MCC

Materials Characterization Center

Workshop on the Leaching Mechanisms of Nuclear Waste Forms, December 7-8, 1982

Summary Report

January 1985

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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MATERIALS CHARACTERIZATION CENTER
WORKSHOP ON THE LEACHING
MECHANISMS OF NUCLEAR WASTE FORMS,
DECEMBER 7-8, 1982, THOUSAND OAKS, CA.
SUMMARY REPORT

J. E. Mendel
A. B. Harker(a)

January 1985

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

Pacific Northwest Laboratory
Richland, Washington 99352

(a) Rockwell Science Center, Thousand Oaks, CA.

FOREWORD

The Leaching of nuclear waste forms is a complex phenomenon that has been studied extensively. There is a basic understanding of the various reactions involved. What remains to be done is to quantify the relationships between the different reactions so that mathematical models can be used to predict the leaching behavior of waste forms for thousands of years, several orders of magnitude beyond experimentally verifiable times. A three-year leaching mechanisms program has been set up by the defense high-level waste lead office to integrate the efforts of several laboratories and outside consultants to develop the requisite data base and demonstrate its application in predictive mathematical models.

The output of this program, which is being coordinated by the Materials Characterization Center (MCC), is expected to be

- Efficient utilization of Department of Energy (DOE) waste management scientific resources through coordination by workshops and special studies that also bring in outside experts when needed.
- Documented, back-up materials data to demonstrate that DOE's predictive mathematical models for defense waste-form leaching are soundly based on mechanistic principles.
- A peer-reviewed, coherent, waste materials data base that relates directly to predictive mathematical models for defense waste-form leaching and can be used to demonstrate the relationship of this leaching behavior to Environmental Protection Agency (EPA) and Nuclear Regulatory Commission (NRC) criteria.

This document is a report of a workshop held in Thousand Oaks, California, December 7-8, 1982. It was the third in a series of leaching mechanisms workshops to be held at about six-month intervals. Reports of the first and second workshops in the series have been issued (PNL-4228, and PNL-4382).

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1.0 INTRODUCTION

1.0 INTRODUCTION

The laboratories and lead investigators participating in the leaching mechanisms program are as follows:

University of Florida (L. L. Hench)
Catholic University of America (P. B. Macedo)
Pennsylvania State University (W. B. White)
Rockwell Science Center (A. B. Harker and D. R. Clarke)
Lawrence Livermore National Laboratory (D. D. Jackson)
Pacific Northwest Laboratory (G. L. McVay)

The program is funded by DOE's defense high-level waste (HLW) lead office and is being coordinated by J. E. Mendel of the Materials Characterization Center. The written proceedings of workshops, held at about six-month intervals, are progress reports for the leaching mechanisms program. This is a report of the third workshop in the series, which was held at Thousand Oaks, California, December 7-8, 1982.

The agenda for the workshop is attached as Appendix A; a list of attendees is in Appendix B.

The first session of the workshop was devoted to progress reports by participants in the leaching mechanisms program. These progress reports, as prepared by the participants, are given in Section 3.0.

The goal of the remainder of the workshop was to exchange information on the development of repository-relevant leach testing techniques, often called interactions testing. To this end, a wide spectrum of investigators, many of whose work is sponsored by DOE's Nuclear Waste Terminal Storage (NWTs) project, made presentations at the workshop. These presentations were a significant and beneficial part of the workshop and are summarized in Sections 4.0 and 5.0 according to the workshop agenda topics. In many cases, the presenters provided a written version of their presentation which has been included verbatim; in the other cases, the workshop chairman has supplied a brief synopsis.

2.0 SUMMARY

2.0 SUMMARY

This report covers the first three sessions of the workshop, the sessions where formal presentations were made. The report either contains complete papers or summaries of presentations from these sessions.

Session I. Progress Report on Leaching Mechanisms

After an overview of the leaching mechanism program, presented by J. E. Mendel, investigators from each of the six laboratories involved in the program presented progress reports. These reports cover research activities since the May 1982 workshop. At that workshop, the laboratories agreed to focus the program on borosilicate glass. A reference glass was prepared at Savannah River Laboratory (SRL) and cast into bars at Pacific Northwest Laboratory (PNL). These bars were distributed to the participants so that they are now working with a common material. While many diverse activities continue, befitting the complexity of the subject, many progress reports described initial tests using the MCC reference glass.

Session II. Characterization of Leached Surfaces

Eight presentations were made in this session. Reports and summaries cover various techniques for characterizing leached surfaces. After an initial overview of the subject by A. Harker, the seven remaining presentations each dealt with a different characterization technique.

Session III. In Situ Characterization of Leaching Surfaces

Three presentations were made in this session. The first and third presentations each covered a different technique of in situ characterization of leaching surfaces. The second presentation was a useful tutorial. Papers from all three presentations are included in full in this report.

3.0 SESSION I. PROGRESS REPORT ON LEACHING MECHANISMS

3.0 SESSION I. PROGRESS REPORT ON LEACHING MECHANISMS

3.1 CATHOLIC UNIVERSITY -- P. B. Macedo

The present report details the progress made so far, and the studies which still need to be completed, towards the preparation of Section 6.1 (Mechanism of Defense Glass Dissolution) in the final report of the leaching mechanism program. Previous periodic reports emphasized specific aspects of the program, and the present report is intended to summarize the general progress in brief, based on the tentative outline submitted with this report.

3.1.1 Leaching Mechanisms at the Constant Environment (High Dilution and/or Rapid Flow) Limit - The Effects of Total Exposure and Time

The principal transient effect in the interaction of a fresh, dry glass surface with water is the formation of a distinct surface layer. Layer formation plays a major role in controlling the initial leaching kinetics and, even more important, the composition and structure of the layer control the resistance of the glass to further attack as shown by Hench, Yastrebova and others. Diffusion-dissolution models of layer build-up, which were originally developed for simple silicate glasses by Douglas, Boksay, Holland, and Doremus were recently extended to complex nuclear waste glasses by Kuhn and by Wicks and Wallace.

The effectiveness of the layer as a protective barrier depends on its structure, porosity and mechanical stability. All of these factors are sensitive functions of the chemical composition and even the thermal history of the glass.

The results of high-dilution tests (IAEA- or ISO-type as well as short-term MCC-1) which were carried out at CUA and at SRL during recent months indicate that in the case of defense borosilicate glasses (SRL-131 and MCC Reference Glass) the surface layer is mechanically unstable and flakes off upon drying, etching and even upon prolonged immersion, because of the development of stresses in the subsurface region. Surface analysis results obtained at CUA, SRL and the ANL indicate the formation of at least two distinct regions: An outer thin dealcalized film and an inner layer where the composition variations

are significant, but dealkalization is less than 20% complete. In addition, CUA and ANL results indicate the formation of fine precipitates both on the surface of the glass and elsewhere in the leach vessel. Complete characterization of the structure and properties of the layer requires using both direct and surface analysis results (e.g., HF etching data) and inferences from leachate analysis.

The results of leach tests carried out at CUA indicate that the dissolution of Si follows an approximately first power law, $C \propto kt$, throughout the entire leaching process monitored in high-dilution tests at 90°C, even including the first day data. Na leaching data show a similar time-dependence from the third day onwards, and only during the first three days it is possible to obtain a reasonable fit with a $C = kt^{1/2}$ assumption. Accordingly, in the case of these particular dependence, 1/2-power kinetics appear to be relevant only for extremely short periods of time, and even during these periods it is quite possible (as shown by Claassen, Grandstaff and others) that this behavior does not imply the process is diffusion-controlled. Moreover, it is observed that boron, which is a soluble but not very mobile species, leaches out as rapidly as Na and with identical kinetic behavior. Accordingly, the extent of the role of diffusion and the relevance of diffusion-based models in interpreting the over-all kinetics of defense waste glass dissolution are still far from certain and require further studies.

3.1.2 Leaching as a Function of Contact Time Between the Glass and the Medium - The Effects of Flow

A major effort is under way at CUA to characterize the effect of flow rate on the rate of material loss from waste-forms using a pulsed-flow technique which permits investigating behavior at flow rates as low as 0.2 m/yr. Continuous-flow studies at the high flow rate region (50-4000 m/yr) have also been carried out at PNL and at the University of Florida. Most of the work prior to July 1982 was carried out on SRL TDS-131 glass and the major conclusions were reported earlier. Briefly, the silica dissolution rates increase due to rising pH when leachant exchange begins to slow down in the rapid flow region. However, over the flow range of interest (1-70 m/yr) the major effect observed is a decrease in dissolution rates with decreasing leachant exchange rates due to

saturation. On the other hand, the leach rates of Na, Li and B show little decrease with decreasing flow rate and these elements continue to leach out preferentially even in the saturation region of silica and alumina, causing a continued increase in pH and in solubility limits. In contrast, Ca, Sr, and, to a lesser extent, Cs undergo hydrozide/silicate precipitation or high-pH-promoted reabsorption and their leach rates drop sharply at slow flow rates. At slow flow rates, in the case of SRL TDS-131 glass as well as of other waste-form materials, the saturation levels, which determine the rate of material loss, are considerably lower when both silica and alumina are present than when one of these oxides is present alone. In all cases, the Al-Si concentration products, as well as the ratios between the concentrations of these two elements indicate that the solubilities of these two species are inter-related through the formation on the surface of the glass of a combined aluminosilicate alteration product.

Recently the flow test program at CUA has been extended in two directions: The use of MCC Reference Glass as an alternative to SRL TDS-131 glass and the use of environments which bear more resemblance to repository media than deionized water. Some preliminary results are shown in Table 3.1. It can be seen that MCC Reference Glass qualitatively displays a behavior similar to that of SRL TDS-165. Quantitatively both the extent of the pH rise and the leach rates are somewhat smaller in the case of MCC Reference Glass.

The second set of data included in Table 3.1 shows that when simulated ground-water, with a composition modeled after water from the Grande Ronde basalt formation, is substituted for deionized water the leach rates of several glass components, such as Si, decrease by as much as a factor of 7; on the other hand, the leach rates of other species, such as Fe, U and Sr do not decrease and even show an increase in the ground-water leachant. The addition of stainless steel, a representative canister material, to the system, using a glass:steel area ratio aimed at simulating repository conditions does not induce a significant decrease in the leach rates observed in the ground water.

Further experiments required to advance the study of the flow and dilution conditions on leach rates include long-term experiments at equivalent flow rates below 0.5 m/yr, establishment of a complete data base for MCC Reference

TABLE 3.1. Effects of Glass and Leachant Composition on the Results of Flow Tests at 70°C: Normalized Leach Rates $\times 10^2$ ($\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) (regular block samples)

Glass Leachant	SRL TDS-135		MCC Reference Glass			
	DI Water	DI Water	DI Water	DI Water	Ground-Water	Ground-Water
Presence of Stainless Steel Flow Rate, m/yr	1.99	10.7	2.42	10.8	12.2	16.2
pH	10.7	10.0	9.70	9.65	9.57	9.55
Si	7.1	10.5	1.85	6.17	0.80	0.93
B	23.2	17.5	2.53	8.78	1.64	1.92
Na	18.7	21.9	2.50	7.84		
Cs	6.9	12.5	3.59	10.83	2.44	2.71
Li	21.4	16.4	2.50	9.37	2.37	2.63
Ca	<0.2	<0.1	0.24	2.35		
Sr	<0.1	0.1	0.13	0.35	1.39	1.68
Al	0.3	6.7	1.45	5.55	0.65	0.80
Fe	0.01	0.06	0.10	0.02	0.10	0.14
Cr				0.36	<0.01	<0.01
Mg				<0.01	<0.01	0.12
U			0.67	0.92	1.05	1.28

Glass, and surface analysis studies (using chemical etching and physical methods) on glass samples which have been leached in pulsed flow experiments until the leachate composition and, presumably, the surface structure have reached steady state. In particular, it is intended to carry out leach tests using samples partially covered with a protective gold coating in order to determine the extent of surface regression relative to the over-all extent of the leached, altered zone.

3.1.3 Effects of the Surface-to-Volume Ratio

Experiments carried out at CUA using the pulsed flow system show that as long as sufficient precautions are taken to exclude extraneous effects, such as gradual contamination of the leachate with species originating in the test environment, larger surface-to-volume ratios are equivalent to longer contact

times. Accordingly, the S/A ratio can be used as a scaling parameter in establishing a normalized contact time scale. These conclusions have been corroborated by findings of other groups. Present findings also indicate that powder tests, based on specific powder areas deduced from comparative leach tests on powders and regular block samples under high dilution conditions, give the same results within experimental error as tests on regular blocks even in the slow flow region. In all cases, observed specific power areas are higher by about 25% than those calculated assuming spherical geometry due to the presence of surface irregularities. These studies will be extended to MCC Reference Glass.

