclide-laden weathered glasses from test set #2 were leached at room temperature in groundwater for a total of 86 days. Periodically, small aliquots of solution were counted to assess the release rate of the radiotracers. The last set of experiments, using stable isotopes and sodium aluminate additive, was conducted to observe any enhanced sequestration in structural cages of zeolitic minerals such as sodalites and cancrinites. These tests were also static weathering tests conducted at 200 °C for 7 days. The resultant solids were then fully characterized.

1.3 Document Outline

This document consists of five chapters. This introduction is followed by Section 2.0, a discussion of the materials and methods used in the experiments;. The results and discussions of the glass-weathering, radionuclide sequestration, and release experiments are given in Section 3.0. The conclusions gathered from the experiments are presented in Chapter 4.0, followed by the references cited in the text in Chapter 5.0.

2.0 Materials and Methods

2.1 Glass Weathering Experiments

The first set of experiments was set up to monitor the formation of secondary crystalline minerals. Because the objectives of the glass-weathering experiments were to identify and characterize the type of secondary minerals formed, no radionuclides or stable isotopes of potentially mobile contaminants were introduced into the glasses. Two kinds of weathering experiments (static and dynamic) were conducted to evaluate the type and quantities of secondary crystalline minerals that would form from waste glasses. The static tests consisted of glasses equilibrated with groundwater in sealed reactors for a specified time period (up to 6 weeks). The dynamic test consisted of glass samples repeatedly reacted with fresh groundwater for shorter time periods (~1 week for each contact time; up to six contacts per test). The methods used to conduct these tests are described in the following sections.

Two glasses of different compositions were used in these experiments (Table 1). The reasons for selecting these glasses were that their physical and chemical characteristics have been well established, and their compositions are similar to specific glass compositions that will be used to stabilize Hanford tank wastes. The LAWBP1 glass is a sodium boro-alumino-silicate glass with ~5% zirconia. Other components in this glass (<3 wt% each on an oxide basis) consisted of chloride, iron, potassium, lanthanum, magnesium, titanium, zinc, and <0.1% of phosphorus and sulfur. The LAWA44 glass is a sodium borosilicate glass that contains less alumina, zirconia, and more iron oxide than the LAWBP1 glass. The LAWA44 glass also contains ~2 wt % calcium oxide. These glasses were prepared for the chemical weathering experiments by crushing and grinding the material to pass through a #325 sieve (<44 µm).

The uncontaminated groundwater used in these experiments was collected from well 699-S3-25 located on the Hanford Site (Table 2). The rationale for using groundwater is that past studies (Serne and Wood 1990; Serne et al. 1993) have suggested that vadose zone sediment porewater has a similar chemical composition to the groundwater. The composition of the groundwater indicates that calcium, magnesium, sodium, and potassium are the principal cationic constituents, with chloride, sulfate, and carbonate the dominant anions. The charge-balance calculations (+5%) indicated that the chemical analysis of this water is complete and accurate.

2.1.1 Static Weathering Experiments

The static weathering experiments were conducted by weighing three 3-g portions of each glass (LAWBP1 and LAWA44) into Teflon™ Parr reactors (Parr Instruments, Moline, Illinois). Hanford Site groundwater was added to the glass samples to achieve a solution-to-solid ratio (ml/g) of 1, 2 and 3, respectively. The reactors were sealed and then placed in an oven preheated to 160 °C. Following 6 weeks of reaction, the solids were separated, washed with deionized distilled water, and dried in an oven at 100 °C.

Table 1. Chemical Composition of Waste Glasses

Elemental Oxide	LAWBP1 (wt%)	LAWA44 (wt%)	Elemental Oxide	LAWBP1 (wt%)	LAWA44 (wt%)
Al ₂ O ₃	10.00	6.20	Na ₂ O	20.00	20.00
B ₂ O ₃	9.25	8.90	P ₂ O ₅	0.08	0.03
CaO	--	1.99	SO ₃	0.10	0.10
Cl	0.58	0.65	SiO ₂	41.89	44.55
Fe ₂ O ₃	2.50	6.98	TiO ₂	2.49	1.99
K ₂ O	2.20	0.50	ZnO	2.60	2.96
La ₂ O ₃	2.00	--	ZrO ₂	5.25	2.99
MgO	1.00	1.99			

Table 2. Chemical Composition of Uncontaminated Hanford Site Groundwater^(a)

Constituent	Conc. (mmol/L)	Constituent	Conc. (mmol/L)
pH	8.4 (SU)	Ba	0.001
Cl	0.677	Ca	1.447
NO ₃	0.027	Fe	0.003
SO ₄	1.135	K	0.358
C (organic)	0.061	Mg	0.658
CO ₃	2.623	Mn	0.001
Al	0.005	Na	1.305
B	0.005	Si	0.577
(a) Filtered (0.45 µm)			

The air-dried weathered glass samples were prepared for X-ray diffraction (XRD) analysis by packing subsamples into quartz sample holders. The samples were scanned through a range of 6 to 80 °C using Cu-K α radiation. The diffraction data were analyzed by using software linked to an international diffraction database.

2.1.2 Dynamic Weathering Experiments

The dynamic weathering experiments were conducted using only LAWBP1 glass. Duplicate 10-g samples of glass were transferred into two Teflon-lined Parr™ reactors. Ten milliliters of Hanford groundwater was added to the glass samples. Each of the sealed reactors was placed in ovens preheated to 95 °C and 160 °C, respectively. At the end of 1 week of reaction, all the reacted solution was removed and saved for analysis of dissolved constituents. Also, a portion of the weathered glass (~1-g) was removed, washed with DI water, air-dried, and analyzed by XRD for the presence of any secondary crystalline phases. Next, a fresh aliquot of Hanford groundwater was added to the remaining glass in the reactor (maintaining the same solution-to-

solid ratio of 1 (ml/g), and reacted again for another week. Each cycle (lasting about a week) consisted of reacting, sampling, and characterizing the solids and solution over a total of 7 weeks.

Portions of solids sampled after every weekly cycle were gently crushed; washed with deionized, distilled water; air dried; and characterized using XRD analysis. The reacted solutions were analyzed for dissolved constituents using inductively coupled plasma/optical emission spectrometry (ICP-OES).

2.2 Radionuclide Sequestration and Mobilization Experiments

Our previous studies with SRL202, LD6, and LAWA33 glasses showed that the weathered glasses exhibited different degrees of sequestration of radionuclides that were spiked into contacting solutions (Mattigod et al. 1998, 2002a). These studies also showed that the secondary crystalline minerals that formed from weathering glasses sequestered portions of the radionuclides. Also, the degree of radionuclide sequestration seemed to depend on the types and quantities of secondary crystalline minerals that were formed. However, the partitioning of the total sequestered activity between the crystalline minerals and the amorphous phases was not determined. Therefore, we conducted two sequential tests to determine the degree of incorporation of radionuclides, spiked into the reacting solution during the hydrothermal weathering portion of the glass testing, followed by a mobilization experiment in which the amount of radionuclide release was monitored by equilibrating an aliquot of fresh solution with the radionuclide-laden weathered glasses/secondary minerals. The methods used in these two sets of experiments follows.

2.2.1 Radionuclide Sequestration Experiments

Five-gram portions of each glass (LAWBP1 and LAWA44) were transferred into Teflon-lined ParrTM reactors. Individual 5-mL aliquots of Hanford Site groundwater were spiked separately with either ⁷⁵Se, ⁹⁹Tc, or ¹²⁵I, and these individually spiked aliquots were added to one of the three sample reactors of each glass. The spike levels ranged from ~0.03 to ~7 µCi. For the Se and I tests with the higher level of radiotracers, 10 ppm of stable Se or I was also added. For control, 5-mL aliquots of similarly spiked groundwater were transferred to three blank reactors. All reactors were sealed and placed in an oven preheated to 160 °C. Also, another experiment was conducted to investigate the effects of very high hydroxide alkalinites on radionuclide sequestration. This test consisted of reacting glass samples with 1M NaOH solution spiked individually with ~0.03 to ~7 µCi of ⁷⁵Se, ⁹⁹Tc, or ¹²⁵I. Again, for the higher spiking 10 ppm of stable Se or I was also present.

At the end of 6 weeks, the weathered glass samples were removed from the oven and cooled. The samples were crushed and washed three times with deionized, distilled water. The wash water was composited and successively filtered through 0.45-µm and Amicon (20 Å) filters (Amicon is a subdivision of Millipore Corporation, Bedford, Massachusetts), and the activities of

⁹⁹Tc in the filtrates were measured by liquid scintillation counting. The activities of ⁷⁵Se and ¹²⁵I, in liquid samples were measured by gamma-ray spectrometry using a calibrated Wallac® 1480 Wizard™ 3-in. NaI detector with built-in software.

2.2.2 Radionuclide Mobilization Experiments

To study the release of radionuclides from the weathered glass, portions (~5 g) of radionuclide-laden glass/secondary mineral solids resulting from the sequestration experiments were equilibrated at room temperature (25 ± 5 °C) with ~150 ml of fresh Hanford groundwater. Periodically (3, 7, 10, 14, 21, 59, and 86 days), 5-ml aliquots of the reacting solutions were removed and counted for radionuclide activities released from the weathered glass.

2.3 Stable Isotope Sequestration Experiments

Weathering studies on a number of waste glasses of differing compositions have established that the degree of radionuclide sequestration depends on the types and quantities of secondary crystalline minerals that form during the reaction. Also, the types of secondary minerals differ in their radionuclide sequestration capacity. For instance, zeolithic minerals such as sodalite [Na₆Al₆Si₆O₂₄(Na₂X)] and cancrinite (Na₆)Al₆Si₆(Na₂X)O₂₄ · 2H₂O (where X represents an anion species) can sequester up to ~8 % of Se, ~22 % of I, and ~27% of Re in their structural cages². Therefore, if the formation of sodalite and cancrinite minerals can be promoted during glass weathering, a higher fraction of the radionuclides could be sequestered in relatively insoluble forms. To examine this possibility, we designed a set of experiments in which stable isotopes, Re and I, were added along with sodium aluminate, an additive that promotes the formation of sodalite and cancrinite minerals from weathering glasses.

Two-gram portions of LAWBP1 and LAWA44 glass samples were transferred into replicate Parr™ reactors. Measured quantities (0.324 g and 0.562 g) of solid sodium perrhenate and sodium aluminate (0.210 g and 0.424g), respectively, were added to each of the LAWBP1 and LAWA44 glass samples.. Similarly, 0.178 g and 0.308 g of solid sodium iodide, and sodium aluminate (0.21 g and 0.424g), respectively, were added to another set of LAWBP1 and LAWA44 glass samples. A third set of glass samples without any spikes or additives was set up as a control. Hanford groundwater was added to each container to achieve a solution-to-solid

² Calculated as the % ratio of mol wt of anionic species to the mol wt of sodalite or cancrinite. For example, assuming all the anionic cage sites in sodalite are occupied by SeO₄, the quantity of Se sequestered can be calculated as, [mol wt of Se/mol wt of Na₆Al₆Si₆O₂₄(Na₂SeO₄)] X 100 = (78.96/1041.3) x100 = 7.6%

ratio of 0.5 ml/g. All reactors were sealed and placed in an oven preheated to 200 °C. Following 7 days of reaction, the solids were separated, washed with deionized distilled water, and dried in an oven at 100 °C. The air-dried weathered glass samples were characterized by XRD analysis and scanning electron microscopy (SEM) analysis.

3.0 Results and Discussion

3.1 Glass Weathering Experiments

The results of the mineralogical characterization of glasses weathered under static and dynamic conditions and the composition of solutions from dynamic tests are presented in this section.

3.1.1 Static Weathering Experiments

The principal weathering product (60 -75 %) of LAWBP1 glass was found to be zeolite P [$\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$], which is a synthetic analog for a sodium-rich zeolite mineral named garrisonite (Figure 1, Table 3). Other zeolite minerals such as analcime [$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$] (15 - 30%) and cancrinite [$\text{Na}_6\text{Al}_6\text{Si}_6(\text{Na}_2\text{X})\text{O}_{24} \cdot 2\text{H}_2\text{O}$] (~10%) were also identified as products of weathering. It is important to note that in the cancrinite structure, the cage positions represented by (X) can be occupied by a variety of anions that include, I, SeO_4 , and TcO_4 (Barrer and Cole 1970; Barrer 1982).

Weathering reactions conducted using LAWA44 glass at a solution-to-solid ratio of unity resulted in the formation of about 65 wt% zeolite P and ~35% analcime (Figure 2, Table 3). However, reactions conducted at higher solution-to-solid ratios (2 and 3 mL/g) produced a single crystalline product, namely, analcime.

Relative quantities of crystalline minerals produced from both waste glasses at various solution-to-solid ratios indicated that typically more zeolite P formed at lower ratios, and increasing relative quantities of analcime were found at higher solution-to-solid ratios. The solution pH values measured at the end of the experiments ranged from 12.54 to 12.72 indicating that glass weathering had created solution conditions with significant hydroxide alkalinites (~0.05M NaOH). Our previous studies have demonstrated that zeolite minerals such as analcime can structurally incorporate radionuclides. The characteristics and the schematic structural diagrams of these zeolite minerals are included in the Appendix.

Table 3. Estimated Quantities of Crystalline Weathering Products

Glass	Soln/Solid ratio (mL/g)	Crystalline Minerals (wt%)			Equilibrium pH (SU)
		Analcime	Zeolite P	Cancrinite	
LAWBP1	1	15	75	10	12.70
LAWBP1	2	30	60	10	12.72
LAWBP1	3	25	65	10	12.66
LAWA44	1	35	65	--	12.54
LAWA44	2	100	--	--	12.72
LAWA44	3	100	--	--	12.66

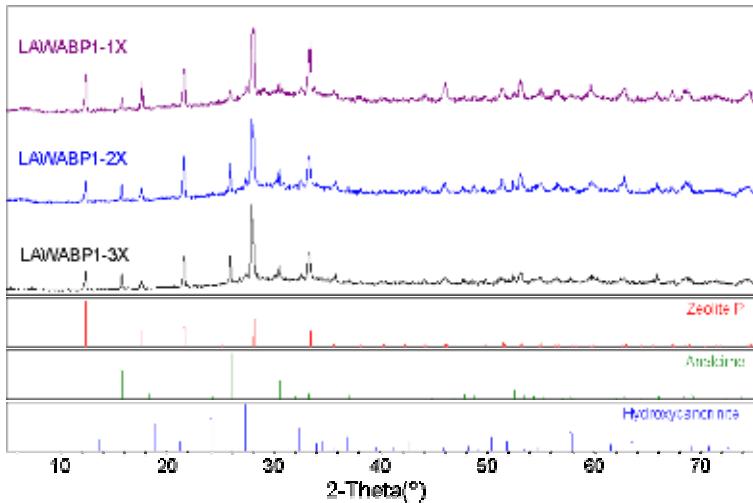


Figure 1. X-Ray Diffraction Data for Crystalline Secondary Phases Formed from Weathered LAWBP1 Glass

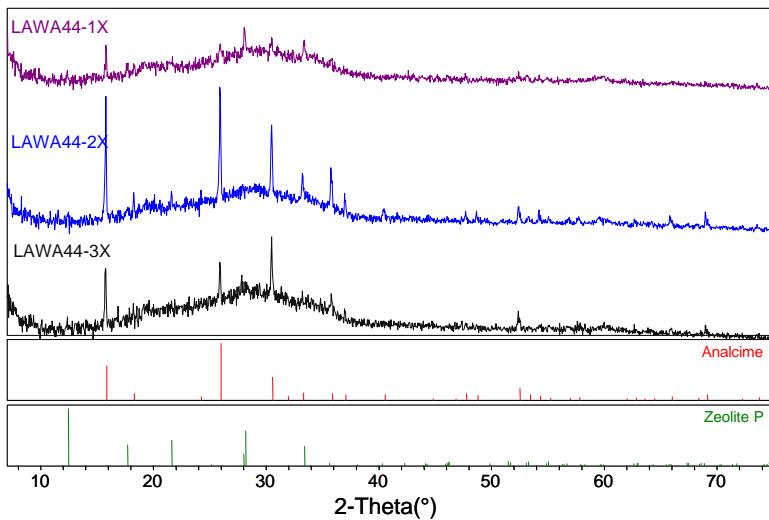


Figure 2. X-Ray Diffraction Data for Crystalline Secondary Phases Formed from Weathered LAWA44 Glass

3.1.2 Dynamic Weathering Experiments

Dynamic weathering of LAWBP1 glass at 95 °C resulted in only trace quantities (<5%) of a “clay-like” crystalline mineral with 9 angstrom [Å] spacing in a matrix of unaltered glass and gel (Figure 3). Comparatively, tests conducted at 160 °C resulted in significant amounts of analcime (Figures 4, 5). Crystalline minerals resulting after 1 week of dynamic weathering of LAWBP1 at 160 °C consisted of approximately 80% analcime, 15% phillipsite, with 5% of a 9Å clay mineral (Figure 5). During subsequent time intervals, the observed crystalline minerals consisted mainly of analcime (~95%) and phillipsite (~5%). It is important to note that static weathering of

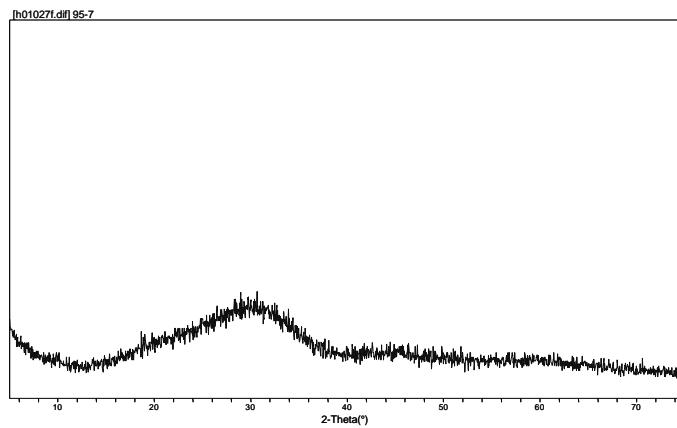


Figure 3. XRD Data for Phases Formed from LAWBP1 Glass Weathered at 95 °C for 7 weeks

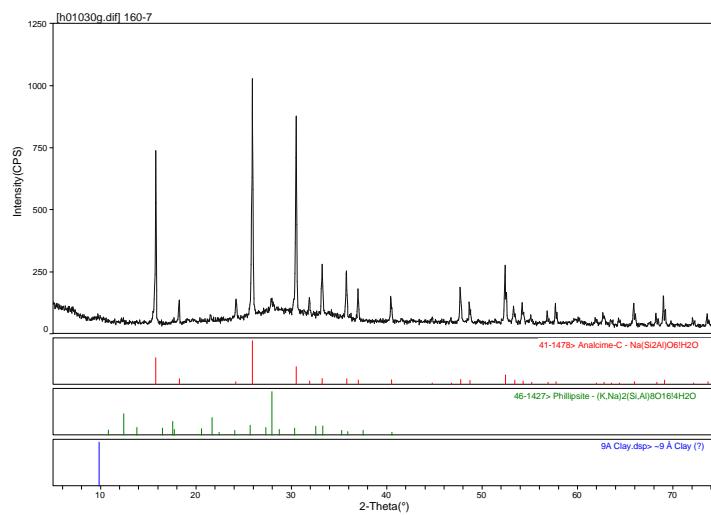


Figure 4. XRD Data for Phases Formed from LAWBP1 Glass Weathered at 160 °C for 7 weeks

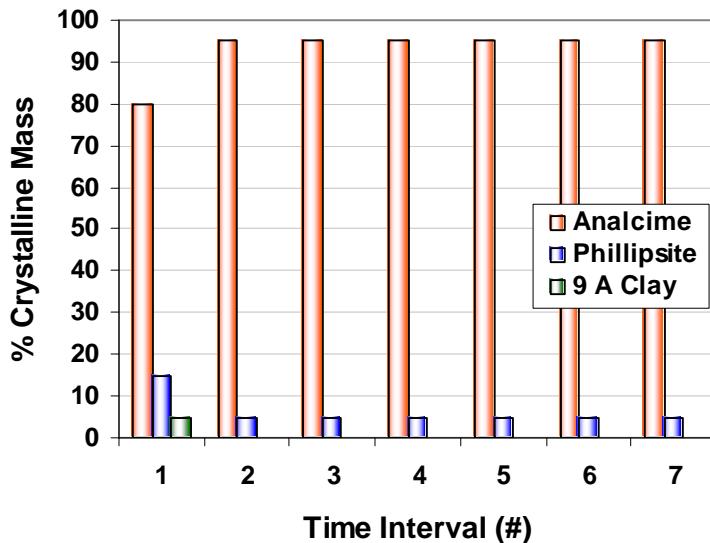


Figure 5. Estimated Quantities of Crystalline Weathering Products From Dynamic Weathering Cycles of LAWBP1 Glass at 160 °C

LAWBP1 glass conducted under similar experimental conditions (same temperature, time span, and solution-to-solid ratio) resulted in ~15% analcime, 75% zeolite P, and 10% hydroxycancrinite (Table 4). These data showed that the weathering regime has a significant affect on the types of secondary mineral assemblages produced from a reacted glass. The pH values of the contacting solution indicated that the hydroxyl concentrations were five times higher (~0.05 M) under static weathering conditions as compared to the dynamic weathering regime. It is well established that higher hydroxyl concentrations are necessary for the formation of cancrinite and zeolite P (Mattigod et al. 2002b). The results from our experiments agree with previous studies of zeolite formation as a function of hydroxyl alkalinity.

Solution pH data from the dynamic experiments (Figure 6) showed that during the initial weathering phase the pH values were relatively high (~12.2 at 95 °C and 13.0 at 160 °C). The pH values were relatively constant for approximately four solution replacements extending over 26 days of weathering. Subsequent solution replacement cycles indicated relatively rapid decline of pH values at both reaction temperatures. At the end of seven solution replacement cycles, the pH of equilibrated solutions had decreased by one to two orders of magnitude from the pH values measured during the initial solution replacement cycle.

Table 4. Estimated Quantities of Crystalline Minerals Resulting from Static and Dynamic Weathering of LAWBP1 Glass^(a)

Weathering Regime	Analcime	Zeolite P	Hydroxy-cancrinite	Phillipsite	Equilibrium Solution pH (SU)
Static	15	75	10	--	12.70
Dynamic	95	--	--	5	12.05

(a) Solution-to-solid ratio, 1.0 mL/g; temperature, 160 °C, Reaction time, 6 weeks.

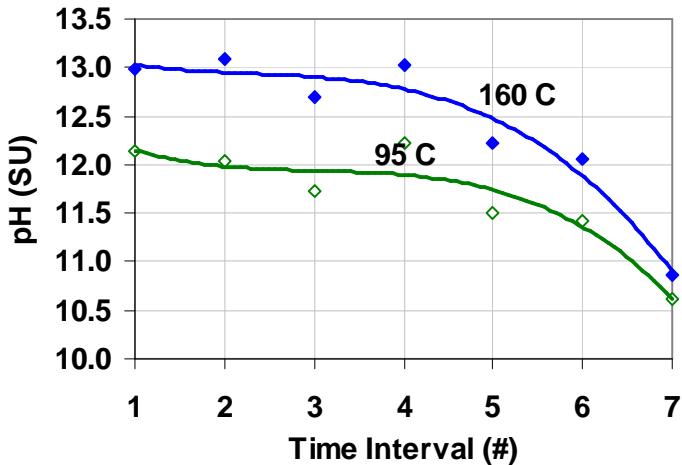


Figure 6. Proton Activity (pH Values) in Contact Solutions as a Function of Dynamic Weathering Cycles of LAWBP1 Glass.

Cumulative fractional release data at 95 °C for major glass components (Na, K, B, Al, and Si) indicated that only minor fractions of these elements were released to the solution phase (Figure 7). As compared to mobilization of Al and Si, about one to two orders of magnitude higher mass fractions of boron and the alkali elements (Na and K) were released at both reaction temperatures. Such elemental release performance from waste glasses have been attributed to a sodium-proton exchange reaction that initiates matrix dissolution of glasses (McGrail et al. 2001). At 95 °C, Al and Si fractional releases were about an order of magnitude less than the releases observed for B and the alkali elements (Figure 7a).

At higher reaction temperature (160 °C) however, significant cumulative mass fractions of B and alkali elements (~0.9 B, ~0.3 Na and K) were released to the solution phase. These releases were about an order of magnitude higher than the releases observed at 95 °C (Figure 7a, b). Similarly, about an order of magnitude higher cumulative mass fraction of Si was released during reaction at higher temperature (160 °C). In contrast, at higher temperature significantly lower cumulative mass fraction (~an order of magnitude lower) release of Al was observed.

Such anomalously lower Al releases at higher temperature can be attributed to the formation of secondary crystalline minerals. At higher temperature, Al released from weathering glasses gets rapidly incorporated into secondary crystalline minerals with limited solubilities; therefore, insignificant mass fractions of this element are partitioned into the solution phase. However, at 95 °C, due to the lack of formation of secondary crystalline minerals and the high solubility of glass and amorphous gel phases, higher fractions of Al are likely be partitioned into the solution phase.