3.1.4 Effects on Initial Leachant Composition

The leachant composition can have major effects on material loss rates both under high dilution or rapid flow conditions and in the slow-flow, saturation-controlled region. For instance, the results shown in Table 3.1 demonstrate that the loss rates of Si and Al are much smaller in a ground-water leachant, which is already close to saturation with respect to these elements, than in deionized water which has reached the same pH level due to selective alkali leaching. This approach to saturation with respect to the major glass elements also induces a smaller decrease in the leach rates of the soluble components (alkalis, B). On the other hand, the leach rates of polyvalent ions (Fe, U) are higher in ground-water, due to the presence of complexing species (CO_3^{2-} , F^- , Cl^-). Even stronger effects may occur in irradiated ground-water where species such as oxalate may be present.

The solubilities of silica and alumina are primarily determined by the highest pH reached in the medium. In the case of SRL TDS-131 glass, where the pH at low flow rates can reach values of at least 12, the pH of the ground-water is not important. On the other hand, in the case of less alkaline waste-forms (e.g., MCC Reference Glass under moderately high flow rate conditions) the rate of corrosion will be significantly higher in highly basic ground-water media (Grande Ronde basaltic water, pH $\approx$ 10) than in near-neutral ground-water.

Further tests on corrosion rates of MCC Reference Glass in synthetic ground-water and in controlled-pH media are under way at CUA.

3.1.5 Temperature Effects

Temperature effects on material loss rates strongly depend on flow rates. Under high-dilution conditions, studies at CUA and PNL are indicative of large effects, consistent with activation energies of 70-100 kJ. Leach tests in the slow-flow saturation region exhibit little temperature dependence, in agreement with findings by White and Tole and others on the solubilities of aluminosilicate species. Most of the leach tests carried out so far at CUA were performed at 70°C; additional tests on MCC Reference Glass at 90°C are planned.

3.1.6 Effect of Glass Composition

Although most of the new tests planned at CUA will be carried on MCC Reference Glass, long-term studies of SRL TDS-131 glass are still in progress. Comparative studies on these two glasses and on other waste-form materials as well as on simple glasses and on aluminosilicate minerals by the various participants in the Leaching Mechanism Program will be utilized in order to reach better understanding of surface layer formation and of the nature of the solubility-controlling species.

3.1.7 Modeling

Proposed mechanisms for the interaction between nuclear waste glasses and water, including diffusion-corrosion models developed by Wicks and Wallace, Kuhn, Lutze and others and alteration-solubility models (Lasaga) will be examined in terms of their relevance at various flow rates and their applicability to experimental data. Every effort will be made to assist in furnishing a data-base and checking calculated predictions of the LLL predictive numerical model under current development (PROTOCOL).

3.1.8 Natural Analogs

The CUA leach studies program is based to a large extent on the assumption that long-term durability predictions, even when supported by well-developed mechanisms consistent with laboratory data, are much more firm when checked against geochemical data on systems in which the interaction between solids and aqueous media has taken place over periods comparable to the service time required of a geologic repository. Leach studies carried out at CUA have already shown that a simple congruent dissolution model based on high-dilution

test data agrees well with observations on the extent of corrosion of 700,000-year old tektite glasses exposed to surface water. The conclusions concerning the inter-relationship between the solubilities of Si and Al which apply to nuclear waste glasses and ceramics have also been shown valid for basalt, granite and nepheline. The composition of subsurface water aged about 20,000 years originating in basalt and granite formations has been successfully correlated with mechanisms based on short-term observations, including aluminosilicate saturation, continued alkali leaching, resorption and ion-exchange of cations and preferential dissolution of inclusion phases. These studies greatly increase the confidence in the validity of proposed models in accounting for long-term interactions and show that, in the absence of extreme conditions of pH and temperature, glasses can be expected to possess the long-term durability required for safe nuclear waste fixation and immobilization.

3.2 UNIVERSITY OF FLORIDA -- L. L. Hench, D. E. Clark, and C. Maurer

3.2.1 Introduction

The objectives of this document are as follows:

1. Compare the range of chemical characteristics of various candidate repository materials.
2. Suggest alternative chemical solutions to be used for comparative studies on nuclear waste glass-rock interactions.

3.2.2 Approach

Twenty-one references were examined to determine the range of values of ground water compositions and other chemical variables relevant to repository-glass interactions. Discussions were also held with SRL personnel concerned with glass-rock interactions. Table 3.2 summarizes the types of repository locations considered and the various conditions considered relevant to potential glass-rock interaction tests.

TABLE 3.2. Baseline Repository Conditions

- Types of Repositories Considered and Their Locations
 - Salt: Carlsbad, New Mexico; Kansas (Permian Basin); Michigan (Salina Basin); Mississippi; Utah (Paradox Basin)
 - Basalt: Wanapum, Washington, Grande Ronde, Washington (both in Columbia Plateau)
 - Tuff: Nevada Test Site
 - Granite: Stripa, Sweden
- Repository Conditions Considered Relevant to Waste Form Corrosion
 - Water Composition (mg/L): Natural and from Deep Pore Holes
 - pH
 - E_h (volts)
 - Temperature ($^{\circ}\text{C}$)
 - Water Content of Rock (%)
 - Water Flow Rate (L/yr)
 - Thermal Conductivity ($K = \text{watts/m/}^{\circ}\text{C}$)

3.2.3 Results

Salt

Table 3.3 presents the range of values reported for potential salt-type repositories. Brine inclusions in salt and bittern brines are compared. Six alternative locations are included. Wide ranges of alkali and chlorine contents are observed for both brine inclusions and the bittern brines. The ranges of the various chemical constituents are summarized in Table 3.7. Little data is available for many chemical species. Flow rates reported range from 0.016 L/yr to 1 L/yr with the exception of the Avery Salt Dome, LA which is high with 15.7 L/yr.

TABLE 3.3. Salt Repositories

Species, mg/L	WIPP A, N.M. (2)	WIPP B, N.M. (2)	Kansas (2)	Michigan (3)	Mississippi (3)	N.M. (3)	Utah (3)
Na	42,000	150,000	43,900	28,000	79,000	44,000	18,800
K	30,000	10	1,900	9,000	7,800	30,250	5,990
Li	20	0	--	--	--	--	--
Rb	20	1	--	--	--	--	--
Cs	1	1	--	--	--	--	--
Mg	32,000	10	51,500	16,000	3,920	62,600	39,200
Ca	600	900	1,200	80,000	34,000	500	52,700
Sr	5	15	--	2,000	2,520	--	2,000
Ba	--	--	--	--	--	--	--
Al	--	--	--	--	--	--	--
Fe	2	2	--	--	--	--	--
Cl	190,000	175,000	223,000	250,000	198,700	251,500	241,000
Br	400	400	3,200	--	2,040	530	3,080
I	--	--	--	--	--	--	--
F	--	--	--	--	--	--	--
SO ₄ ⁻²	3,500	3,500	7,500	--	176	3,300	4
CO ₃ ⁻²	--	--	--	--	--	--	--
HCO ₃ ⁻	700	10	--	--	--	--	--
HNO ₃ ⁻	0	0	--	--	--	--	--
B ₃ ⁻³	1,200	10	--	--	--	--	--
PO ₄ ⁻³	--	--	--	--	--	--	--
H ₃ SiO ₄ ⁻	--	--	--	--	--	--	--
SiO ₂	--	--	--	--	--	--	--
pH	6.5	6.5	--	--	--	--	--
E _h	--	--	--	--	--	--	--

Temp (°C)

Water Content (%) - Range is 0.016 + 1.16 (Ref. 4,5,6,7)

Flow Rate (L/yr) - Range is 0.016 + 1 (Ref 1,6,8,9)

Thermal Conductivity (watts/m/°C) - Range is 2.59 + 4.20 (Ref. 2)

*Flow Rate (50°C) - 15.7 L/yr for Avery Salt Dome, LA (Ref. 9)

--Not reported

Basalt

The chemical species from two different layers of Washington basalt are compared in Table 3.4. The variations are much less than present in salt but there is still considerable difference in Na, Ca, Cl^- , SO_4^{-2} , and HCO_3^- content. A wide range in pH from 7.4 to 10.1 is also reported.

T. E. Jones of Rockwell International has developed a synthetic Grande Ronde ground water recipe which is based upon water samples collected just below the Umtanum Basalt flow (3242-3529 ft). The recipe establishes two stable concentrated stock solutions from which 40 L of synthetic ground water can be prepared from 1 L of each stock solution. The advantage of this approach is that it permits preparation of the synthetic ground waters as fresh solutions which enables the high pH of the basalt to be simulated in laboratory experiments. Because of the potential importance of this method to the Basic Leach Mechanisms Program, a copy of Jones' report is included as Appendix A.

Tuff

Relatively little data was discovered for tuff; Table 3.5 is a summary. Table 3.7 shows that the ground water chemistry of tuff is intermediate within the ranges reported for basalt and granite. The lower pH and variable flow, depending upon saturation or unsaturation, are major differences from the other silicate based alternatives.

Granite

STRIPA granite in Sweden has been well characterized with respect to hydrology and ground water chemistry. The ground water chemistry from deep STRIPA bore holes is presented in Table 3.6 for several locations. As summarized in Table 3.7 there is a wide range in Na, Ca, Cl, SO_4^{-2} , and HCO_3^{-2} content in the granitic ground waters. However the range of pH and flow rates is small.

3.2.4 Options

Tables 3.8, 3.9 and 3.10 present three options for selection of test conditions for testing of nuclear waste glass-rock interactions. The logic of each is the following.

TABLE 3.4. Basalt Repositories

Species, mg/L	Wanapum Layer, Washington(2)	Grande Ronde Layer, Washington(2,15,16)				
		182	242	250	250	-
Na	17-80	182	242	250	250	-
K	5.9-19	3.3	3.2	1.9	1.9	-
Li	-	-	-	-	-	-
Rb	-	-	-	-	-	-
Cs	-	-	-	-	-	-
Mg	0.2-25	0.0	2.0	0.04	0.04	-
Ca	1.6-24	0.8	1.3	1.3	1.3	-
Sr	-	-	-	-	-	-
Ba	-	-	-	-	-	-
Al	-	-	-	-	-	-
Fe	-	-	-	-	-	-
Cl	3.8-15	52	70	34	148	130
Br	-	-	-	-	-	-
I	-	-	-	-	-	-
F	3.8-15	21	-	37	37	29
SO ₄ ⁻²	0.2-32	98	148	148	108	-
CO ₃ ⁻²	-	-	-	-	21	-
HCO ₃ ⁻	141-216	66	88	43	25	-
NO ₃ ⁻	-	-	-	-	-	-
BO ₃ ⁻³	-	-	-	-	-	-
PO ₄ ⁻³	-	-	-	-	-	-
H ₃ SiO ₄ ⁻	-	-	-	-	145	-
SiO ₂	41-63	116	115	121	-	-
pH	-	10.1	10.1	10.1	7.4-9.9	10.1
E _h (volts)	-	-	-	-	-0.5	-0.4k
Temp. (°C) - 60-70°C (Umtanum Layer)						
Water Content (%) -						
Flow Rate (L/yr) -						
Thermal Conductivity (Watts/m/°C) - Range is 1.40-4.18 (Ref. 2)						
- Not Reported						

TABLE 3.5. Tuff Repositories

Species, mg/L	Nevada Test Site
Na	51
K	4.9
Li	0.05
Rb	-
Cs	-
Mg	2.1
Ca	14
Sr	0.05
Ba	0.003
Al	0.03
Fe	0.04
Cl	7.5
Br	-
I	-
F	2.2
SO ₄ ⁻²	22
CO ₃ ⁻²	0.0
HCO ₃ ⁻	120
HNO ₃ ⁻	5.6
BO ₃ ⁻³	-
PO ₄ ⁻³	0.12
H ₃ SiO ₄	-
SiO ₂	61
pH	7.1
E _h (volts)	Mildly Reducing
Temp. (°C)	35°C (Ref. 19)
Water Content	2-10 (welded; volcanic ash that has been heated to 600°C) 10-25 (nonwelded: volcanic ash)
Flow Rate (L/yr)	1015 (at 220°C), Ref. 13
Thermal Conductivity (Watts/m/°C)	1.2-1.9, welded (Ref. 2) 0.4-0.8, nonwelded (Ref. 2)