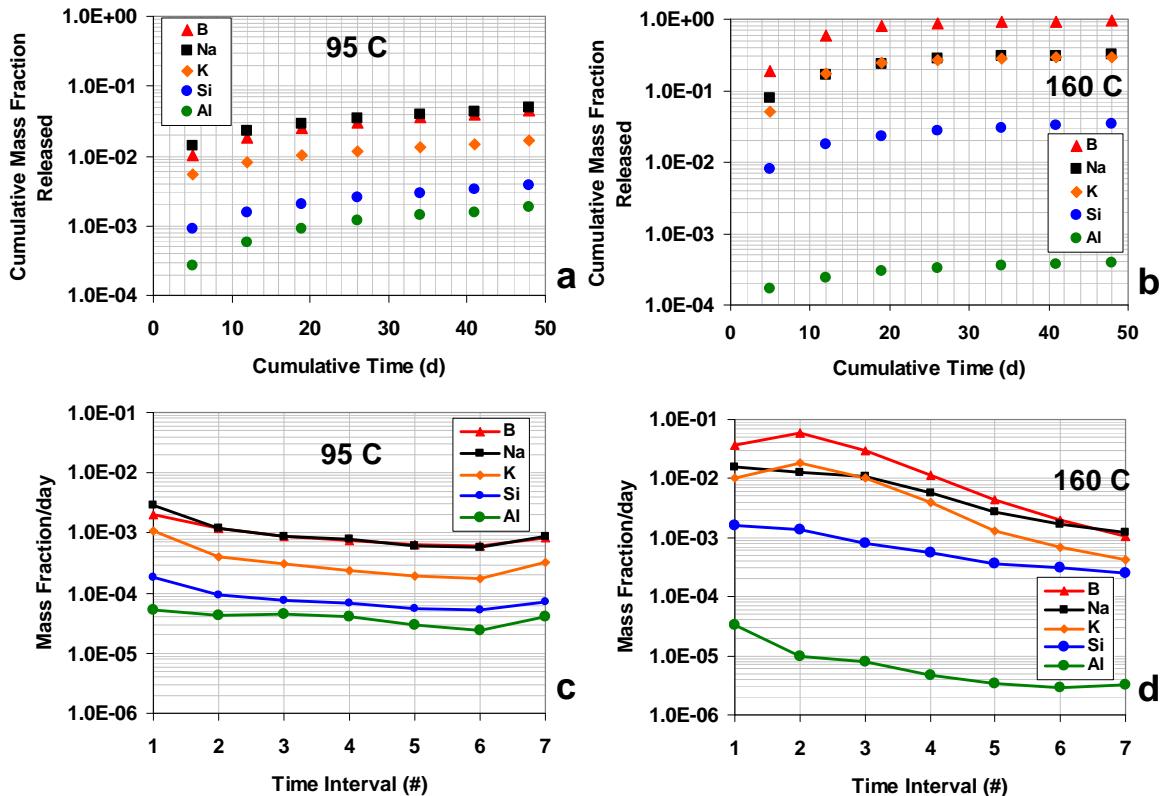


Figure 7. Cumulative and Rates of Elemental Mass Fraction Released During Dynamic Weathering of LAWBP1 Glass at 95 °C (a, c) and at 160 °C (b, d).

Additionally, a comparison of releases of B and the Na indicated that at 95 °C similar cumulative mass fractions of B and Na were released, whereas at 160 °C about three times less mass fraction of Na was released. These differences can also be attributed to the formation of crystalline minerals such as zeolites that preferentially incorporate Na into their structures.

During dynamic weathering at 95 °C, the mass fraction release rates for all major elements were relatively low ($\sim 4 \times 10^{-5}$ to 2×10^{-3} /day) and constant during all reaction intervals (Figure 7c), whereas at 160 °C the initial mass fraction release rates of $\sim 3 \times 10^{-5}$ to 5×10^{-2} /day declined with each successive time interval after the second solution exchange (Figure 7d), and at the end of the experiment appeared to be reaching a steady state that ranged from $\sim 3 \times 10^{-6}$ to 1×10^{-3} /day. Such declines in mass fraction release rates were probably due to longer diffusion paths created by the increasing thickness of the hydrated gel layer on the glass and/or the drop in solution pH.

In summary, the dynamic weathering of glasses indicated that the assemblage of secondary crystalline minerals formed were notably different from the assemblages resulting from static

weathering. These results indicated that an analysis of solution data in conjunction with solid phase characterization leads to a better understanding of the phenomenon that control dynamic weathering of waste glasses.

3.2 Radionuclide Sequestration in Secondary Minerals

The results of the radionuclide sequestration and mobilization experiments are discussed in the following sections. Data from both these experiments were used to determine the partitioning of the radionuclides between the secondary crystalline phases and the hydrated gel phase in weathered glasses.

3.2.1 Radionuclide Sequestration Experiments

The data from radionuclide-spiked HGW experiments indicated that ~16 to 18% of ^{125}I , ~7 to 13% of ^{75}Se , and ~5 to 12% of ^{99}Tc were sequestered in reaction products (the secondary crystalline phases and the hydrated gel layer) formed from weathering of LAWBP1 glass (Table 5). Comparatively, an identical experiment conducted with radionuclide-spiked 1M NaOH solution showed similar degrees of sequestration of Se^{75} (~8 to 14%) but a noticeably lower degree of sequestration of ^{125}I activity (~12 to 13%). Data for ^{99}Tc could not be obtained because of interferences in detecting the Tc in the alkaline solutions.

Table 5. Radionuclide Fractions Sequestered in Weathered LAWBP1 Glass

Activity Partitioning	^{125}I	$^{125}\text{I} + \text{I}^{(\text{a})}$	^{75}Se	$^{75}\text{Se} + \text{Se}^*$	^{99}Tc	^{99}Tc
Hanford Groundwater						
Initial activity in solution (nCi)	25.9	229.1	399.1	4107.5	670.1	6984.1
Final activity in solution (nCi)	21.4	192.0	370.3	3573.6	593.3	6630.6
<i>Activity in solids (nCi)</i>	<i>4.5</i>	<i>37.1</i>	<i>28.8</i>	<i>533.9</i>	<i>76.8</i>	<i>353.5</i>
Activity in solids (% of spike)	18	16	7	13	12	5
Total activity released (nCi)	2.0	8.3	11.7	146.0	27.4	231.8
<i>Activity in Crystalline minerals (nCi)</i>	<i>2.5</i>	<i>28.8</i>	<i>17.1</i>	<i>387.9</i>	<i>49.4</i>	<i>121.7</i>
Activity in Crystalline minerals (%)	10	13	4	9	7	2
1M NaOH						
Initial activity in solution (nCi)	24.7	227.9	397.3	3942.2	243.6	2095.1
Final activity in solution (nCi)	21.7	199.0	364.9	3411.6	-- ^(b)	-- ^(b)
<i>Activity in solids (nCi)</i>	<i>3.0</i>	<i>28.9</i>	<i>32.4</i>	<i>530.6</i>	--	--
Activity in solids (% of spike)	12	13	8	14	--	--
Total activity released (nCi)	1.8	10.1	13.2	172.9	27.1	214.0
<i>Activity in Crystalline minerals (nCi)</i>	<i>1.2</i>	<i>17.8</i>	<i>19.2</i>	<i>357.7</i>	--	--
Activity in Crystalline minerals (%)	5	8	5	9	--	--
(a) 10 ppm stable isotope						
(b) caustic solution interfered with ^{99}Tc analyses						

Experiments conducted with samples of LAWA44 waste glass reacted with radionuclide- and stable isotope-laden HGW resulted in sequestration of ~9 to 16 % of ^{125}I , ~6 to 15% of ^{75}Se , and ~<1 to 6 of ^{99}Tc and sequestration from 1M NaOH solution of ~8 to 11 % of ^{125}I and ~8 to 13% of ^{75}Se , respectively (Table 6). The degree of sequestration of ^{99}Tc in experiments using 1M NaOH solutions could not be assessed due to matrix interference during scintillation counting.

Table 6. Radionuclide Fractions Sequestered in Weathered LAWBP1 Glass

Activity Partitioning	^{125}I	$^{125}\text{I} + \text{I}^{\text{(a)}}$	^{75}Se	$^{75}\text{Se} + \text{Se}^*$	^{99}Tc	^{99}Tc
Hanford Groundwater						
Initial activity in solution (nCi)	25.8	230.1	398.4	4533.0	714.0	7053.8
Final activity in solution (nCi)	23.6	193.1	375.8	3852.9	711.0	6649.8
<i>Activity in solids (nCi)</i>	2.2	37.0	22.6	680.1	3.0	404.0
Activity in solids (% of spike)	9	16	6	15	<1	6
Total activity released (nCi)	1.6	3.0	5.4	77.8	--	128.6
<i>Activity in Crystalline minerals (nCi)</i>	0.6	34.0	17.2	602.3	--	275.4
Activity in Crystalline minerals (%)	2	15	4	13	--	4
1M NaOH Medium						
Initial activity in solution (nCi)	24.8	227.1	398.9	3942.2	244.1	2091.1
Final activity in solution (nCi)	22.2	208.1	365.6	3420.1	--(b)	--(b)
<i>Activity in solids (nCi)</i>	2.6	19.0	33.3	522.1	--	--
Activity in solids (%)	11	8	8	13	--	--
Total activity released (nCi)	--	10.2	22.6	188.5	30.3	377.9
<i>Activity in Crystalline minerals (nCi)</i>	--	9.0	10.7	333.6	--	--
Activity in Crystalline minerals (%)	--	4	3	9	--	--
(a) 10 ppm stable isotope						
(b) caustic solution interfered with ^{99}Tc analyses						

The degree of radionuclide sequestration observed for these waste glasses was comparable to the previous data obtained for other weathered glasses (LD6 and LAWA33) containing zeolitic minerals as the crystalline weathering products (Mattigod et al. 1998, 2002a). These data indicate that one of the critical factors in radionuclide sequestration is the types and quantities of secondary minerals that form from weathering glasses.

3.2.2 Radionuclide Mobilization Experiments

Radionuclide-laden solids from the sequestration experiments were placed in contact with uncontaminated groundwater and the release of radiotracers monitored. The results showed that at the end of 3 days, the portion of releasable ^{125}I , ^{75}Se , and ^{99}Tc in the solution phase approached a steady-state value (Figure 8). Subsequent measurements extending up to 86 days showed that no further release of radionuclides occurred; that is, no significant changes in solution activities were found after decay corrections for the short half-lives of ^{125}I and ^{75}Se .