TABLE 3.6. Granite Repositories

Species	STRIPA, Sweden				
Na	43-121	40.6-51.5	64.0	176-177	125
K	0.2-5.4	0.13-0.2	0.2	0.5-0.55	0.4
Li	-	-	-	-	-
Rb	-	-	-	-	-
Cs	-	-	-	-	-
Mg	0.5	0.25-0.27	0.29	0.18-0.2	0.5
Ca	10-59	15.4-18.0	19.6	109-110	59
Sr	-	-	-	-	-
Ba	-	-	-	-	0
Al	-	-	-	-	0
Fe	0.29-0.24	-	-	-	0.02
Cl	52-283	35.4-56.0	90.5	439-449	283
Br	-	-	-	-	-
I	-	-	-	-	-
F	-	-	-	-	-
SO ₄ ⁻²	2.7-19	1.3-3.1	5.4	42.9-55.4	19
CO ₃ ⁻²	-	-	-	-	3
HCO ₃ ⁻	15.4-78.7	68.4-97.4	50.3	8.3-9.4	13
NO ₃ ⁻	-	-	-	-	-
BO ₃ ⁻³	-	-	-	-	-
PO ₄ ⁻³	-	-	-	-	-
H ₃ SiO ₄ ⁻	-	-	-	-	-
SiO ₂	11.0-12.89	11.1-12.1	11.3	10.2-10.3	11
pH	8.85-9.75	8.55-9.10	9.16	9.44-9.6	9.0
E _h (volts)	-	-	-	+0.17	
Temp. (°C)	-	11.7-14.5	8.2	8.0	-
Water Content (%)					
Flow Rate (L/yr) - Range is <0.52 + 3.54 (Ref. 13,14)					
Thermal Conductivity (Watts/m/°C) - 3.69 (Ref. 2)					
Range is 2.34 + 3.29 (Nevada) (Ref. 2)					

- Not Reported

TABLE 3.7. Range of Values for Various Types of Repositories

Brine	Silicate	Species, mg/L	Brine Inclusions	Bittern Brine	Basalt	Tuff	Granite
35,400	49	Na	42,000-150,000	18,800-79,000	17-250	51±	40.6-177
25,300	--	K	10-30,000	5,900-30,250	1.9-19	4.9	0.13-5.4
--	--	Li	0-20	--	--	0.05	--
--	--	Rb	1-20	--	--	--	--
--	--	Cs	1	--	--	--	--
39,600	--	Mg	10-51,500	3,920-62,600	0.15	2.1	0.18-0.5
--	--	Ca	600-1,200	800-80,000	0.8-24	14	10-110
--	--	Sr	5-15	1,520-2,000	--	0.05	--
--	--	Ba	--	--	--	0.003	0
--	--	Al	--	--	--	0.03	0
--	--	Fe	2	--	--	0.04	0.02-0.24
165,000	--	Cl	175,000-223,000	198,700-251,500	3.8-148	7.5	35.4-449
--	--	Br	400-3,200	530-3,080	--	--	--
--	--	I	10	--	--	--	--
--	--	F	--	--	3.8-37	2.2	3.7
--	--	SO ₄ ⁻²	3,500-7,500	4-3,300	0.2-148	22	1.3-55.4
--	--	CO ₃ ⁻²	--	--	21	0.0	3
--	130	HCO ₃ ⁻	10-700	--	25-216	120	8.3-97.4
--	--	NO ₃ ⁻	0	--	--	5.6	--
--	--	BO ₃ ⁻³	10-1,200	--	--	--	--
--	--	PO ₄ ⁻³	--	--	--	0.12	0
--	16.9	H ₃ SiO ₄ ⁻	--	--	145	--	--
--	16.9	SiO ₂	--	--	41-121	61	10.2-12.8
6.5	7.5	pH	6.5	--	9.4-10.1	7.1	8.85-9.6
--	--	E _h (volts)	--	--	-0.4-0.5	Mildly Reducing	+0.17
x	x	Temp (°C)	--	--	60-70	35	8-14.5
x	x	Water Content (%)	0-1.6	--	--	2.25	--
x	x	Flow Rate (L/yr)	0.016-1	--	--	1,051	<0.52-314
x	x	Thermal Conductivity (watts/m/°C)	2.59-4.20	--	1.4-4.18	0.4-1.9	2.34-3.29

-- Not reported

* Calculated based on Reference 20

Calculated as H₂SiO₃·H₂O

x Not relevant

TABLE 3.8. Option #1: Upper and Lower Limits - Recommended Solutions for Testing Glass-Rock Interactions

Species, mg/L	Saline A	Saline B	Silicate A	Silicate B
Na	15,000	150,000	15	250
K	10	30,000	0.1	20
Li	0	20	0	0.1
Rb	0	20	0	0
Cs	0	1	0	0
Mg	10	60,000	0	15
Ca	600	80,000	0.8	100
Sr	5	2,000	0	0.5
Ba	0	0	0	0
Al	0	0	0	0.03
Fe	0	2	0	0.2
Cl	175,000	250,000	3.8	450
Br	400	3,200	0	0
I	0	10	0	0
F	0	0	2.2	37
SO ₄ ⁻²	4	7,500	0.2	150
CO ₃ ⁻²	0	0	0	21
HCO ₃ ⁻	10	700	8	216
NO ₃ ⁻	0	0	0	5.6
BO ₃ ⁻³	10	1,200	0	0
PO ₄ ⁻³	0	0	0	.12
H ₃ SiO ₄ ⁻	0	0	0	145
SiO ₂	0	0	10	121
pH	6.5	6.5	7.5	9.5
Test Conditions				
Temp.	90°C	90°C	90°C	90°C
SA/V	0.1 cm ⁻¹	0.1 cm ⁻¹	0.1 cm ⁻¹	0.1 cm ⁻¹
Flow	Static vs 10 ML/hr	Static vs 10 ML/hr	Static vs 10 ML/hr	Static vs 10 ML/hr
Time:	28 days 90 days	28 days 90 days	28 days 90 days	28 days 90 days

**TABLE 3.9. Option #2: Average Rock Type - Recommended Solutions
For Testing Glass-Rock Interactions**

Species, mg/L	Inclusions	Bittern Brine	Basalt	Tuff	Granite
Na	95,000	58,000	133	51	109
K	15,000	18,000	10	5	3
Li	10	-	-	0.05	-
Rb	10	-	-	-	-
Cs	1	-	-	-	-
Mg	25,000	33,000	7	2	0.3
Ca	900	40,000	12	14	60
Sr	10	1,800	-	.05	-
Ba	-	-	-	-	-
Al	-	-	-	.03	-
Fe	2	-	-	.04	.12
Cl	200,000	225,000	75	7.5	242
Br	1,800	1,800	-	-	-
I	10	-	-	-	-
F	-	-	20	2.2	3.7
SO ₄ ⁻²	5,500	1,600	75	22	28
CO ₃ ⁻²	-	-	21	-	3
HCO ₃ ⁻	350	-	120	120	53
NO ₃ ⁻	-	-	-	5.6	-
BO ₃ ⁻³	600	-	-	-	-
PO ₄ ⁻³	-	-	-	0.12	-
H ₃ SiO ₄ ⁻	-	-	145	-	-
SiO ₂	-	-	80	61	11.5
pH	6.5	6.5	9.7	7.1	9.0
Test Conditions					
Temp.	90°C	90°C	90°C	90°C	90°C
SA/V	0.1 cm ⁻¹	0.1 cm ⁻¹	0.1 cm ⁻¹	0.1 cm ⁻¹	0.1 cm ⁻¹
Flow	Static vs 10 ML/hr	Static vs 10 ML/hr	Static	Static	Static
Time	28 days 90 days	28 days 90 days	28 days 90 days	28 days 90 days	28 days 90 days

TABLE 3.10. Option #3: Most Relevant Solutions for Testing
Glass-Rock Interactions

Saline	
Solution A:	Dissolved salt representative of being inclusions from potential repository site
B:	Dissolved salt representative of bittern brine from potential repository site
Silicate	Solution A: Basalt simulated groundwater based upon Jones report

Option #1 is to determine the range of effects that may occur as a result of glass-rock-water interactions. Data is already available for many glass compositions exposed to static or flow conditions in the presence of D.I. water, MCC brine solutions or MCC silicate water solutions. Table 3.7 shows that the MCC brine solution does not approximate the average of the various saline repository solutions reported. The MCC brine solution is high in Mg and low in Cl and the numerous other constituents present in real ground waters are missing. The sensitivity of glass leach rate and formation of reaction layers to the range of species present in repository saline solutions could be determined by testing in upper and lower limits of the measured brine inclusions and bittern brines. Table 3.8 presents two saline test solutions that represent the extremes that could be encountered. Table 3.7 also shows that the MCC silicate water is a poor approximation of silicate ground waters. Thus, a similar pair of silicate solutions representing the upper and lower limits of chemical concentrations encountered in basalt, tuff, and granite are also given in Table 3.8.

The hypothesis of this option is that a comparison of leach mechanism and leach rates in upper and lower limit saline and silicate solutions with MCC DI water, brine, and silicate waters should be sufficient to establish whether important synergistic interactions will occur. If the mechanisms of the glass-water interfacial reactions remain the same and leach rates alter by only 2-3X as a function of the extreme ground water chemistry ranges studied, then there is little need to explore further details. However, if major changes in

mechanisms or leach rates are detected then the important chemical species responsible for the differences can be examined using a statistical based comparison experiment.

Option #2 is to conduct a series of glass-rock-solution tests using solutions that represent the average chemistry for each of the five major rock types: salt with brine inclusions, bittern brines, basalt, tuff, and granite. A rationale for this option is that baseline data is essential if the kinetics of glass-repository interactions are to be modeled. Data from tests of the average or mean of the alternative repositories is more relevant to such models than are the extremes of Option #1.

Option #3 is to use site specific solutions for the tests, similar to the approach being taken at SRL. In such an approach representative samples from a saline based site would need to be obtained. The silicate based solution could be restricted to the basalt ground water formula proposed by Jones.

3.2.5 Recommendations

Our recommendation is to adopt Option #1 with the Jones basalt simulated ground water, Silicate Solution A of Option #3, to replace Silicate A of Option #1. The rationale of this recommendation is that the lower limit Silicate A solution of Option #1 is close enough to the MCC silicate water and therefore data is available for the lower limit. There is little effect observed. Using the Jones simulated basalt ground water will couple our studies more closely with a leading candidate site and other tests being conducted. A comparison of results from that solution to the upper limit Silicate B solution should be sufficient to examine the effect of ground water chemistry on solubility limited leaching, a principal objective of the program.

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REFERENCE MATERIAL CHEMISTRY --
SYNTHETIC GROUNDWATER FORMULATION

T. E. Jones

BWIP Material Testing Group
Waste Package Department
Basalt Waste Isolation Project

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Rockwell Hanford Operations
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ABSTRACT

A recipe has been developed for the preparation of a synthetic Grande Ronde Basalt groundwater. The recipe is based on water samples collected from the test horizon just below the Umtanum flow (3,242 to 3,529 ft). The recipe presented establishes two stable concentrated stock solutions. Forty liters of synthetic groundwater can be prepared from 1 L of each stock solution. Limitations of the synthetic groundwater recipe are discussed. It was perceived that water from this test horizon would be the most likely to migrate into either of the two candidate repository horizons within the Grande Ronde Basalt (i.e., the Umtanum and middle Sentinel Bluffs flows).

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REFERENCE MATERIAL CHEMISTRY--SYNTHETIC GROUNDWATER
FORMATION--T. E. Jones^(a)

INTRODUCTION

The basalt formations underlying the Hanford Site near Richland, Washington are being evaluated as a possible repository site for the long-term storage of nuclear wastes. As part of this evaluation, extensive laboratory tests will be conducted. These tests will include the interaction of groundwater with basalt rock, waste forms, and engineered barriers. A broad spectrum of leach, sorption, hydrothermal, corrosion, and radionuclide transport experiments is planned.

To evaluate the results of these tests, it is imperative that the experiments be carried out using a common groundwater of known stable constituents. It is not practical to use natural groundwater for these tests because of the instability of the water system and the logistical problems associated with collecting and shipping large volumes of groundwater over long distances. Thus, it was necessary to develop a reference synthetic groundwater recipe that could be transmitted to laboratories involved in the testing program. This synthetic groundwater can then be prepared in the participating facility as needed for the studies that are to be performed.

The reference synthetic groundwater recipe was based on water samples from the Grande Ronde Basin, since that formation appeared to be the most likely location of a repository system. There are considerable variations (both vertically and horizontally) in the chemistry of water samples collected from test horizons within the Grande Ronde Basalt. However, the

(a) RHO-BW-ST-37P, April 1982, reprinted with permission of the author.

completed analyses indicate that the major chemical characteristics of groundwater throughout the Grande Ronde Basalt (e.g., high pH, high dissolved solids, and unusually high concentrations of fluoride) are distinct and consistent. A water sample from just below the Umtanum flow (3,242 to 3,529 ft) was chosen as the model for the reference synthetic Grande Ronde groundwater.

DISCUSSION

A number of boreholes penetrate the Grande Ronde Basalt that underlies the Hanford Site. The concentration of major chemical constituents observed in water samples collected from this formation vary over a fairly wide range. Sodium, chloride, and sulfate ion concentrations fluctuate by as much as 100 mg/L and pH measurements vary by more than one pH unit. In developing the reference synthetic Grande Ronde groundwater recipe, data from a specific test horizon were used as the model. A specific test horizon was chosen, rather than a composite or average value, so that a comparison of behavior could be made between synthetic and natural groundwater in certain selected experiments. Water samples were obtained from an artesian well, borehole DC-6, located near the old Hanford townsite.

The synthetic Grande Ronde groundwater recipe involves the preparation of two concentrated stock solutions: one containing the basic salts and the other the acidic components. One liter of each stock solution is sufficient material for the preparation of 40 L of synthetic groundwater. The concentrated stock solutions are stable. However, exposure of the

basic solution to air must be kept to a minimum to avoid absorption of atmospheric carbon dioxide. A comparison of actual and synthetic groundwater composition is given in Table 1. Table 2 is a listing of the pH of synthetic and natural groundwaters as a function of temperature over the range of 25° to 65°C.

Certain aspects of the natural groundwater cannot be easily reproduced in the laboratory. These include solution oxidation-reduction potential or E_h , trace metal ions, dissolved gases, and trace amounts of organic species. No attempt was made to reproduce dissolved gas or trace metal ion compositions. Although it is believed that low levels of naturally occurring organic material can influence the mobilization and transport behavior of radionuclides (Silviera, 1981), little data are available on the amounts or identity of organic species that may be present in water samples from the Grande Ronde Basalt.

The oxidation-reduction potential measured in water samples from test horizons within the Grande Ronde Basalt generally fall between 0.0 and -0.2 V (versus the standard hydrogen electrode). However, the interpretation of oxidation-reduction potential measurements made in groundwater samples is the subject of much discussion (Garrels and Christ, 1965; Whitfield, 1974). The chemical species present in groundwater that give rise to the potential measured at a platinum electrode are usually not known. In addition, the concentration of these unknown species is so low that it is questionable whether an electrochemically valid measurement can be made. Even so, solution oxidation-reduction potential is an important variable in any leach, sorption, or radionuclide transport experiment because the oxidation-reduction potential will ultimately control the oxidation state

TABLE 1. Comparison of Actual and Synthetic Grande Ronde Groundwater Compositions at 25°C.

Chemical species	Actual composition		Synthetic composition	
	mg/L	meq/L	mg/L	meq/L
Na	363	15.8	358	15.6
K	3.43	8.87×10^{-2}	3.43	8.78×10^{-2}
Ca	2.76	0.138	2.78	0.138
Mg	0.032	3.1×10^{-4}	0.032	3.1×10^{-4}
Total cations		16.00		
F	33.4	1.76	33.4	1.76
Cl	310	8.75	312	8.81
SO ₄	173	3.604	173	3.61
Alkalinity* (as HCO ₃ ⁻)		1.82		
Total anions		16.06		

*Actual = 9.03×10^{-4} mol/L inorganic carbon; 76.1 mg/L silica.
 Synthetic = 8.96×10^{-4} mol/L inorganic carbon; 76.2 mg/L silica.

TABLE 2. pH as a Function of Temperature for Synthetic and Natural Grande Ronde Groundwater.

Temperature	Natural (DC-6)	Synthetic (Grande Ronde)
Room temperature	9.75	9.77
25°C	9.71	9.74
45°C	9.47	9.49
65°C	9.19	9.19

of the radionuclide. Some workers have added reducing agents, such as hydrazine, to simulate reducing conditions found in the groundwaters (Salter et al., 1981). Other workers have attempted to control solution oxidation-reduction potential by controlled potential electrolysis using a commercially available potentiostat (Giblin et al., 1981). Recent experiments in the Basalt Materials Research Laboratory suggest basalt/water interactions at high pressure and temperature may control solution oxidation-reduction potential.

PROCEDURES FOR PREPARATION OF GRANDE RONDE GROUNDWATER

Two concentrated stock solutions are prepared. Stock solution A contains the sodium salts of carbonate, silicate, sulfate, fluoride, and hydroxide. Stock solution B contains hydrochloric acid and the chloride salts of potassium, calcium, and magnesium. Recipes for the preparation of 1 L of each stock solution are given in Tables 3 and 4. General procedures for the reagents are given in the appendix. Synthetic groundwater samples and stock solutions should be stored in tightly capped polyethylene or Teflon containers.

To prepare 1 L of synthetic Grande Ronde groundwater, 25-mL aliquots of stock solutions A and B are added to 900 mL of deionized water. Minor pH adjustments are made with either 0.10M HCl or 0.10M NaOH to bring the final pH to 9.75 at room temperature. After the pH adjustment has been made, the solution is diluted to exactly 1 L. This procedure can be scaled up to any volume needed.

TABLE 3. Reagents Required for the Preparation of Stock Solution A.

Chemical species	g
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	14.4
Na_2CO_3	3.80
NaF	2.95
Na_2SO_4	10.2
NaOH (50 wt%)	18.8

Salts are dissolved in 750 mL of deionized water and then diluted to exactly 1 L. Partially filled bottles of this solution should be stored in an argon or nitrogen envelope.

TABLE 4. Reagents Required for the Preparation of Stock Solution B.

Chemical species	Amount and unit of measure
KCl	0.262 g
CaCl_2	2.75 mmol (i.e., 27.5 mL of 0.100M Ca^{+2})
MgCl_2	5.26×10^{-2} mmol (i.e., 10.5 mL of 5.00×10^{-3} M Mg^{+2})
HCl	3.43×10^2 mmol (i.e., 171.6 mL of 2.00M HCl)

Specified portions of each stock solution and the salt are added to 500 mL of deionized water then diluted to exactly 1 L.

QUALITY CONTROL

All solutions should be stored in nonglass containers, such as polyethylene or Teflon. A sample of the synthetic water should be submitted for chemical analysis. The analyzed concentration for each component should be within 5% of the specified concentration. The pH of the synthetic groundwater should be 9.75 ± 0.10 pH unit.

The concentrated stock solutions are relatively stable. These solutions are tentatively assigned a 1-yr shelf life. The synthetic groundwater (diluted mixture of stock solutions) is much less stable. It should be stored in tightly sealed, completely filled, nonglass vessels. The synthetic groundwater must be protected from atmospheric carbon dioxide. The shelf life should be limited to 2 wk. (The natural Grande Ronde groundwaters have been observed to decrease about 0.1 pH unit per month, even though they are stored in completely filled, tightly sealed polyethylene bottles.)

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APPENDIX
REAGENTS REQUIRED

- Water - Freshly deionized or distilled water should be used as the solvent. If exposed to the atmosphere, it should be boiled or purged with nitrogen to remove dissolved carbon dioxide.
- Na_2CO_3 - Commercially available, primary standard-grade sodium carbonate should be dried at 120°C for 2 hr and stored in a desiccator.
- $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ - Reagent-grade sodium silicate should be used. The number of waters of hydration is uncertain. Therefore, the "effective" formula weight of sodium silicate must be determined. This is done by analyzing a solution containing a weighed amount of sodium silicate by either atomic emission, atomic absorption, or wet chemical methods, for total dissolved silica.
- NaOH - 50 wt% solutions of reagent-grade NaOH are commercially available or can be prepared from reagent-grade sodium hydroxide pellets.
- KCl - Reagent-grade potassium chloride should be dried at 120°C for 1 hr and stored in a desiccator.

- Na_2SO_4 - Reagent-grade sodium sulfate should be dried at 80°C for 1 hr and stored in a desiccator.
- NaF - Reagent-grade sodium fluoride should be dried at 80°C for 1 hr and stored in a desiccator.
- HCl - A 2.00M stock solution of hydrochloric acid is prepared by diluting 167 mL of concentrated HCl to 1 L. This solution can be standardized by diluting it from 25.00 mL to 500.00 mL and titrating against sodium carbonate.
- CaCl_2 - Calcium chloride is extremely hygroscopic. For that reason, a 0.10M stock solution is prepared by dissolving 14.7 g of reagent-grade $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in 1 L of water. The Ca^{+2} concentration is determined by either atomic emission, atomic absorption, or wet chemical methods.
- MgCl_2 - Magnesium chloride is extremely hygroscopic. For that reason, a $5 \times 10^{-3}\text{M}$ stock solution is prepared by dissolving 1.02 g of reagent-grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in 1 L of water. The Mg^{+2} concentration is determined by either atomic emission, atomic absorption, or wet chemical methods.

3.3 PENNSYLVANIA STATE UNIVERSITY -- W. B. White, C. G. Pantano,
W. P. Freeborn, D. S. Knight, S. D. Atkinson, J. A. Garland,
T. D. Henderson, Y. Khalil and J. A. Nacklas

3.3.1 Dissolution of Specific Radionuclides

Uranium

Slabs were cut from bars of the MCC reference defense waste glass and polished to give smooth regular surfaces. They are being leached in solvents to investigate the role of both pH and Eh on the extraction of uranium from the glass. Solvents used thus far are:

Deionized water (pH = 5.8)

H₂O₂ (pH = 5.0)

NH₄OH (pH = 11.0)

HCl (pH = 1.0)

Samples are taken after uniform time intervals and analyzed for uranium with the Scintrex Uranium Analyzer, a fluorometric device that will detect uranium down to the ppb level. Some initial results are shown in Figure 3.1. As expected, there is a pronounced pH effect, with the dissolution in highly

FIGURE 3.1. Dissolution of Uranium From MCC Reference Defense Glass Various Solvents

acidic solution some three orders of magnitude higher than dissolution in deionized water. Somewhat surprisingly, the dissolution rate in base is also higher. Hydrogen peroxide was used as a solvent to simulate a highly oxidizing environment, with Eh near the upper bound of the stability of water. There appears to be a small effect of redox potential over this range but it is small and in view of a small pH difference between the DI water and the hydrogen peroxide solution, may be even smaller.

The concentrations in all of the solutions are essentially independent of time which suggests that some steady-state situation has already been reached at the first sampling point. Further experiments will address the short time scale. Other solutions are needed to determine the functional form of the pH control. A set of experiments in bubbling hydrogen or other Eh buffer is needed to determine uranium solubility at the lower limit of the water stability field. The effect of bicarbonate complexing should be investigated. The mechanism responsible for the apparent shown in the figure must also be examined.

Technetium

The dissolution of ^{99}Tc from glass waste forms is expected to be strongly influenced by pH and Eh because of the large number of valence states shown by technetium.

The MCC reference defense waste glass does not contain technetium and the first step was to see if technetium could be dissolved in it. Small rods cut from the glass bars were sealed in 5 mm platinum tubes with a small quantity TcO_2 . The platinum tube was then sealed in a 1-cm diameter silica glass tube and the assembly heated to temperatures in the range of 950 to 1100°C. Some care is needed because the platinum tubes leak at temperatures above 1150°C and will rupture at lower temperatures if the technetium concentrations exceed 5 wt%. TcO_2 is volatile at high temperatures and builds up a high vapor pressure. The optimum conditions appear to be 2.5 wt% Tc at 1100°C. The tubes were rotated in the furnace to cause the molten glass to flow. The final result was a glass bar. Chips from the center and edges of the bar all showed uniform technetium concentrations by beta counting so it appears that glass samples suitable for dissolution experiments have been prepared.

3.3.2 Oxidation Potential in Glass Dissolution

Concepts and Definitions

The basic concepts, equations, and diagrams commonly used in Eh studies were reviewed at the May 1982 workshop and appear in workshop report.