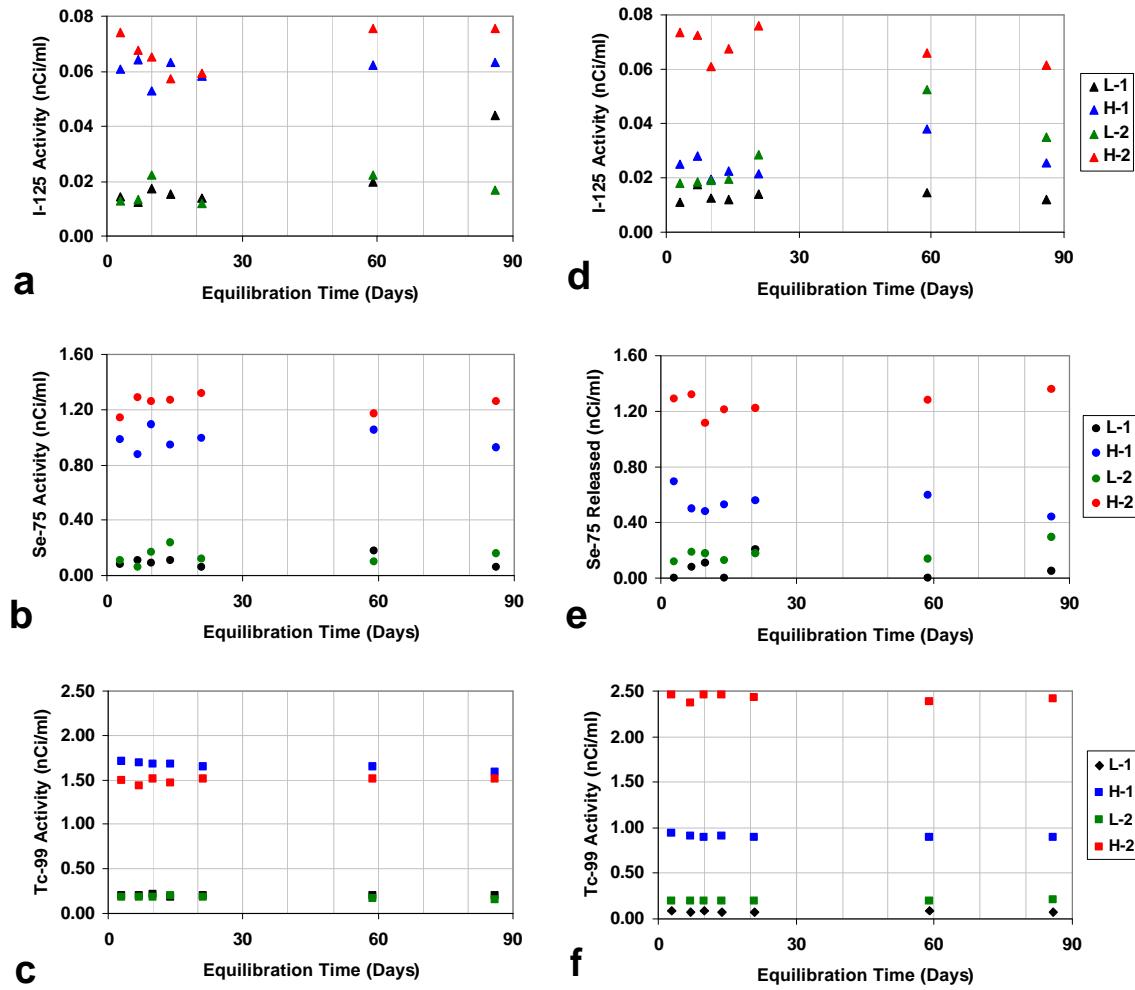


Figure 8. Radionuclide Activities in Solution as a Function of Time. Figures a, b, and c show the activities of ^{125}I , ^{75}Se , and ^{99}Tc in groundwater equilibrated with weathered radionuclide-laden LAWBP1 glass. Figures d, e, and f show the activities of ^{125}I , ^{75}Se , and ^{99}Tc in groundwater solutions equilibrated with weathered radionuclide-laden LAWA44 glass/secondary minerals. L-1 and H-1 indicate the low and high radionuclide spike levels used in weathering and sequestration experiments conducted in Hanford groundwater, and L-2 and H-2 indicate the low and high radionuclide spike levels in 1M NaOH solution used in weathering sequestration experiments.

(Figure 8). Such early release and relative constancy of solution activities over an extended period indicated that the fractions of readily leachable radionuclide activities were associated with an easily desorbable fraction or a readily soluble solid phase such as a hydrated gel.

Moderate increases in solution pH values (~0.5 Standard Units or SU) during the early phase of equilibration indicated that gel dissolution was probably occurring from sodium-proton exchange (Figure 9). The pH values remained relatively constant up to 60 days followed by

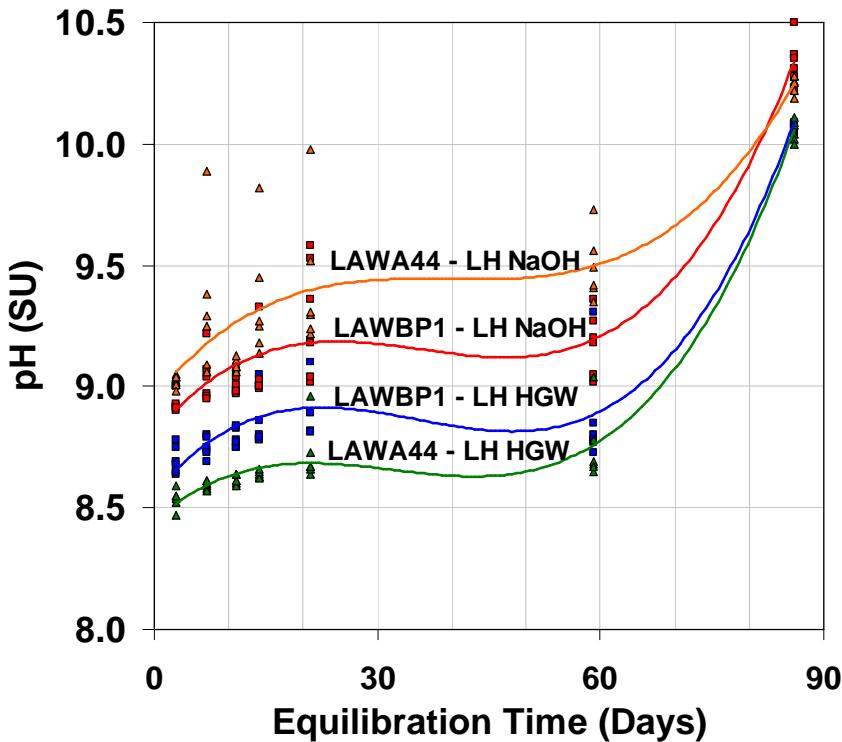


Figure 9. Time-Dependent pH Values of Hanford Groundwater Equilibrated with Weathered (in HGW and in 1M NaOH) and Radionuclide (LH - Low and High Spiked)-Sequestered LAWBP1 and LAWA44 Glasses.

precipitous increases (~0.8 -1.0 SU) that indicated a probable second episode of sodium-proton exchange and concomitant matrix dissolution. Despite these episodic matrix dissolutions signaled by pH changes, there were no changes in radionuclide activities in solution. Therefore, non-leachable fractions of radioactivity in the solid phase appeared to be sequestered by relatively insoluble crystalline phases such as zeolites.

Calculations based on results of radionuclide sequestration and mobilization experiments indicated that substantial fractions of radionuclides sequestered in the solid phase of the weathered glasses resided in the crystalline minerals (Table 5, 6). For instance, ~55 to 80% and ~30 to 90% of the sequestered ^{125}I activities were associated with crystalline minerals (zeolite P and analcime) in the weathered LAWBP1 and LAWA44 glasses, respectively. Similarly, ~60 to 70% and 30 to 90% of solid phase activities of ^{75}Se were sequestered in crystalline minerals in the weathered LAWBP1 and LAWA44 glasses, respectively. In these weathered glasses, crystalline minerals contained significant fractions of ^{99}Tc activities (~35 to 70%) associated with the solid phase.

The crystalline phases identified in these weathered glasses consisted of zeolite P (75%), analcime (15%), and hydroxycancrinite (10%) (LAWBP1), and zeolite P (65%) and analcime (35%) (LAWA44). Our previous study has established that a zeolite mineral, analcime, resulting

from weathered glasses (LD6 and LAWA33) structurally sequestered I, Re (an analog of Tc), and Se. An assessment of the tendencies of the crystalline phases to incorporate mobile contaminants has indicated that analcime has a greater tendency to incorporate I, whereas other zeolite minerals such as herschelite and phillipsite/paragonite have enhanced tendencies to sequester Re (Mattigod et al. 2002a). Therefore, radionuclide sequestration tendencies of various crystalline minerals appear to be a function of their structural type and the relative kinetics of their formation.

3.3 Stable Isotope Sequestration Experiments

In these experiments, the data indicated that weathering of stable isotope solids spiked with solid sodium aluminate to waste glass samples (LAWBP1 and LAWA44) placed in contact with HGW resulted in the formation of the cage-structured zeolitic mineral sodalite as the dominant crystalline fraction (Table 7, Figures 10, 11). Contrastingly, analcime was the principal zeolitic crystalline mineral found in both weathered glass samples that did not contain any spikes or aluminate additives. Also, in all cases the weathered LAWA44 glass contained a minor amount (~5%) of an unidentified crystalline mineral.

The scanning electron micrographs of sodalite crystals formed from stable isotope (either Re or I) and sodium aluminate-spiked weathered glasses (Figures 12 – 19) show several distinct morphologies belonging to the cubic system. Because sodalite formation is initiated by the templating action of anions, the morphology of sodalite crystals is dictated by the stereochemical configurations of the salt molecules trapped in the structural cages. For instance, large multifaceted spherical sodalite crystals were found in Re-spiked weathered LAWBP1 glass (Figures 12, 13), whereas individual dipoidal sodalite crystals formed from Re- and sodium aluminate-spiked LAWA44 glass (Figures 16, 17). Similar differences were noted in the morphology of sodalite crystals formed from I-spiked LAWBP1 and LAWA44 glasses (see Figures 14, 15 versus Figures 18, 19). The sodalite crystals formed from I- spiked LAWBP1 glass crystallized as hexoctahedrons, whereas sodalite crystallized from I-spiked LAWA44 glass occurred as aggregates of gyroids.

Table 7. Estimated Quantities of Crystalline Weathering Products from Re- and I-Spiked LAWBP1 and LAWA44 Glasses with an Additive

Glass	Spike/Additive	Crystalline Minerals (wt%)		
		Analcime	Sodalite	Unidentified
LAWBP1	--	100	--	--
LAWBP1	Re/NaAlO ₂	--	100	--
LAWBP1	I/NaAlO ₂	10	90	
LAWA44	--	95	--	5
LAWA44	Re/NaAlO ₂	--	95	5
LAWA44	I/NaAlO ₂	--	95	5

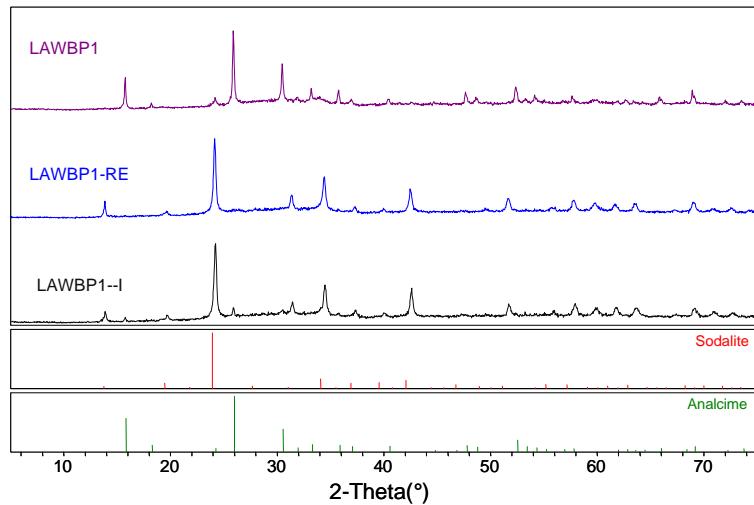


Figure 10. XRD Data for Phases Formed from LAWBP1 Glass Weathered with Stable Isotope Spikes

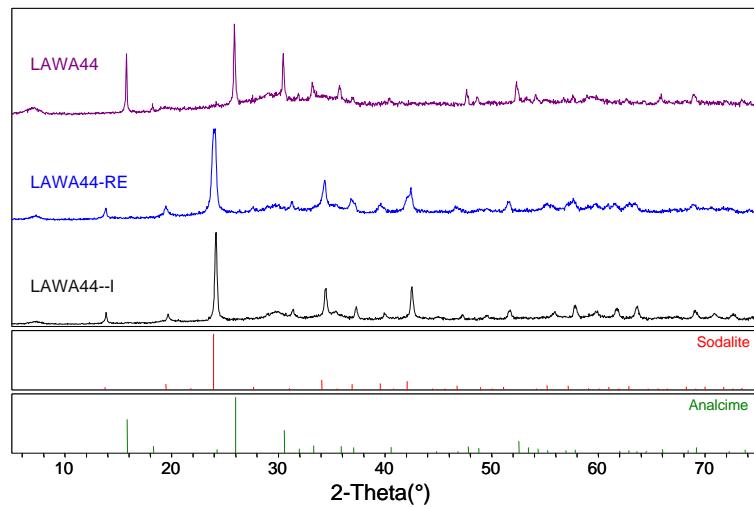


Figure 11. XRD Data for Phases Formed from LAWA44 Glass Weathered with Stable Isotope Spikes