Measurement of Eh

From a rather large literature on Eh measurement and control, three methods have been selected for detailed investigation with regard to glass waste form dissolution. These are:

Conventional platinum electrode measurements

Calculation of Eh from variable valence element speciation

Electrical conductivity of palladium electrodes

Conventional Eh measurements have been criticized as being too uncertain and taking too long to reach equilibrium. We are simply applying the method to some of the leach experiments to see how they perform in these specific instances. Back calculation of Eh from known activities is a useful check on instrumental measurements. Iron-containing solutions are being used for most of the experimental work because the necessary thermodynamic quantities are much better known for this system.

The palladium-hydrogen system provides a possible novel approach to Eh measurement, especially under highly reducing conditions. The concept is shown in Figure 3.2. Redox reactions in solution generate a certain hydrogen fugacity. This in turn drives hydrogen into or out of the palladium wire coil and the final hydrogen concentration in the metal is determined by its electrical resistance (Figure 3.3). Two devices have been constructed: a coil of 25 μm wire wound on a teflon mandrel and a palladium film sputtered onto a glass substrate with electrodes at each end. The diffusivity of hydrogen in palladium is known ($2 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$) and the time to reach saturation with a 25 μm cylinder should be on the order of 10 seconds. In the first experiments, the system required some hours to reach steady state. There are also some experimental problems with shorting out the coils in highly conducting (e.g., brine) solutions. More experimentation is needed but so far the technique seems to hold promise.

FIGURE 3.2. Schematic Drawing for an Eh Sensor Based on Palladium-Hydrogen Exchange

FIGURE 3.3. Dependence of the Resistance of Palladium on the Equilibrium Hydrogen Pressure

Experimental Control of Eh

After consideration of a number of possible Eh buffer techniques and considering their possible effects on other aspects of the glass dissolution chemistry, we have returned to a consideration of bubbling hydrogen as a means of achieving low Eh. Solutions of 0.01 M FeCl_3 could be reduced in about 1 week in the presence of a palladium catalyst. The next step will be to monitor the rate of reduction and compare it with calculations from the iron speciation.

3.3.3 Rate Theory for Complex Glasses

A rather large body of experimental results on the dissolution kinetics of silicate crystals have been accumulated. In almost all cases, the kinetics are controlled by surface reactions and not by diffusion through a leached surface layer. A detailed comparison is being made between the dissolution rates for glasses and crystals of similar composition so that a quantitative comparison can be made between diffusion-controlled kinetics, surface-reaction-controlled kinetics, and the kinetics of glass recrystallization. One might expect transfer between these mechanisms depending on temperature and fluid chemistry.

3.3.4 Surface Effects

Zeta Potentials

An automated streaming potential apparatus (Figure 3.4) has been employed to study the zeta potential of Vycor and the MCC reference defense waste glass. The apparatus consists of a glass cell in which crushed glass (-25 +45 mesh) is packed between two permeable platinum electrodes. Deionized water is passed in alternate directions from two different flasks through the crushed glass plug by nitrogen gas pressure. A potential difference between the electrodes created by the movement of charged species in the liquid medium relative to the glass surface is measured by an electrometer and recorded. The streaming potential is used to calculate the zeta potential. The conductivity of the water changes as ions are leached from the glass and this has an influence on the streaming potential that must be accounted for.

A study of Vycor glass was initiated to compare experimental results with literature values. In deionized water, the measured zeta potential was extremely high; unfortunately, no values have been reported in the literature for SiO_2 in DI water so a similar study was begun in a weak electrolyte solution (10^{-3} M NaCl). Observed values decreased by a factor of 100 compared to DI water and compare favorably with reported values. This indicated that the presence of electrolytes in solution may serve to compress the double layer near the particle surfaces and thereby cause the zeta potential to decrease. These results may explain the time-dependent decrease in zeta potential observed for multicomponent silicate glasses in deionized water. In other words, the continuous leaching of electrolytes from the multicomponent glass surfaces brings about a compression of the double layer and a corresponding decrease in the zeta potential. Thus the time dependent changes observed in zeta potential for alkali silicate glasses may be a consequence of the corrosion kinetics and not a controlling factor.

Similar surface studies on the MCC reference defense waste glass were initiated in DI water. These are underway at the present time.

In an effort to determine whether the solution or the glass surface potential has the greatest influence on the corrosion kinetics, the streaming

FIGURE 3.4. Apparatus Used for Zeta Potential Measurements

potential apparatus will be filled with fresh deionized water but not a new sample once the measured potentials and pH reach equilibrium. Any differences observed in the measured zeta potential would indicate the role of solution species while the absence of a zeta potential change would show the role of the leached layer as being most critical. Zeta potentials of the MCC waste glass will be determined as a function of pH and compared with zeta potentials of sample colloidal hydrates of Fe, Al, Zr, Ni, Mn, etc., in an effort to determine which species are accumulating at the surface.

3.3.5 Dissolution of Crystalline Precipitates

Dissolution Kinetics of Spinel NiFe_2O_4 and NiAl_2O_4

Transition metals tend to precipitate from many of the nuclear waste glasses as dispersed spinel structure crystals. NiFe_2O_4 and NiAl_2O_4 were selected as representative compositions. Figure 3.5 shows some kinetics data for NiFe_2O_4 . In acid solutions the spinels dissolve according to a simple linear kinetics with no evidence for saturation or precipitation under the time periods investigated. Indeed, the dissolution at pH = 0 was interrupted by the complete dissolution of the sample! As the pH rises, both an oxidation reaction of ferrous to ferric iron and a precipitation reaction of iron and nickel hydroxides appears. Equilibrium solubilities plunge by 6 to 8 orders of magnitude and the concentrations of elements in solution falls below limits of detection.

When completed, this study will map the range of expected effects of pH and Eh on spinel phase solubility and will distinguish between release rates controlled by kinetics and release rates controlled by equilibrium solubility.

FIGURE 3.5. Some Representative Rate Curves for the Dissolution of NiFe_2O_4 Spinel in the Dissolution of NiFe_2O_2

Dissolution of Technetium from Spinel Structures

Technetium, being a transition metal, is expected to follow the other iron group metals and might be expected to occur in the precipitate phases. Because of the very low limit of detectability of Tc by beta counting techniques, the dissolution of Tc from spinel structures can be followed even under dissolution conditions where the host spinel phase is very soluble. Figure 3.6 shows some preliminary data. Here again, both pH and Eh are expected to have a controlling influence.

FIGURE 3.6. Dissolution of Technetium From Magnesium Titanate Spinel at Various pH and Temperature as Shown

3.4 ROCKWELL SCIENTIFIC SCIENCE CENTER -- A. B. Harker, D. R. Clark, and T. Shaw

Since the Gaithersburg Leach Mechanism workshop, activity at the Science Center has focused upon completing studies on the leaching of polyphase ceramic forms and initiating investigation of surface layer formation in the MCC-boro-silicate glass. The experimental work on the ceramic forms is essentially

complete, with only long-term leach tests still in progress. The results of the 12-month study on ceramic leach mechanisms are summarized in slides 1 through 8.

Slide 1: The short-term (<3-day) static and flowing leach tests in deionized water matches pure phase nepheline dissolution behavior. However, after 3 days the solution levels drop well below that predicted by simple nepheline dissolution, indicating that saturation and precipitation is occurring.

Slide 2: (No hard copy) SEM micrograph of the RSC-S29 ceramic saw-cut surface after 3 days of exposure at 90°C to deionized water. Nepheline dissolution is observable and precipitate build-up can be seen.

Slide 3: Precipitate formation can be seen from XRD surface analysis; however, the low angle peaks are not unambiguous. Two possible phases are Gibbsite, $\text{Al}(\text{OH})_3$, or stratlingite, $\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$.

Slides 4 and 5: The saturation and precipitation is a pH-dependent process. At high SA/V ratios the pH climbs to ~9.2 and is accompanied by a significant increase in the solution concentrations of all elements.

Slide 5: In simulated silicate ground water the SA/V variation tests show a rapid stabilization of the pH at 8.9 to 9.0.

Slide 6: In silicate water no precipitate is observed in 100 days and only very little penetration of the water into the form is seen by SEM.

Slide 7: XPS does show the ceramic becoming Si enriched on the surface in silicate water, possibly stabilizing the nepheline phase.

Slides 8, 9, 10, 11: (No hard copy) Variation of the green packing density of the ceramic before consolidation produces variations in the shape and degree of connection between the nepheline grains. The larger and more connected grains, produced by low green densities, show an increased dissolution rate. This demonstrates the role of diffusional pathways in limiting leaching of the nepheline grains.

Summary: The polyphase ceramic leaching process is pH dependent. Under pH conditions between 7 and 9 in initially deionized water, precipitation limits

dissolution very rapidly. Silicate water rapidly stabilizes the form at a pH of 8.9 to 9.0 with little observable dissolution occurring and no precipitate formation in 100 days at 90°C.

Modeling of dissolution must include thermodynamically-controlled phase-specific leach rates, saturation-controlled precipitation, and limiting diffusional effects in the solid-state for the nepheline phase.

Initial work on characterizing the performance of the MCC borosilicate glass has included static leach testing, XPS, SIMS, SEM and TEM analysis. Initial depth profiling and in-situ Raman microprobe analysis have been carried out. EPR studies of the Fe in the gel layers have also been performed.

Specific results include:

Slide 12: MCC-1 tests with four replicates have been carried out to 28 days in silicate water on monolithic forms. Results are reported as molar concentrations rather than leach rates. Note Fe and U limiting concentration behavior.

Slide 13: SA/V tests in DI water show the pH to continue to increase $>>10$ before stabilizing.

Slides 14 and 15: 21 days of leaching in silicate water produces a pH of 9.25 and a gel layer shown to be ~6 microns thick by ion-beam profiling and SEM analysis. SIMS Fe and B profiles compared with XPS profiling show complete leaching of B, Li, Zr, U and Na, from the gel layer. Al, Si and Fe and O are fairly uniform in the gel layer with Mg highly concentrated at the surface.

Slide 16: EPR analysis confirms Fe to be in the 3+ state in the MCC-7668 gel layer (formed in DI water). EPR also shows a minor crystalline phase.

Slide 17: XPS indicates Fe is primarily +3 in the MCC borosilicate defense waste.

Summary of borosilicate glass leach results:

1. pH and SA/V is highly important in establishing leach conditions.
2. The gel layer has a very structured morphology.
3. The gel layer contains a minor crystalline phase.

4. Depth profiling shows somek specific element buildup in the gel layer (Mg, Al, Si, Fe, and O).
5. Solution analysis indicates that Fe and U are probably forming a colloidal phase.

SLIDE 1. Comparison of Short Term Leach Rates of the RSC-S29 Form with Those of Pure Phase Nepheline and the LLNL, Ceramic Waste Form

SLIDE 2. SEM Micrographs of Polished RSC-S29 Ceramic Surfaces After 3 Days of Exposure at 90°C to Deionized Water. Nepheline dissolution is observable and precipitate formation can be seen.

SLIDE 3. The X-Ray Diffraction Patterns Recorded From the Surfaces of the RSC-S29 Ceramic After 28 Days at 90°C and 215°C Compared With That From the Unexposed Material. At the elevated temperature x-ray peaks consistent with the formation of a calcium-alumina silicate (stratlingite) are detectable.

SLIDE 4. pH Stabilization with Effective Exposure Time to Leach Solutions

SLIDE 5. Molar Concentration Changes With Effective Time of Leaching

SLIDE 6. SEM Comparison of Polished Monoliths Exposed Under MCC-1 Conditions to Deionized and Silicate Waters at 90 C for 100 Days. The precipitate formed in the deionized water experiment is absent in the silicate water system. The silicate water appears to stabilize the nepheline phase and inhibit the leaching process.

SLIDE 7. XPS Spectra Recorded From the Surface of the Ceramic Before and After exposure to the Silicate Water for 28 Days. A silicon-rich surface layer, as evidenced by the enhancement of the Si peak, slowly forms.

ELEMENT	Concentration (M)		
	7 Days	14 Days	28 Days
Li	$1.4 \pm 0.2 \times 10^{-3}$	$1.8 \pm 0.06 \times 10^{-3}$	$2.2 \pm 0.2 \times 10^{-3}$
B	$7.1 \pm 0.8 \times 10^{-5}$	$9.8 \pm 0.3 \times 10^{-5}$	$1.1 \pm 0.1 \times 10^{-4}$
Na	$2.4 \pm 0.0 \times 10^{-3}$		
Si	$1.4 \pm 0.03 \times 10^{-3}$	$1.4 \pm 0.05 \times 10^{-3}$	$1.6 \pm 0.06 \times 10^{-3}$
Al	$4.9 \pm 0.4 \times 10^{-5}$	$5.5 \pm 0.1 \times 10^{-5}$	$5.9 \pm 0.4 \times 10^{-5}$
Ca	$8.2 \pm 1.6 \times 10^{-6}$	$9.4 \pm 1.0 \times 10^{-6}$	$8.9 \pm 1.9 \times 10^{-6}$
Mn	$8.2 \pm 2.2 \times 10^{-7}$	$1.4 \pm 0.5 \times 10^{-6}$	$1.0 \pm 0.3 \times 10^{-6}$
Fe	$7.0 \pm 3.0 \times 10^{-6}$	$8.0 \pm 0.3 \times 10^{-6}$	$2.5 \pm 0.8 \times 10^{-6}$
Sr	$7 \pm 2 \times 10^{-7}$	$7 \pm 2 \times 10^{-7}$	$5 \pm 2 \times 10^{-7}$
Cs	$1.0 \pm 0.4 \times 10^{-6}$	$6.8 \pm 1.0 \times 10^{-6}$	$6.3 \pm 1.0 \times 10^{-6}$
U	$3.3 \pm 0.5 \times 10^{-6}$	$4.4 \pm 0.3 \times 10^{-6}$	$4.7 \pm 0.3 \times 10^{-6}$

SLIDE 12. Results of MCC-1 Static Leach Testing of the MCC-Borosilicate Glass in Silicate Water at 90°C

SLIDE 13. Normalized pH Versus Time Plot for the Borosilicate Glass Samples Leached at the Various SA/V Ratios Shown. The data have been normalized to an SA/V ratio of 6.9 (cm⁻¹).

Elemental Ratios*	Clean Surfaces	Leach Surface	Sputter TIME		
			1 hour	2 hours	2 3/4 hours
Si/O	0.10 0.099	0.070	0.093	0.088	0.086
Fe/O	0.078 0.092	0.10	0.10	0.14	0.125
Mg/O	0.032 0.030	0.23	0.21	0.18	0.16
AR/D	0.020 0.021	0.022	0.022	0.021	0.022
U/O	0.080 0.072	< 0.005	< 0.005	< 0.005	0.03
Na/O	0.33 0.26	0.10	0.13	0.16	0.19
Zr/O	0.012 0.012	< 0.005	< 0.005	< 0.005	0.005
B/O	0.011 0.012	< 0.005	< 0.005	< 0.005	0.005

*Elemental ratios not normalized for spectroscopic sensitivities

SLIDE 14. XPS Depth Profile of MCC-BSG Gel-Layer
Formed at 90°C in Silicate Water

Leach Time - 21 days

Final pH - 9.25

Solution Concentrations

	Mg/l	M	Blank (mg/l)
Al =	1.62	6×10^{-5}	< .03
Si =	30.7	1.1×10^{-3}	12.5
Na =	53	2.3×10^{-3}	47
B =	1.55	1.4×10^{-4}	0.008
Li =	1.56	2.3×10^{-4}	< 0.01
Fe =	0.30	5.4×10^{-6}	0.02
Mg =	0.15	6.2×10^{-6}	0.30
Mn =	0.19	3.5×10^{-6}	0.02

SLIDE 15. Solution Analyses and Silicate Water Blank for
the Leach Test Producing the Gel Profile in
Slide 14

SLIDE 16. EPR Spectrum of Gel Layer from MCC Borosilicate Glass

SLIDE 17. XPS Spectra of Fe in the Gel-Layer of DI Water Leached MCC Borosilicate Glass. Fe^{3+} is the most probable state for the element.

3.5. PACIFIC NORTHWEST LABORATORY -- G. L. McVay

An understanding of the mechanisms of glass-water interactions involves evaluating several important parameters and their interactions. The parameters to be considered in this paper are the effects of sample surface-area-to-solution-volume ratio (SA/V) coupled with silicon solubility, the effects of soft iron, and of colloid generation. These effects are all interrelated and will be discussed in the text.

When samples of a glass are exposed to different volumes of leachate for similar experimental times, the results can be interpreted in various ways. If large volumes of water are used, then saturation effects are less important during normal experimental times and higher leach rates, sustained for longer periods of time, are usually observed. When small volumes of water are used relative to the exposed glass surface area, saturation effects can be important early in the experiment and smaller leach rates are normally measured. Not only are these effects important for experimental design and data interpretation, they can be used for accelerated testing purposes as well.

It has been shown that silicon removal by leaching from a silicate glass does not exceed the solubility limit of fused silica (Pederson et al. 1982). This has been demonstrated for several glasses ranging from simple four-component glasses to complex 30-component borosilicate waste glass.

Consistent with the conclusion that silicate glass dissolution rates are strongly influenced by the saturation fraction of silica in solution is the finding of Figure 3.7 that leaching data for different SA/V values and leaching times can be represented by a single curve. For any combination of SA/V and leaching time where the product is a constant, concentrations of glass components in the leachate are equal. The results shown in Figure 3.7 are for PNL 76-68 glass. Similar curves were generated for all of the glass elements. Leached layer thicknesses were not equal, since less material is required to be leached, per unit surface area, at high SA/V than at low SA/V to reach the same solution concentration. Since the shapes of the leaching curves were identical at different SA/V values, despite major differences in the leached layer thicknesses, it must be true that the presence of the leached layer does little to modify glass dissolution rates.

FIGURE 3.7. Log Silicon Concentration Versus SA/V x Time. Leaching data for a range of SA/V values in M⁻¹ and times generate a single curve.

To further demonstrate the importance of silicone-in-solution on the leachability of PNL 76-68 glass, samples were leached in silicic acid solutions of varying concentrations and in two actual groundwaters that contained dissolved silicon. Boron dissolution amounts following 28-day leach tests are plotted versus initial silicon concentrations in Figure 3.8. Dissolution of boron (as well as other soluble glass components) shows an approximate inverse relationship to the amount of dissolved silicon in both silicic acid solutions and in the more complex groundwaters. Dissolved silicon saturation fractions clearly are important in modifying glass dissolution rates.

Elemental release data, when plotted versus the product of SA/V and leaching time, generates only one curve for a given glass, such as that of Figure 3.7. Because of this, changes in the SA/V ratio can be used as a method of accelerated leach testing as it pertains to the solution concentrations. Solution data for MCC-1 tests at low SA/V values can be predicted on the basis of much shorter tests at high SA/V, following the curve of Figure 3.7. The highest practical SA/V value that can be used for monolithic samples and one that yet allows sufficient leachate solution for ICP analysis in typical laboratory experiments is approximately 10⁴ m⁻¹. Thus, a 10³ acceleration factor

FIGURE 3.8. Boron Release Following 28 Days of Leaching Versus the Initial Silicon Concentration. Dissolution of all soluble components was sharply reduced by dissolved silicon.

can be realized at this SA/V ratio over the more standard value of 10 m^{-1} . Even greater acceleration factors may be possible using glass powders carefully prepared to remove adhering fine particles.

While accelerated leach testing using varied SA/V and MCC-1 static leaching procedures appears possible, complications arise when other components of the waste package system are considered, which may limit the usefulness of the method. If, for example, the waste package contains a reactive ferrous material, glass dissolution rates are expected to be accelerated because iron silicate colloids form, which lower the activity of the dissolved silicon (McVay and Buckwalter 1983).

In essentially all static leaching experiments that have been conducted on glass in simple water systems, such as deionized water, the elemental release rates are initially rapid and then decrease as leaching progresses (El-Shamy et al. 1972; Clark et al 1979; Hudson and Bacon 1958; McVay and Buckwalter 1980; Hency et al. 1980). An approximately constant leach rate is typically achieved due to the relatively short experimental times and the sufficiently low sample surface-area-to-leachate-solution-volume ratios (SA/V) used. One of the primary reasons for the decrease in elemental release rate as leaching progresses

is the accumulation of elements in solution that act to retard leaching. This is best illustrated by the previously discussed effects of varying the SA/V ratio on leaching characteristics. Increasing the volume of water to which a sample is exposed (lowering the SA/V) results in the higher initial elemental release rates being maintained for a longer period of time before solution concentrations are high enough to slow the leach rate. Thus, the total elemental removal from the sample is greater with lower SA/V ratios (Buckwalter et al. 1982).

A similar phenomenon exists for leaching in complex groundwaters. As can be seen from the compositions of basalt and tuff groundwaters used in this investigation, many elements such as Ca, Na, and Si, which would normally be present in simpler waters after leaching a glass sample, are already present in the starting water composition. The basalt water contains the greatest concentration of elements with the tuff water being intermediate between deionized and basalt waters. Therefore, one might expect the initial leaching characteristics of the glass in basalt and tuff groundwaters to be similar to those observed at longer times in deionized water if one primarily considers solubility.

Time-dependent leaching results for PNL 76-68 glass in deionized, tuff, and basalt waters are shown in Figure 3.9 by solid and dashed lines for boron and cesium, respectively. These elements were chosen for illustration because they are not in the original groundwater composition and because boron and cesium represent both matrix and mobile modifier elements. Solution concentrations were normalized by the elemental fractions in the sample and by the sample surface areas for ease of comparison. As can be seen from Figure 3.9, the leaching characteristics of the glass are quite different in the various leachates. The deionized water results show the characteristic initial rapid release rate which decreases with leach time. Tuff water, which has more elements than deionized water, shows lower beginning leach rates and less total leaching. Basalt water, which has the most elements prior to leaching, has the lowest starting release rates and the lowest total leaching. In fact, there is little evidence for an initial enhanced leach rate in basalt water. These observations are consistent with the theory that for a given waste form the

FIGURE 3.9. Illustration of Two Effects on Leaching Characteristics of PNL 76-68 Glass. Effect of groundwater composition without iron present and effect of having iron present during leaching.

solution composition controls the leaching characteristics and, as elemental concentrations increase in the leachate, elemental release rates decrease (Buckwalter et al. 1982).

However, when the experiments were repeated in an identical manner, except for the inclusion of a piece of ductile iron of the same approximate surface area as the glass sample, a totally different result occurred. The starting solution composition had little effect on the leaching characteristics of the glass samples. These results are illustrated by the cross-hatched region in Figure 3.9. This cross-hatched region includes the boron and cesium leaching results from deionized, tuff, and basalt waters. Elemental removal rates in all of the leachates are initially similar to those observed for early leaching in deionized water without the presence of iron. However, in the presence of iron, the leach rates do not decrease as rapidly with time as they do in deionized water alone. Consequently, more elemental removal occurs from the glass samples.

Identical results were also observed in salt brine solutions. These effects can be attributed to the formation of iron-silicate precipitates, which cause significant changes in the reactions of both glass and ductile iron with groundwaters. This is due primarily to effectively removing elements from solution by precipitate formation and thus reducing the saturation effects that normally occur in static leaching. In addition to the effects of elemental removal from waste glass, the presence of iron causes many of the removed elements to be incorporated in the precipitates.

The above discussions have focused upon PNL 76-68 glass. This is due primarily to the fact that the data are available and more extensive than for MCC reference defense waste glass. However, some data are available for the MCC glass and will be discussed and compared to that from PNL 76-68 glass.

A representative sampling of the MCC glass data is shown in Figure 3.10. Although both 40 and 90°C leaching data are available for all of the elements in the glass, the boron data in Figure 3.10 are presented for comparison to 76-68 data in Figure 3.9. The DI water from Figure 3.9 is identical to the

FIGURE 3.10. Effects of 90°C Groundwater and of Iron on Boron Release from MCC Reference Defense Waste Glass (Q-H₂O is same as DI water)

Q-water from Figure 3.10. As can be seen from Figure 3.10, leaching without soft iron results in a reduced boron release in groundwaters of increasing complexity. This is the same result observed for PNL 76-68 glass in Figure 3.9. However, the MCC glass releases approximately half as much boron, in all of the groundwaters evaluated, as was observed in PNL 76-68 glass (Figure 3.9). This improved durability is in part due to the aluminum present in the MCC glass (PNL 76-68 glass has no Al).