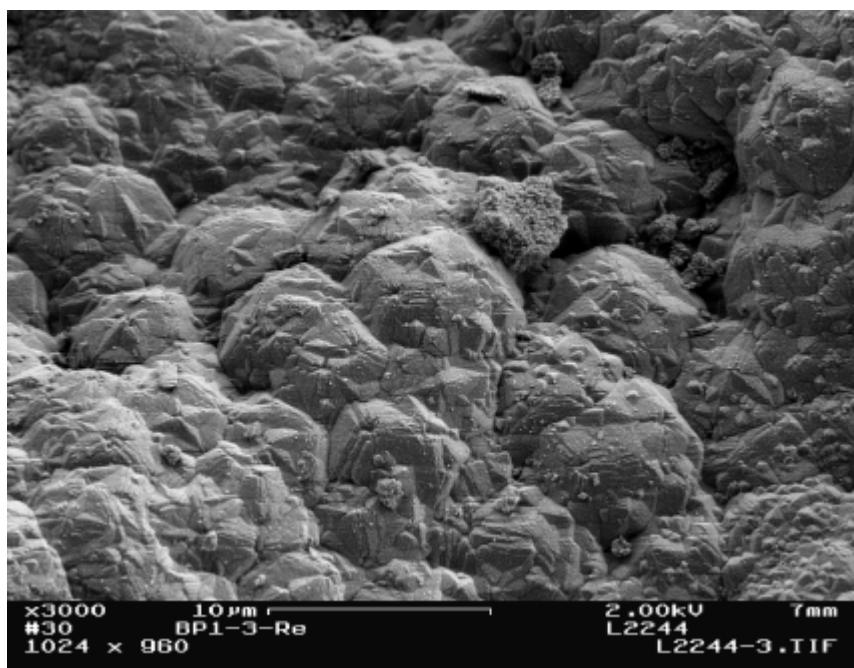


Figure 12. A Dense Mass of dodecatrapezohexoctahedral Sodalite Crystals Formed from Re-Spiked Weathered LAWBP1 Glass

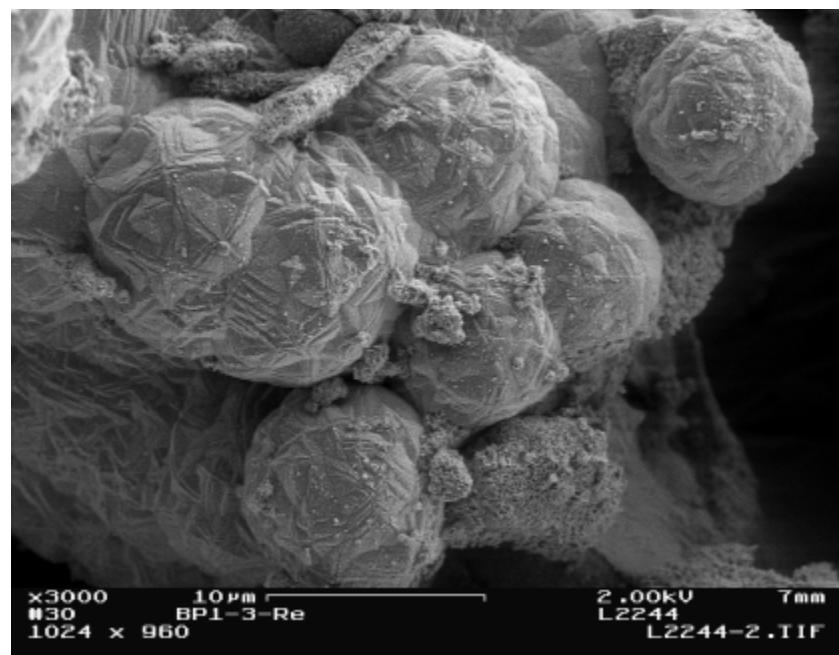


Figure 13. Detailed Morphology of Sodalite Crystals Formed from Re-Spiked Weathered LAWBP1 Glass

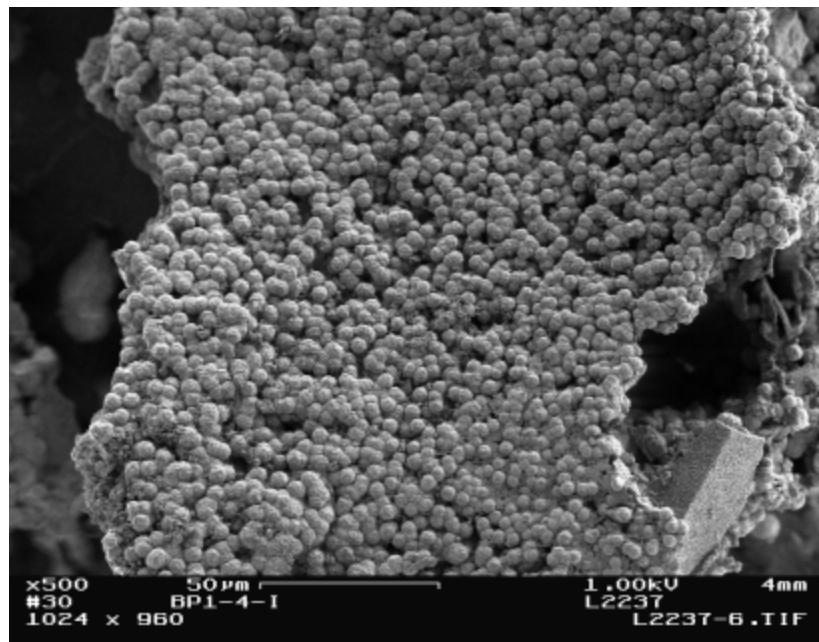


Figure 14. A Large Cluster of Sodalite Crystals formed From I-Spiked Weathered LAWBP1 Glass

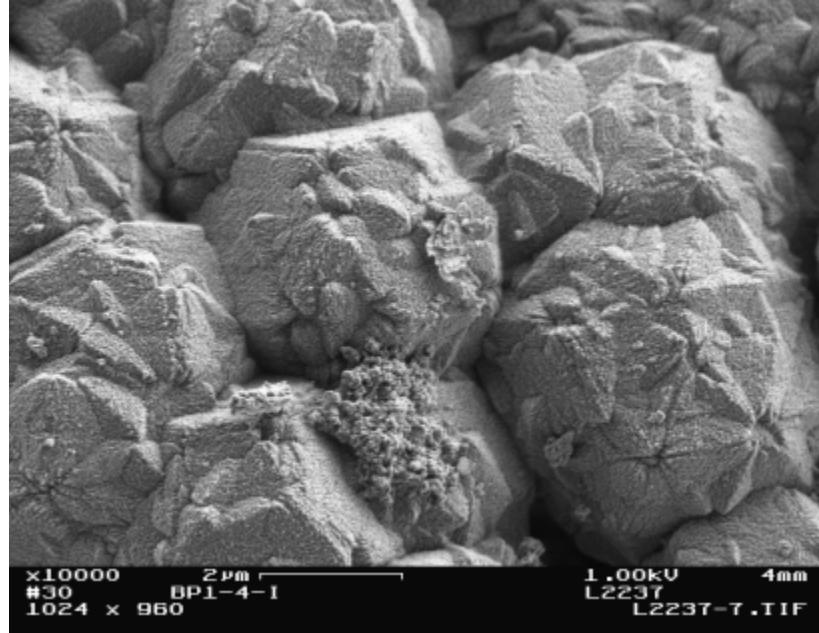


Figure 15. A Close-up View of Hexoctahedral Sodalite Crystals Formed from I-Spiked Weathered LAWBP1 Glass

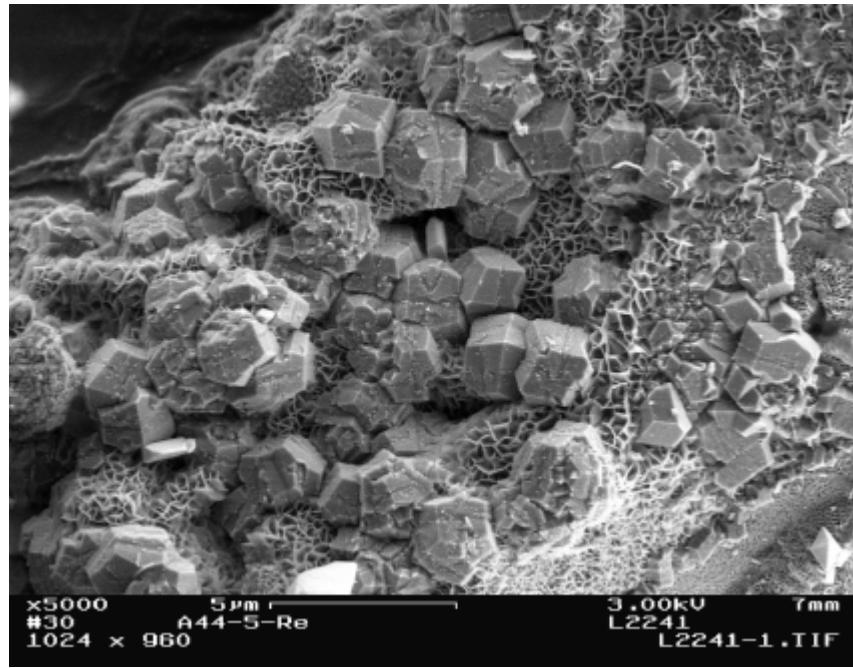


Figure 16. An Assemblage of Diploidal Sodalite Crystals Formed on the Gel-layer in Re-Spiked Weathered LAWA44 Glass

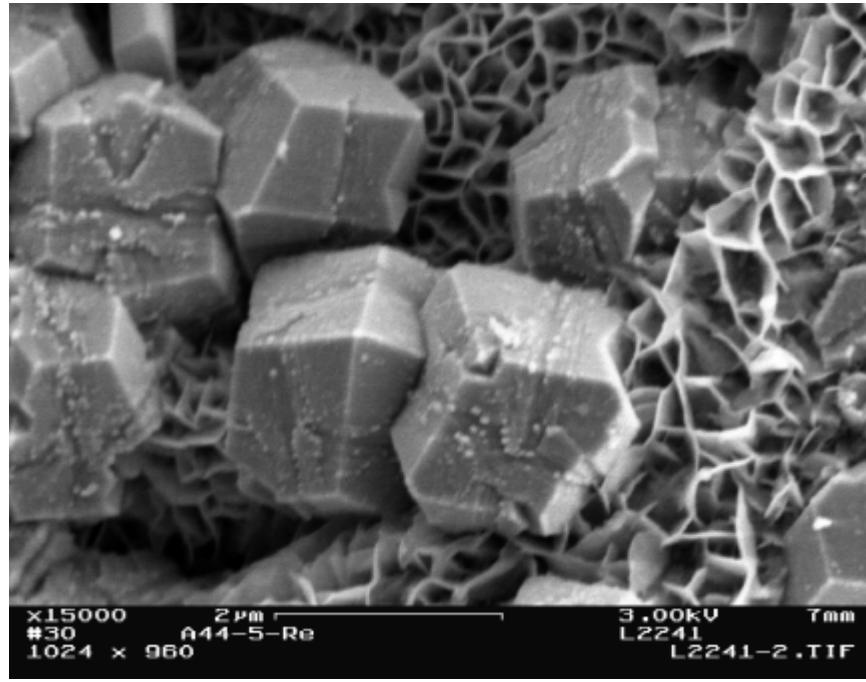


Figure 17. An Enlarged View of Diploidal Sodalite Crystals Formed from Re-Spiked Weathered LAWA44 Glass

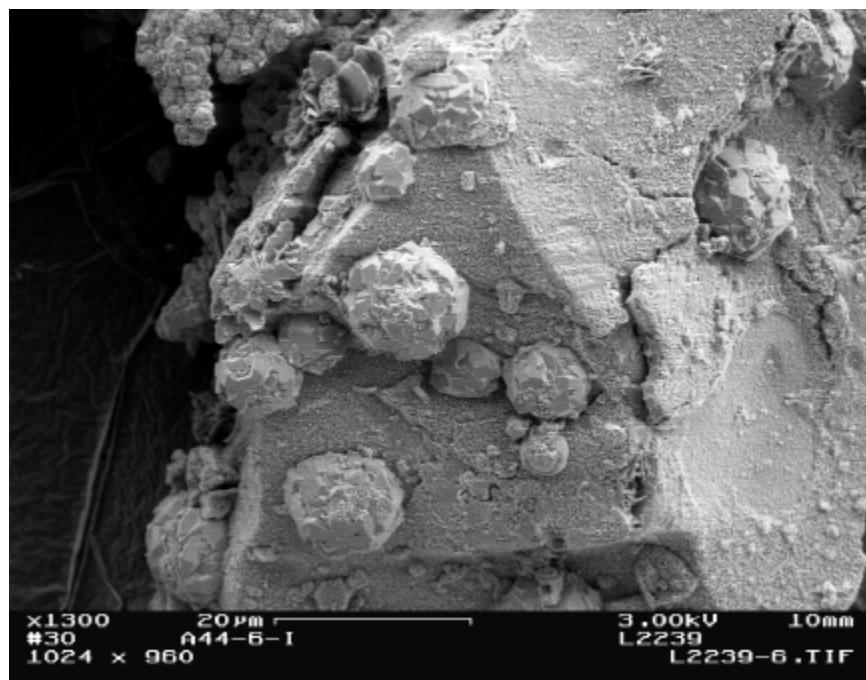


Figure 18. A Magnified View of Intergrown Gyroidal Sodalite Crystals Formed from I-Spiked Weathered LAWA44 Glass