Addition of soft iron to the MCC glass leaching experiments results in enhanced boron removal as was observed for PNL 76-68 glass. However, the total amount removed was again approximately half of that observed for PNL 76-68 glass, and the spread between groundwaters remained about the same as when no iron was present. This is in apparent contrast to observations for PNL 76-68 glass, which had little difference in boron release characteristics when soft iron was present. More data on the MCC glass is needed before firm conclusions can be drawn on the effects of iron.

It appears that the silicon solubility has been lowered in the MCC glass relative to that observed in PNL 76-68 glass. This is possible if rapid formation of aluminosilicate alternation products (which have lower silicon solubility than amorphous silica) occurs. This would cause both release rates and total amount released (of elements with release rates comparable to or higher than Si) to be lowered compared to glasses such as PNL 76-68. It should have minimal effect on slow release or low solubility elements such as the actinides.

Actinide release from the MCC glass is represented by ^{239}Pu in Figure 3.5. The glass was doped with ^{239}Pu to a level of .03 wt%. As can be seen from Figure 3.5, similar amounts of Pu ended up in solution and on the container walls. Unfortunately, filtration was not possible at the time, so the solution analyses include both Pu in colloidal form and in solution. As can be seen from the upturn of the Pu concentration in solution with time, colloidal formation is having a significant effect on the results. Later experiments, where filtration was done, show that the upturn is due totally to colloid formation. The concentration of Pu in solution (minus colloids) from the MCC glass is nearly identical to that observed with PNL 76-68 glass. Apparently, the Pu solubility

FIGURE 3.11. Pu-239 Release from MCC Reference Defense Waste Glass into 90°C DI Water

(at least under these experimental conditions) from the two glasses is similar and not affected by silicon solubility variations.

Rutherford backscattering of the leached uranium-containing MCC glass gives insight into reaction layer development and is illustrated in Figure 3.12. It can be seen that the uranium concentration increases with time in the reaction layer and that its distribution is uniform through the reaction layer. The iron can be seen to increase on the reaction layer surface with time and is not uniformly distributed through the gel layer. It is unclear at this time whether other actinides enhance on the surface or are uniformly distributed in the gel layer. This has a large impact on the amount of alpha radiolysis to which the groundwaters will be exposed. Unfortunately, due to the similarity in mass of all the actinides, Rutherford backscattering cannot differentiate between Pu, Np, or U; and since U is present in the largest concentrations, it is all that is observed.

Colloids fall into two general categories, i.e., true and pseudo. The true colloid is generally formed by actinide reaction with water constituents, such as hydroxides, and are normally small in size and long lasting. Pseudo colloids are typically formed by precipitate reactions which then sorb

FIGURE 3.12. Rutherford Backscattering Spectra of MCC Reference Defense Waste Glass Leaching in DI Water at 90°C

actinides onto their surfaces. The pseudo colloids tend to be larger and less stable than true colloids. Collectively, they represent the possibility of transporting larger quantities of actinides than solubility limits alone would allow.

Investigations of the actinide sorption characteristics of two pseudo colloids, iron-silicate precipitates and Na-bentonite, are illustrated in Figures 3.13a and 3.13b. The speciation as a function of Eh and pH are shown in the top two curves of Figure 3.13a for U and Pu. At constant Eh, the charge of the stable species varies from positive to negative as the pH goes from acidic to basic. Over the same pH variation, the surface charge (as determined by the zeta potential) becomes more negative but does not go positive even at pH 2. These results are shown in the bottom curve of Figure 3.13a for both Na-bentonite and Fe-silicate. Therefore, one would expect that when the colloid and the actinide species have opposite charge, they would attract; and when they are similarly charged, they would repel each other. Thus, actinide sorption (U and Pu) should occur in the acidic region and not in the basic region. That this is the case is illustrated in Figure 3.13b for iron-silicate

FIGURES 3.13a and 3.13b. Uranium and Plutonium Speciation, the pH Dependence of Colloid Zeta Potentials, and Pu and U Sorption on Fe-Silicate and Na-Bentonite Colloids. (All results are at room temperature in DI water.)

precipitates (top curve) and Na-bentonite (bottom curve). Since groundwaters typically range from neutral to basic pH values, we are on the edge of the colloid sorption problem.

Much understanding has been gained about glass-water interactions in realistic repository environments. There still needs to be a significant increase in understanding about the effect of radiolysis (particularly alpha) on the repository environment, about particle size distribution and stability of generated colloids, and about solubility in near-field repository environments.

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3.6 LAWRENCE LIVERMORE NATIONAL LABORATORY -- D. D. Jackson

3.6.1 Dissolution Model Development

Several useful features have been added to PROTOCOL to extend its competence to more types of leaching systems. Techniques for coupling to experimental configurations and data were developed. It can now be directed to do

simulations of congruent dissolution. It can accept water volume and composition changes due to sampling at scheduled intervals, with water replacement. It has been modified to run larger problems, and to provide more information on mass balance in the system.

3.6.2 New Options

Dissolution rate data sets that have been used as test problems in the development of PROTOCOL have involved the concentrations of elements that were actually measured in solution. Another important and recurring type of problem is to examine the consequences of congruent reactions. I have now added an option to have congruent rates calculated automatically, and based on the rate for any component that is selected. This option makes it possible to study the effects of assuming that a constant fraction of the whole waste form reacts as a specified rate. Of course, it cannot require that all elements actually dissolve at that rate, but allows precipitation and dissolution to occur. This option has been debugged and simple test cases run. Congruency was confirmed by agreement of the leached depths of component elements.

Another option was added to help interpret experiments in which water changes are made at intervals. In the model, specified fractions of the resident water volume are replaced on a schedule listed in the input instruction file. This will make it possible to examine the effects of various sampling techniques on release, including complete water replacement. The coding for this option has been completed, but test cases have not yet been run.

Logic was added to the timer subroutine to do a few very early time calculations, no matter what other timing options are selected. This was done because some very insoluble phases precipitate immediately, and it was useful to increase the resolution enough to determine when such events happen. However, the output must be interpreted with caution, since as the time increments become very small, the assumption of a quasi-equilibrium in the aqueous/surface part of the system becomes unrealistic.

3.6.3 Surface Chemistry

Greater emphasis is now being placed on properties and reactions in the near surface material that accumulates during leaching. This can be visualized

as an amorphous silicate or protosilicate, and it seems essential to monitor its composition during leaching. This requires a feature that has not been readily available in the model; a mass balance for the system. It is necessary to calculate and retrieve several quantities; the depth of depletion of each element, masses and composition of residual material in the leached zone, in new phases that are precipitated by MINEQL, in the resident water volume and in the outflow volume, if any. The surface layer stoichiometry can then be obtained by difference.

Although the current version of PROTOCOL cannot generate concentration profiles in the solid, the depth of depletion of elements in the near surface has been calculated as a step function, assuming a zone of 100% depletion with a sharp boundary, and is now printed out in the data summary.

The masses of precipitated phases could previously be obtained only from a very detailed printout at each time step. However, it is not feasible to print all the chemical details that are potentially available during a run. These masses have now been retrieved and are now tabulated in the summary output file.

Aqueous concentrations can now also be extracted at each time step without excessive output. As a test case, silicon and aluminum species are now tabulated, and this will eventually be converted to an option to retrieve and print species concentrations for any specified list of elements.

3.6.4 Expanded Capabilities

Modifications are being made to the model allowing it to run a more realistic waste glass composition, with many more component elements. There is a (temporary) machine limitation on array sizes. Some unused space has been recovered by reducing and reshaping of the arrays. It is now possible to run a ten-element (plus pH and Pe) problem with the full existing data file for 363K, and a further expansion will be made in the near future. However, effects of problem size may well recur as more complex and realistic glass and solution compositions are approached.

An improvement was made in the way analytical expressions for leach rates are extrapolated. The original expedient scheme for computing mass fluxes from

rate functions was numerical integration by a simple summation of rate-area-time products in the series of time increments. This has now been replaced with a subroutine that carries out an N-point Gaussian quadrature, which will allow much closer tracking of rate functions.

3.6.5 Interactions with Experimental Data

It has been found very useful to run simulations of actual experimental data. Model capabilities needing the most attention could be quickly identified. For example, dissolution data for nepheline (Tole 1980) were used to develop and verify a capability for geometry-independent area input (irregular shapes, powders), and suitable techniques for converting experimental data to a PROTOCOL-compatible format.

I first examined the question of optimum functional form for representing data. For the present, curve fitting is done off-line with an in-house analysis program. Functions were generated and sample runs were made for a series at pH = 3, T = 298K, and a run time of 1 month, with the component set K, Na, Al and SiO₂. It was found that, providing the rates are adequately represented by the functions used, and that the thermochemical data is correct, the next event in the system would have been saturation with respect to kaolinite. Al₂Si₂O₅(OH)₄ at about 6 months.

These direct comparisons indicate that the coding is correct insofar as tracking experimental data is concerned, that the chemical extrapolation of empirical rate functions is working, and producing reasonable results. The generation of analytical expressions to represent experimental data, however, is not a completely satisfactory process. In order to reduce the subjective element, an automatic curve-fitting algorithm should probably be used in the future: It will have the advantage that the criteria for goodness of fit will then be preset and documented.

The next data used in model development, and more nearly representative of waste glass chemistry, was an experimental series submitted by D. E. Clark (SRL 131-TDS-3A) at 363K (90°C). For elements with enough data (Si, Na, Li, Mg), the main feature was an evident inflection point between 1 and 2 weeks. Bilinear fits were therefore made for these elements.

The runs showed no intrinsic evidence, such as precipitation, of the cause of such rate changes. However, it was thought possible to deduce something of the reactions by assuming congruent reaction, at least at early times and very dilute solutions. The question was whether any of the observed release rates could be a consequence of the formation of identifiable insoluble phases at the interface. It was at this point that the congruency option was added. The rates for elements in the glass were computed, assuming congruency with respect to silica, and the PROTOCOL simulations carried out.

The first set examined contained the elements actually reported in solution: Si, B, Na, Ca, Li, Mg, Al, and Mn. This combination of component species led to the selection of so many solid phases that the species arrays overflowed, requiring the problem in parts. It was at this point that array modifications were started.

Precipitation occurred only when the reaction was accelerated by increasing the surface area 100 times. The first solid phase to be formed was amorphous silica, no doubt due to the large excess of silica in the glass, and a relatively high dissolution rate. This was followed much later by the appearance of talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, and shortly after that by the redissolution of the amorphous silica.

Since no solubility constraints for measured elements were found in the simulations, using either actual or congruent rates, the apparent changes in slope at about 1 week are not related to a chemical saturation with respect to materials in the data base. They may result either from decreases in specific surface areas with time, or from the formation of unknown solid phases.

The elements Ti, La, Zr, Fe and Ni were present in the waste glass, but not detected in solution. In order to examine their possible reactions, they were arbitrarily assigned congruent release rates. The result was an immediate precipitation of Fe_2O_3 , ZrO_2 , $\text{La}(\text{OH})_3$ and TiO_2 , indicating as expected that missing species result from solubility constraints.

Even with a 12-component capability, it was not possible yet to run a complete glass composition. The system will be re-examined as missing data that have been identified are added to the data base, and the appropriate coding fixes have been made.

3.6.6 Works in Progress: Extensions to the Model

The problem of how best to extend PROTOCOL to the numerical modeling of solid-state corrosion/diffusion processes is under consideration. A relatively simple submodel for the solid-state transport is possible where there are not strong interactions between migrating species and host matrix (White and Claassen 1980). However, most elements do not move so freely between glass and solution: The chemical complexity of a glass/gel/water system probably precludes closed form numerical models based entirely on physical transport, and chemical reactivity must also be considered. That is, chemical reactions should be monitored, as is now done in the aqueous phase. We might, for example, consider a sequence of coupled subsystems, with the glass as the first element and water as the last. In this concept, each zone would be a discrete chemical subsystem in which transport (both ways) precipitation and dissolution could take place.

There is an existing reactive flow model (Nikolakopoulou et al. 1982) that might be applied to that problem. This is a finite element code that was written for a relatively simple diffusion/precipitation process. Its use in a system with multiple components and with a large number of possible solubility constraints implies a formidable amount of computation. The main questions are whether the method can reasonably be extended to glass dissolution, and whether such a detailed treatment is necessary and would justify the cost of its development.

In addition to the reactivity of diffusing species, the chemical properties of the altered surface material are not well defined. It is nonstoichiometric and effectively amorphous, that is, in various stages of ordering. It is thought not to be chemically inert, but its thermochemical properties as a function of composition are not presently known. This may well be a topic that must be addressed experimentally.