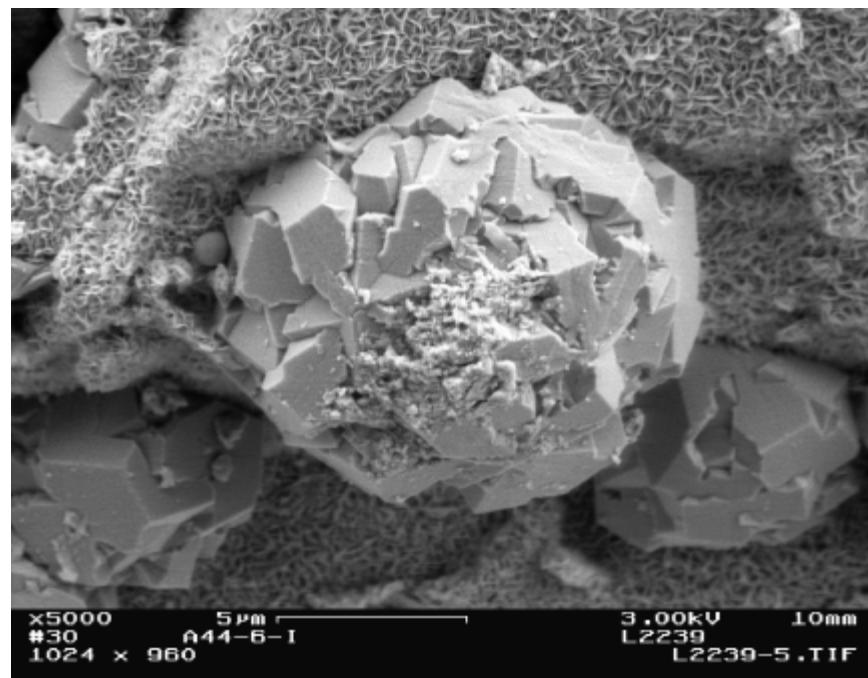


Figure 19. Intergrown Sodalite Crystals Formed from I-Spiked Weathered LAWA44 Glass

The structural formula of sodalite $[Na_6Al_6Si_6O_{24}(Na_2X)]$ indicates that the cage positions (represented by X) can sequester significant quantities of Tc (an Re analog) and I. As an example, sodalite with the composition $Na_6Al_6Si_6O_{24}(NaReO_4)_2$ contains ~27% of Re. Similarly, a sodalite containing mainly I in the cage positions $[Na_6Al_6Si_6O_{24}(NaI)_2]$ can sequester about 22% by weight of I. Considering that the two glasses studied contained about 30 - 35% by mass of sodalite when soluble sodium aluminate was present, we calculated the theoretical maximum quantities of Re and I that could be sequestered in the sodalite phase of the weathered glass to be ~9% Re and ~7% I, respectively. The calculated degree and type of sequestration need to be verified by chemical and extended X-ray absorption fine structure (EXAFS) spectroscopic analysis. These levels of sequestration of Re and I exceed by orders of magnitude the degree of sequestration of these isotopes that can be substituted into analcime. These experiments demonstrated that radionuclide sequestration can be significantly enhanced by promoting the formation of cage-structured minerals such as sodalite from weathering glasses.

As discussed previously (Mattigod et al. 1998), sequestration of radionuclides during glass weathering can occur as a result of either adsorption (exchange) and/or precipitation of secondary minerals. In this study, we showed that small fractions of the sequestered radionuclides that were adsorbed onto the amorphous gel phase were readily mobilized. Comparatively, significant fractions of sequestered radionuclides were relatively leach-resistant because they were integrated into secondary crystalline mineral structures. Also, the formation of secondary minerals may involve precipitation of either a pure or a solid solution phase. For trace components such as radionuclides, the precipitation reactions involve incorporation in secondary minerals as solid solution phases. Based on extensive studies and literature surveys, Barrer (1982) identified a number of mechanisms that result in incorporation of various ionic components into zeolite structures:

- isomorphous (similar coordination-related ionic radii) substitution for tetrahedral Si and Al
- occupation of cation-exchange sites
- substitution of framework oxygen by other anionic species
- entrapment as salt molecules in zeolitic channels and cages.

Each of these mechanisms was evaluated in a previous report (Mattigod et al. 1998) to assess the type of ionic incorporation that can account for the observed sequestration of radionuclides and stable isotopes in secondary crystalline minerals (Table 8).

The salt-molecules are typically entrapped by minerals such as sodalite and cancrinite, which have cage-like structures (Barrer 1982). The principal secondary minerals observed in these spiked weathering experiments (zeolite P and analcime) are not known to trap salt molecules; therefore, the radionuclide incorporation mechanisms for these minerals appear to be mainly isomorphic substitution of Se and Re in tetrahedral sites and iodide substituting for framework oxygen. Because hydroxycancrinite was one of the crystalline products (Table 3) present in weathered LAWBP1 glass, some fractions of radionuclides were probably entrapped in the cage-like structure of this mineral.

Table 8. Mechanisms of Radionuclide Incorporation in Zeolite Minerals

Radio-nuclide	Isomorphous Substitution for Al and Si in Tetrahedral Coordination	Occupation of Cation-Exchange Site	Framework Oxygen Substitution	Salt Molecule Entrapment in cages of sodalites and cancrinites
⁷⁵ Se	Possible; ionic radius compatible with Si	Oxyanion species (SeO_4^{2-}); cannot occupy cationic site	Oxyanion substitutions not observed	Known to occur as Na_2SeO_4 molecule
⁹⁹ Tc	Possible; ionic radius compatible with Al	Oxyanion species (TcO_4^-); cannot occupy cationic site	Oxyanion substitutions not observed	Possible as alkali-oxyanion salt
¹²⁵ I	Anionic species; substitution not possible	Anionic species (I^-); cannot occupy cationic sites	Halide substitution possible	Known to occur as NaI and KI molecules

The stable isotope-spiked weathering experiments conducted in this study were designed to promote the formation of cage-structured sodalite and/or cancrinite minerals that could entrap higher concentrations of Re and I. The results showed that it was possible to attain a large degree of radionuclide sequestration in sodalite cages. Additional studies need to be conducted that include synthesis of pure sodalite phases containing Re and I and an assessment of the degree of sodalite solubility and concomitant mobilization of the entrapped ions.

Additional experiments and thermodynamic calculations are needed to assess whether the secondary minerals that formed by contacting LAWBP1 and LAWA44 glasses with groundwater or caustic solutions at elevated temperatures and testing in the presence of a source of soluble aluminum (such as the tests with sodium aluminate) also form at the lower temperatures that will be found in the ILAW vadose zone. Another challenge is to evaluate whether these minerals remain stable for thousands of years in the ILAW vadose zone environment. If these secondary minerals can be shown to form and remain stable for thousands of years, then another mechanism for contaminant sequestration that is not currently included in the conceptual models of the fate of the ILAW glass can be included in future PA calculations/predictions.

4.0 Conclusions

Static weathering of LAWBP1 conducted at 160 °C (solution-to-solid ratios ranging from 1 – 3 mL/g) resulted in the formation of 60 -75%, zeolite P [$\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$]. Other zeolite minerals such as analcime [$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$] (15 -30%) and cancrinite [$\text{Na}_6\text{Al}_6\text{Si}_6(\text{Na}_2\text{X})\text{O}_{24} \cdot 2\text{H}_2\text{O}$] (~10%) were also identified as products of weathering. Similar weathering reactions conducted using LAWA44 glass at a solution-to-solid ratio of unity resulted in the formation of about 65 wt% zeolite P and ~35% analcime. Reactions conducted at higher solution-to-solid ratios (2 and 3mL/g) produced a single crystalline product, namely, analcime.

Dynamic weathering of LAWBP1 glass at 95 °C resulted in only trace quantities (<5%) of a “clay-like” crystalline mineral with a 9 Å spacing in a matrix of unaltered glass and gel. Similar tests conducted at 160 °C resulted in the formation of significant amounts of analcime. Crystalline minerals produced after 1 week of dynamic weathering at 160 °C consisted of approximately 80% analcime, 15% phillipsite, with 5% of a 9 Å clay mineral. A comparison of results of static and dynamic weathering of LAWBP1 glass showed that weathering regime is a significant factor in the types of secondary mineral assemblages that form from waste glass.

During dynamic weathering of LAWBP1 glass at 95 °C, the mass fraction release rates for all major elements were relatively low (~ 4×10^{-5} to 2×10^{-3} /day) and constant during all reaction intervals, whereas at 160 °C the initial mass fraction release rates of ~ 3×10^{-5} to 5×10^{-2} /day declined with successive time intervals and at the end of the experiment appeared to be reaching a steady state that ranged from ~ 3×10^{-6} to 1×10^{-3} /day. Such decline in mass fraction release rates was probably due to longer diffusion paths created by increasing the thickness of the hydrated gel layer or the decrease in pH.

The radionuclide-spiked HGW experiments indicated that ~16 - 18% of ^{125}I , ~7 - 13% of ^{75}Se , and ~5 - 12% of ^{99}Tc were sequestered in reaction products (the secondary crystalline phases and the hydrated gel layer) formed from the weathering of LAWBP1 glass. Similar degrees of sequestration of ^{75}Se (~8 -14%) but noticeably lower degree of sequestration of ^{125}I activity (~12 – 13%) was observed when the spiked solution consisted of 1M NaOH. Experiments conducted using samples of LAWA44 waste glass reacted with radionuclide-spiked HGW solution resulted in sequestration of ~9 -16 % of ^{125}I , ~6 - 15% of ^{75}Se , and ~<1 - 6 of ^{99}Tc , while sequestration of radionuclides from a 1M NaOH solution was ~8 -11 % for ^{125}I and ~8 - 13% for ^{75}Se , respectively. Sequestration of ^{99}Tc from caustic solutions was not determined because of analytical problems.

Radionuclide re-mobilization (desorption) tests showed that at the end of 3 days, the released radionuclides reached steady state concentrations in solution. Subsequent measurements

extending up to 86 days showed no significant changes in solution activities. Such early release and relative constancy over an extended period indicated that these fractions of the activities were most likely associated with an easily soluble solid phase such as the hydrated gel. Calculations based on results of radionuclide sequestration and mobilization experiments indicated that ~55 – 80% and ~30 – 90% of the sequestered ^{125}I , and about 60 – 70% and 30 – 90% of solid phase activities of ^{75}Se in the weathered LAWBP1 and LAWA44 glasses, were sequestered in crystalline minerals such as zeolite P and analcime.

Weathering of stable isotope- and sodium aluminate-spiked waste glass samples (LAWBP1 and LAWA44) resulted in the formation of a cage-structured mineral, sodalite, as the dominant crystalline mineral. The quantities of Re and I sequestered in the sodalite structure were estimated to be ~9% and ~7%, respectively. These experiments demonstrated that radionuclide sequestration can be significantly enhanced by promoting the formation of a cage-structured mineral such as sodalite from weathering glasses.

These results have some important implications regarding the radionuclide mobilization aspects of ILAW performance assessment:

- Secondary crystalline phases, typically zeolitic minerals, form rapidly from weathering waste glasses, and the metastable fast-forming phases that initially form subsequently convert to more stable crystalline phases.
- Substantial fractions of radionuclides ^{129}I , ^{79}Se , and ^{99}Tc that are initially present in waste glasses are likely to be isomorphically incorporated into the structures of crystalline minerals, and the tendency and the degree of sequestration depends on the mineral structure and their relative formation kinetics.
- Minor fractions of radionuclides adsorbed on to the hydrated amorphous gel are mobilized rapidly when immersed in water that does not contain the radionuclides, whereas radionuclides isomorphically substituted in the zeolitic mineral structures are leach-resistant due to the relative insolubilities of these minerals.
- Radionuclide sequestration in weathering waste glasses can be significantly enhanced by using additives such as sodium aluminate, which promote the formation of cage-structured zeolitic minerals such as sodalite and cancrinite.
- The upper limits of radionuclide activities released from secondary crystalline minerals can be predicted from the equilibrium solubilities of secondary crystalline solid phases.

An improved understanding of radionuclide sequestration and their subsequent mobilization is expected to help refine certain aspects of the waste form release part of the ILAW PA. A set

of follow-on studies is needed to develop a comprehensive understanding of the phenomenon. These are:

- Determine the types of secondary minerals that form at expected disposal site temperatures from weathering of specific ILAW waste glass compositions when the radionuclides are present in glass and not in contacting solutions.
- Enhance the degree of radionuclide sequestration by promoting the formation of cage-structured zeolitic minerals such as sodalite and cancrinite.
- Measure the upper limits of radionuclide sequestration that occur in secondary crystalline minerals
- Assess the kinetics of dissolution of each radionuclide-bearing synthetic secondary crystalline phase or the long-term release of the contaminants from the secondary minerals under near-field environmental conditions encountered the ILAW facility.
- Evaluate the upper limits of radionuclide activity in aqueous phase from studies of equilibrium solubilities of each radionuclide-bearing secondary crystalline phase.

5.0 References

- Barrer R.M. 1982. *Hydrothermal chemistry of zeolites*. Academic Press, New York.
- Barrer R. M. and J. F. Cole, 1970. "Chemistry of Soil Minerals. Part VI. Salt Entrainment by Sodalite and Cancrinite during their Synthesis." *J. Chem. Soc. (A)* 1516-1523.
- Caurel J, D. Beaufort, and E.Y. Vernaz. 1988. Mineral Phase Identification Along Two Profiles from LWR French Reference Glass: Use of an X-Ray Position Sensitive Detector. *Material Research Society Symposium Proceedings*, v. 112, pp. 663-672, Material Research Society, Pittsburgh, Pennsylvania.
- Collella C, R. Aiello, and C. Porcelli. 1978. "Hydration as an Early Stage in the Zeolitization of Natural Glass." *Natural Zeolites*, L.B. Sand and F.A. Mumpton (eds.), Pergamon Press, Oxford, pp. 345-350.
- Ebert W.L., and S.W. Tam. 1997. "Dissolution Rates of DWPF Glasses from Long-Term PCT". *Scientific Basis for Nuclear Waste Management XX*, W.J. Gray and I. Triay (eds.), v. 465, pp. 149-156, Material Research Society, Pittsburgh, Pennsylvania.
- Fortner J.A., S.F. Wolf, E.C. Buck, C.J. Mertz, and J.K. Bates. 1997. "Solution-Borne Colloids from Drip Tests Using Actinide-Doped and Fully-Radioactive Waste Glasses." *Scientific Basis for Nuclear Waste Management XX*, W.J. Gray and I. Triay (eds.), v. 465, pp. 165-172, Material Research Society, Pittsburgh, Pennsylvania.
- Haaker R, G. Malow, and P. Offerman. 1985. "The Effects of phase Formation on Glass Leaching. *Material Research Society Symposium Proceedings*, v. 44, pp. 121-128, Material Research Society, Pittsburgh, Pennsylvania.
- Holler H., and U. Wirsching. 1978. "Experiments on the Formation of Zeolites by Hydrothermal Alteration of Volcanic Glasses." *Natural Zeolites*, L.B. Sand and F.A. Mumpton (eds.), Pergamon Press, Oxford, pp. 329-336.
- Luo J.S., W.L. Ebert, J.J. Mazer, and J.K. Bates. 1997. "Simulation of Natural Corrosion of Vapor Hydration Test: Seven Year Results." *Scientific Basis for Nuclear Waste Management XX*, W.J. Gray and I. Triay (eds.), v. 465, pp. 157-163, Material Research Society, Pittsburgh, Pennsylvania.

Lutze W., R. Muller, and W. Montserrat. 1988. "Chemical Corrosion of COGEMA Glass R7T7 in High Saline Brines." *Material Research Society Symposium Proceedings*, v. 112, pp. 575-584, Material Research Society, Pittsburgh, Pennsylvania.

Mann F.M., R.J. Puigh, II, P.D. Rittmann, N.W. Kline, J.A. Voogd, Y. Chen, C.R. Eiholzer, CT Kincaid, BP McGrail, AH Lu, GF Williamson, NR Brown, and PE LaMont. 1998. *Hanford Immobilized Low-Activity Tank Waste Performance Assessment*. DOE/RL-97-69, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Mann, F.M., K.C. Burgard, W.R. Root, P.E. LaMont, R.J. Puigh, S.H. Finfrock, R. Khaleel, D.H. Bacon, EJ Freeman, BP McGrail, SK Wurstner. 2001. *Hanford Immobilized Low-Activity Waste Performance Assessment: 2001 Version*. DOE/ORP-2000-24, Office of River Protection, Richland, Washington.

Mattigod S.V., D.I. Kaplan, V.L. LeGore, R.D. Orr, H.T. Schaef, and J.S. Young. 1998. *Radionuclide incorporation in Secondary Crystalline Minerals Resulting from Chemical Weathering of Selected Waste Glasses: Progress Report for Subtask 3d*. PNNL-12005, Pacific Northwest National Laboratory, Richland, Washington.

Mattigod S.V., R.J. Serne, B.P. McGrail and V.L. LeGore 2002a. "Radionuclide Incorporation in Secondary Crystalline Minerals from Chemical Weathering of Waste Glasses." *Scientific Basis for Nuclear Waste Management XX*, B.P. McGrail and G. Craglano (eds.), v. 713, pp. 597-604, Material Research Society, Pittsburgh, Pennsylvania.

Mattigod, S. V., D. T. Hobbs, K. E. Parker, D. E. McCready 2002b. *Precipitation of Aluminum Containing Species In Tank Wastes*. PNNL-13881 Pacific Northwest National Laboratory, Richland, Washington.

McGrail B.P., W.L. Ebert, A.J. Bakel, and D.K. Peeler. 1997a. "Measurement of Kinetic Rate Law Parameters on a Na-Ca-Al Borosilicate Glass for Low-Activity Waste." *Journal of Nuclear Material* 249:175-179.

McGrail B.P., P.F. Martin, and C.W. Lindenmeier. 1997b. "Accelerated Testing of Waste Forms Using a Novel Pressurized Unsaturated Flow (PUF) Method." *Scientific Basis for Nuclear Waste Management XX*, W.J. Gray and I. Triay (eds.), v. 465, pp. 253-260, Material Research Society, Pittsburgh, Pennsylvania.

McGrail B.P., W.L. Ebert, D.H. Bacon, and D.M. Strachan. 1998. *A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface*

Disposal System at Hanford. PNNL-11834, Pacific Northwest National Laboratory, Richland, Washington.

McGrail B.P., J.P. Icenhower, D.K. Shuh, P. Liu, J.G. Darab, D.R. Baer, S. Thevuthasan, V. Shuttanandan, M.H. Englehard, C.H. Booth and P. Nachimuthu 2001. “The Structure of Na₂O-Al₂O₃-SiO₂ glass: impact on sodium ion exchange in H₂O and D₂O.” *J. Non-Crystal. Solids.* 296: 10-26.

Newman A.C.D, and G. Brown. 1987. “The Chemical Constitution of Clays.” *Chemistry of Clays and Clay Minerals*, A.C.D. Newman (ed.), pp. 1-128, John Wiley and Sons, New York.

Serne R.J., and M.I. Wood. 1990. *Hanford Waste-Form Release and Sediment Interaction.* PNL-7297, Pacific Northwest Laboratory, Richland, Washington.

Serne R.J., J.L. Conca, V.L. Legore, K.J. Cantrell, C.E. Lindenmeier, J.A. Campbell, J.E. Amonette, and M.I. Wood. 1993. *Solid-Waste Leach Characteristics and Contaminant-Sediment Interactions. Volume 1: Batch Leach and Adsorption Tests and Sediment Characterization.* PNL-8889 vol. 1, Pacific Northwest Laboratory, Richland, Washington.

Van Iseghem P.P., W. Timmermans, and R. De Batist. 1985. “Parametric Study of the Corrosion Behavior in Static Distilled Water of Simulated European Reference High-Level Waste Glasses.” *Material Research Society Symposium Proceedings*, v. 44, pp. 55-62, Material Research Society, Pittsburgh, Pennsylvania.

Van Iseghem P.P., and B. Grambow. 1988. “The Long-Term Corrosion and Modelling of Two Simulated Belgian Reference High-Level Waste Glasses.” *Material Research Society Symposium Proceedings*, v. 112, pp. 631-639, Material Research Society, Pittsburgh, Pennsylvania.

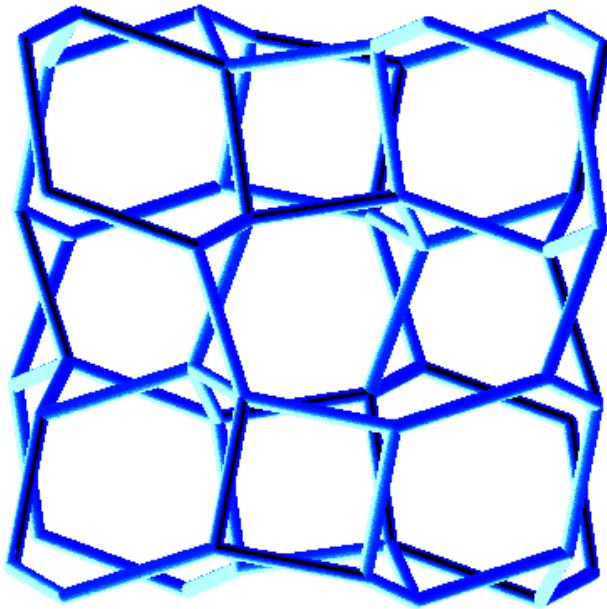
Appendix

Crystallographic Details on Glass Weathering Products

ANALCIME

Chemical Composition: $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$.
Zeolite Structure Type: ANA

Crystal Symmetry: Cubic

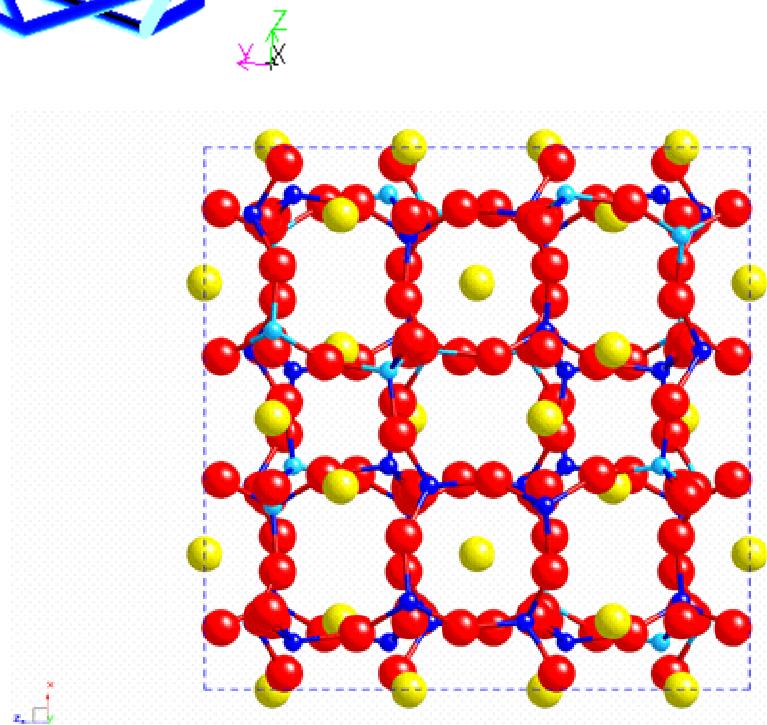


Secondary Building Units (SBU) in analcime consist of four linked tetrahedra (SiO_4 and AlO_4) designated as S4R. These S4R units in turn are linked to form larger units comprising a ring of 6 tetrahedral units (S6R) with a 2.6 Å aperture. View Normal to 001 Crystallographic planes.

View Normal to 100
Crystallographic planes
Showing cation Positions. The
ions in the structure are color
coded as Lt Blue, Al; Dk Blue,
Si; Red, O; Yellow, Na.

Potential Isomorphous
Substitutions in Tetrahedral
Positions: B, Be, Cr(III),
Fe(III), Ga, Ge, Mg, P, Re,
Se(IV), Se(VI), Tc(VII), Ti, and
Zr.

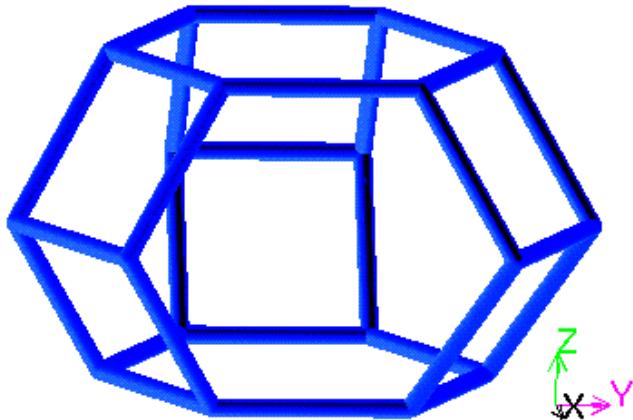
Potential Framework Oxygen
Substitutions:
Br, Cl, F, I, and N.



CANCRINITE

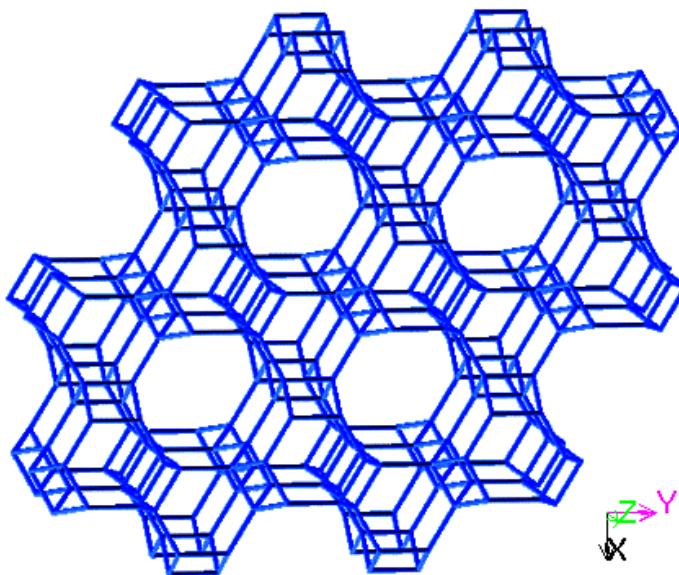
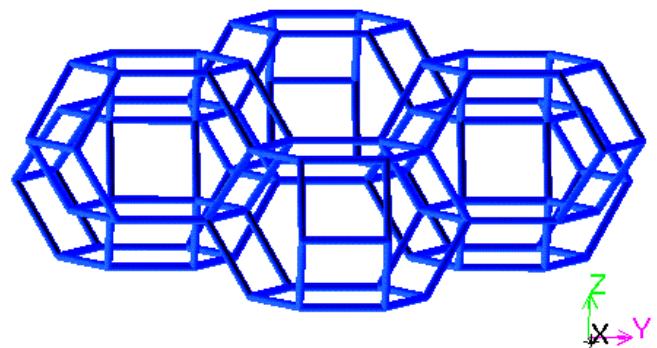
Chemical Composition: $(\text{Na}_6\text{Al}_6\text{Si}_6(\text{Na}_2\text{X})\text{O}_{24} \cdot 2\text{H}_2\text{O}$
Zeolite structure Type: CAN

Crystal Symmetry: Hexagonal



The SBUs in cancrinite consist of S4R, and 6SR linked to form 11-faced polyhedra known as an e-cage.

Six e-cages (polyhedra) form ringed units by alternatively sharing S4R and S6R faces (View normal to [100] crystallographic plane).



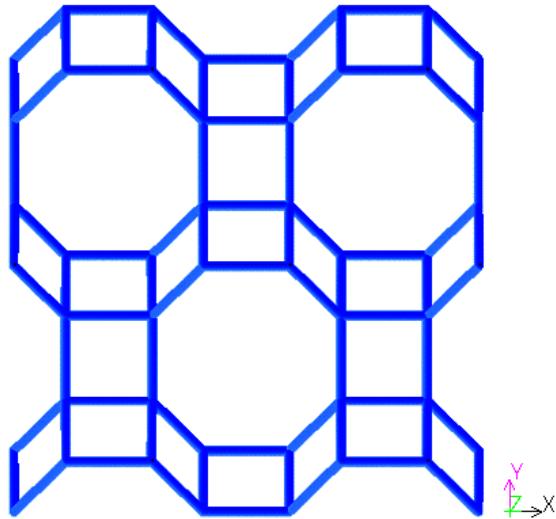
View normal to [001] crystallographic plane showing overall structure of cancrinite.

Potential e-cage trappable Anions (represented by X in chemical compositions) : OH , CO_3 , CrO_4 , I , IO_3 , NO_3 , MoO_4 , VO_4 , TeO_4 , SeO_3 , SeO_4 , SO_4 , Br , TcO_4

PHILLIPSITE

Chemical Composition: $(K,Ca,Na_2)Al_3Si_5O_{16} \cdot 6H_2O$
Zeolite Structure Type: PHI

Crystal Symmetry: Orthorhombic

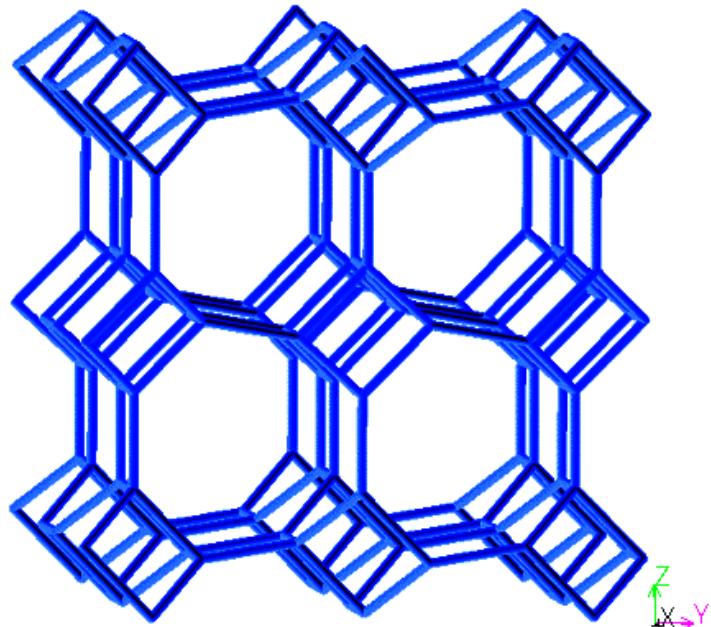


The SBU in phillipsite consists of S4R units linked to form larger S8R units. These S8R units are cross-linked to form chains. View normal to [001] crystallographic plane.

View normal to [100] crystallographic plane showing the parallel linkages of S8R units.

Potential Isomorphous Substitutions in Tetrahedral Positions: B, Be, Cr(III), Fe(III), Ga, Ge, Mg, P, Re, Se(IV), Se(VI), Tc(VII), Ti, and Zr.

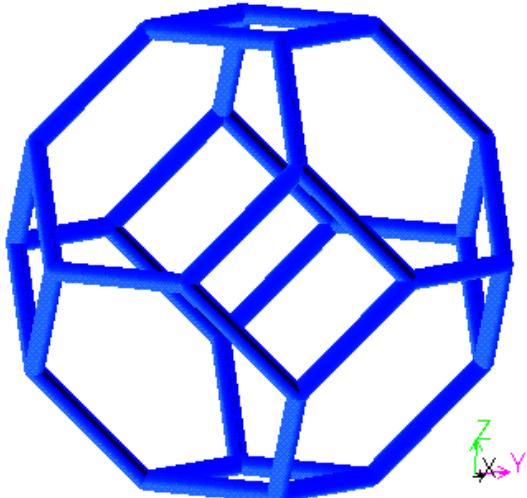
Potential Framework Oxygen Substitutions: Br, Cl, F, I, and N.



SODALITE

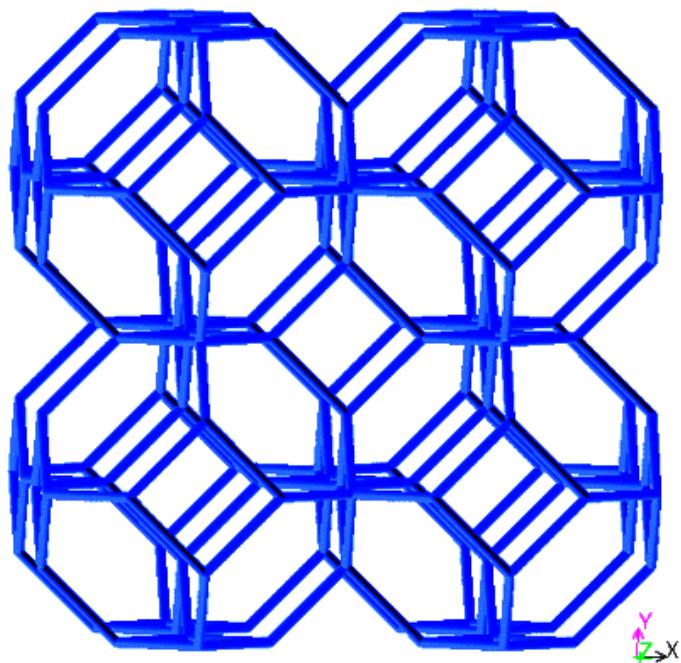
Chemical Composition: $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}(\text{Na}_2\text{X})$
Zeolite Structure Type: SOD

Crystal Symmetry: Cubic



The SBUs in sodalite consist of S4R, and S6R units linked to form a 14-faced polyhedral unit known as a β -cage.

(Eight β -cages (polyhedra) share S4R faces to form larger cubic units. View normal to [001] crystallographic plane (figure to right).

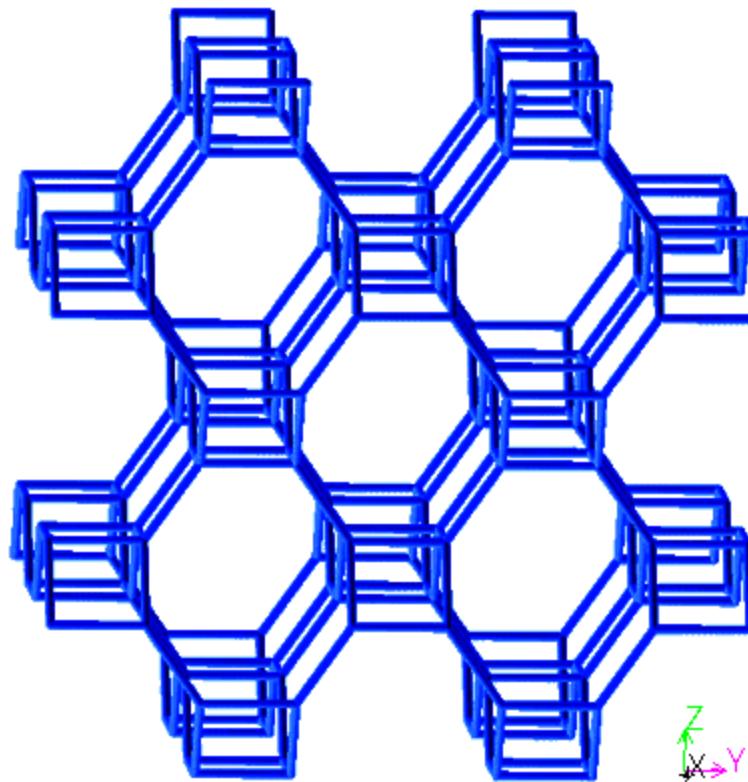


Potential β -cage trappable Anions (represented by X in chemical composition): OH , ClO_4 , C_2O_4 , WO_4 , PO_4 , NO_3 , N_3 , SeO_4 , SO_4 , Cl , I , IO_3 , Br , ReO_4 , TcO_4 .

ZEOLITE P

Chemical Composition: $\text{Na}_4\text{Al}_4\text{Si}_4\text{O}_{16} \cdot \text{H}_2\text{O}$
Zeolite Structure Type: GIS

Crystal Symmetry: Monoclinic



The SBU in zeolite P consists of S4R units linked to larger form S8R units that are cross-linked to form parallel chains. Viewed normal to [100] crystallographic plane.

Potential Isomorphous Substitutions in Tetrahedral Positions: B, Be, Cr(III), Fe(III), Ga, Ge, Mg, P, Re, Se(IV), Se(VI), Tc(VII), Ti, and Zr.

Potential Framework Oxygen Substitutions:
Br, Cl, F, I, and N.

Distribution

<u>No. of Copies</u>	<u>No. of Copies</u>
ONSITE	16 Pacific Northwest National Laboratory
11 CH2M Hill Hanford Group	8 CDs, 8 Hardcopies
<i>7 CDs, 4 Hardcopies</i>	
K.C. Burgard	C.T. Kincaid
M.P. Connelly	G.V. Last
E.A. Fredenburg	B.P. McGrail
T.E. Jones	S.V. Mattigod (<i>4 hardcopies</i>)
A.J. Knepp	R.D. Orr
F.M. Mann (<i>4 hardcopies</i>)	R.J. Serne (<i>1 hardcopy</i>)
G. Parsons	D.E. McCready
R.J. Puigh	V.L. LeGore
	J.S. Young
	K.E. Parker
2 Fluor Hanford	K.M. Krupka (<i>1 hardcopy</i>)
<i>2 CDs</i>	<i>Technical Library (2 hardcopies)</i>
B.H. Ford	E6-35
M.I. Wood	H8-14