3.6.7 References

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4.0 SESSION II. CHARACTERIZATION OF LEACHED SURFACES

4.0 SESSION II. CHARACTERIZATION OF LEACHED SURFACES

4.1 INTRODUCTION OF SURFACE CHARACTERIZATION TECHNIQUES -- A. B. Harker

4.1.1 Overview of Session II

The major purpose of the second workshop session was to provide both a broad overview of existing surface analysis techniques and to present recent results on alteration layer studies in leached nuclear waste forms. Thirteen speakers described the application of spectroscopic, microscopic, and chemical techniques for determining the chemical composition and elemental depth profiles of leached layers. The descriptive names of these techniques are commonly shortened to acronyms, which will be used in this summary. Table 4.1 gives an index of the analysis techniques and their most common acronyms.

TABLE 4.1. Common Abbreviations and Acronyms for
Surface Analysis Techniques

Scanning Electron Microscopy	SEM
Energy Dispersive X-Ray Analysis	EDAX
Transmission Electron Microscopy	TEM
Analytical Scanning Transmission Electron Microscopy	STEM
X-Ray Photoelectron Spectroscopy	XPS or ESCA
Auger Electron Spectroscopy	AES
Scanning Auger Microscopy	SAM
Secondary Ion Mass Spectroscopy	SIMS
Ion Scattering Spectroscopy	ISS
Sputter Induced Photon Spectroscopy	SIPS
Rutherford Backscattering	RBS
Laser Raman Microprobe	LRM or LRS
Fourier Transform-Infrared Reflectance Spectroscopy	FT-IRRS

The techniques listed in Table 4.1 each have unique capabilities for elemental or chemical state identification, however, they can be grouped in several major categories by spatial and depth resolution. Those techniques which provide the poorest spatial resolution include XPS, AES, RBS, and FT-IRRS. These techniques typically use unfocused beams and have spatial resolution of about 1 mm. The ion beam based techniques, typically used for depth profiling, offer a wide range of spatial resolution, depending upon the ion source used. SIMS, SIPS, and ISS are available with resolution of 1 to 5 microns, but typically use beams with less than 50 micron discrimination. The microprobe techniques, SEM/EDAX, STEM, and LRM all offer submicron optical resolution, but often are greatly degraded when performing analytical work.

The technique which has been the most quantitative in describing the elemental composition of leached layers in nuclear waste forms has been SEM/EDAX. This method offers the ability to produce high resolution micrographs of the morphology and quantitative elemental analysis of a physical volume on the order of 3 to 10 cubic microns. XPS and AES have also been widely used to provide semi-quantitative elemental analysis of leached surfaces. Both these techniques detect electrons emitted from the top 10 to 50 angstroms of the surface and offer chemical state information. XPS uses an x-ray source under 1500 eV to stimulate photoelectron emission and is the only technique which detects all elements without requiring the analyst to be concerned about sample heating and charging which can lead to elemental migration.

All of the techniques listed in Table 4.1 were discussed in detail by the speakers with respect to their capabilities and limitations in the characterization of leached layers in nuclear waste forms.

4.1.2 Introduction of Surface Characterization Techniques

Surface analysis techniques can be grouped into several classes based upon the type of information provided, the environment in which the analysis takes place (vacuum, ambient, etc), and the spatial resolution they offer. The techniques also vary in the degree to which the sample must be pretreated and the degree to which they are nondestructive.

The greatest number of surface analysis techniques operate in high or ultra high vacuum and require that the sample surface be pretreated by polishing, coating, or thinning to obtain the best experimental data. These vacuum based techniques are generally available on multiple capability instruments that take advantage of a variety of excitation sources and detectors. Such instruments often offer a combination of XPS, AES/SAM, SIMs, ISS, SIPS, and SEM. The other vacuum based techniques, generally stand alone systems, are SEM/EDAX, analytical STEM with x-ray analysis, and Rutherford backscattering. The multi-capability instruments are generally ultra-high vacuum, 10^{-10} torr, and are designed to provide both surface analysis and depth profiling capabilities with limited spatial resolution in the horizontal plane. The electron-microscope-based techniques are designed to provide physical morphology, elemental distribution, and crystallographic information with submicron spatial resolution.

Tables 4.2 through 4.4 give a break down of the various analysis techniques used in characterization of leached waste form surfaces. The techniques are classed by their operating environment: ultra-high vacuum, high vacuum, or ambient.

The application of the techniques described in the tables in characterizing leached layers requires that proper attention be given to sample treatment in drying, evacuation, coating, or polishing. In addition the effects of sample heating and charging during analysis must also be considered in data analysis. In all cases the application of multiple techniques to confirm results is recommended.

TABLE 4.2. Description of Major UHV Surface Analysis Techniques

X-ray Photoelectron Spectroscopy:

X-ray induced photoemission of core electrons.

Electrons have kinetic energies characteristic of element and chemical state.

Sensitivity varies according to element, typically 0.5 to 0.2 mole%.

TABLE 4.2. (contd)

Analysis depth 10 to 50 angstroms.

Spatial resolution 1-2 mm, focused units are available with 250 micron beam.

No sample preparation required, polished samples give more reproducible data.

Technique is primarily for surface analysis, is semi-quantative, and can be used with ion sputtering for depth profiling.

Auger Electron Spectroscopy & Scanning Auger Microscopy:

Electron Beam (2 to 5 Kv) induced emission of secondary electrons.

Kinetic energy of emitted electrons characteristic of element, some chemical state information.

Sensitivity varies according to element, typically 0.5 to 0.2 mole%.

Analysis depth 10 to 50 angstroms.

Spatial resolution dependent on spot size of electron beam, less than 0.2 microns is possible, 1 to 5 microns is more generally used.

Technique is generally used for bulk elemental analysis, is semi-quantative, and is suitable for depth profiling with ion beam sputtering.

Polished samples provide more uniform data and care must be taken to assure that nonconductive samples do not experience adverse heating or charging during analysis. Liquid nitrogen cooling of nonconducting samples is recommended.

Secondary Ion Mass Spectroscopy:

Primary ion beam sputters surface and creates secondary ions.

Secondary ions are mass analyzed.

Sensitivity is dependent upon elemental ionization coefficient, and chemical environment, variation of 100 to 1000 between elements common. Typical sensitivities 0.1 to 0.0001 mole%.

Technique is typically non-quantitative.

TABLE 4.2. (contd)

Spatial resolution of 500 to 0.5 microns available.

Technique is primarily for determining relative depth profile variations in elemental composition.

Heating charging problems are found with glass samples, liquid nitrogen cooling of nonconducting samples recommended.

Sputter Induced Photon Spectroscopy:

Primary ion beam produces excited neutral atomic species which relax by emitting a photon.

Standard optical spectroscopic techniques used in detection.

Sensitivity varies greatly with element, best sensitivity for alkali elements.

Same applications and restrictions as SIMS.

Ion Scattering Spectroscopy:

Low energy primary ions are scattered with kinetic energy characteristic of element and bonding environment on sputtered surface.

Technique has low sensitivity, but has monolayer depth resolution. Major applications involve surface reactions and adsorption phenomena.

Rutherford Backscattering

High energy (~ 2 MeV) positive helium ions are elastically and inelastically scattered from the analysis surface, providing quantitative elemental content and profile data to a depth of about 2 microns.

Technique requires smooth conductive or coated samples of uniform density. Sensitivity proportional to atomic number squared, but for Z over 40 elemental scattering cannot be resolved.

TABLE 4.3. High Vacuum Surface Analysis Techniques

The two principle high vacuum techniques used in analysis of surface layers are the electron microscopy techniques coupled with x-ray fluorescence analysis of elemental content.

Scanning Electron Microscopy with EDAX:

Highly focused electron beam provides submicron imaging of surface.

Samples must be coated with a conductive material such as gold to avoid charging effects.

Electron beam induced x-ray fluorescence provides elemental analysis and imaging.

EDAX sensitivity low for elements of Z less than 12.

Depth profiling depends upon careful preparation of polished or cracked surface representative of actual average properties.

EDAX analysis has spatial resolution of 1 to 2 microns, but integrates over a volume element of perhaps 3 to 10 cubic microns.

Density effects must always be considered.

With good calibration quantitative measurements can be made to about 10% accuracy.

Scanning Transmission Electron Microscopy with X-Ray Analysis:

Focused electron beam transmitted through an ion beam thinned substrate, less than 50 nm thick, provides 10 to 20 angstrom physical resolution of microstructure.

Specially thinned samples can be leached and their microstructure and elemental content studied.

Technique is best suited for crystalline materials, amorphous materials undergo decomposition during electron beam heating.

TABLE 4.4. Surface Analysis Techniques Suitable for Ambient Applications

Fourier Transform-Infrared Reflectance Spectroscopy:

Technique uses standard reflectance FF-IRRS on dry or wet samples.

Broad bank IR absorptions provide surface bonding information.

Spatial resolution is noise limited to several square mm area.

Laser Raman Spectroscopy:

Raman scattering from a highly focused laser provides bonding information.

Crystalline materials or localized crystalline precipitates can be observed.

In-situ measurements using wet samples can be carried out to observe broad spectral changes.

4.2 APPLICATION OF SCANNING ELECTRON MICROSCOPE/MICROPROBE ANALYSIS --

J. L. Daniel

4.2.1 Summary

SEM and SEM/EDAX are the best established and most widely applied microprobe techniques in the nuclear waste leaching community. Most instrument manufacturers supply fully computer automated x-ray analysis options for the electron microscope user to permit quantitative elemental analysis and mapping. Of primary importance in using the EDAX microprobe technique is the use of correct standards and orientation in the instrument. Specific attention must be given to determining the effects of density variations and any sample preparation including polishing and coating.

In the case of using the SEM/EDAX techniques with leach layers one must consider the heating effects in the very porous, thin layers. Often physical distortion and elemental migration can occur.

Data were presented from leach samples demonstrating that mass balances could be obtained in both leach layers and bulk glasses with accuracy approaching 5% in best cases. In routine cases good qualitative and semi-

quantitative work can be readily carried out if data are properly treated. Preparation of the samples by careful polishing to expose an edge and the use of fracture surfaces can be used to obtain depth profiles. Profiles have a depth resolution of only about 1 micron however, and must be compared with sputter profiles (SIMS, SAM, etc) for confirmation. In addition other methods must be found for the low Z elements as the EDAX technique is only quantitative for elements above Na in the periodic table.

4.3 APPLICATIONS OF ANALYTICAL TRANSMISSION MICROSCOPY -- T. Shaw

4.3.1 Summary

The STEM technique has the highest resolution of the analytical techniques, providing detailed qualitative and quantitative elemental distribution information on the microstructure of materials. The technique can be applied to the study of leached surfaces through the use of specially prepared samples. STEM analysis requires a sample of less than 50 μ m thickness for detailed resolution. Such samples can be prepared by polishing and ion beam thinning. After thinning such samples can be leached for short periods of time to observe the surfaces which occur in the material. In ceramic waste forms detailed information has been obtained in the role of grain boundary leaching and on the leach mechanisms of individual crystalline phases by this thin-foil leaching technique. With glass samples it has been demonstrated that gel layer formation can be observed by this technique and that individual crystalline grains can be observed reacting in the glass matrix. However the extensive sample preparation involved in this technique makes general application prohibitive. The EDAX technique in the STEM system requires careful calibration to be quantitative, but is extremely powerful if microstructure plays an important role in the leach process.

4.4 APPLICATIONS OF AUGER SPECTROSCOPY AND XPS -- L. Pederson

4.4.1 Summary

XPS and AES are the two major techniques by which chemical state and elemental ratio data can be obtained on reacted surfaces. Both methods require ultra-high vacuum and use kinetic energy discrimination to determine the

elemental source of the emitted photo or auger electrons. The common analysis technique allows both types of data to be collected on the same instrument. The combination of these two spectroscopic techniques is a powerful tool for determining the role of such processes as ion-exchange, adsorption, precipitation, oxidation/reduction, etc. in waste form leaching.

The XPS method is based upon the detection of photoelectrons emitted from the core levels of elements irradiated with monochromatic x-rays. Typical instruments use Al and Mg k alpha x-rays of energies 1486.6 and 1253.6 eV respectively. These low energy x-rays usually do no damage to a solid sample and provide photoelectrons whose escape depth is less than 40 to 50 angstroms from the surface. Secondary Auger electrons are also emitted from the x-ray irradiated samples and can be detected simultaneously, however much greater sensitivity can be obtained by using a 1 to 5 KeV electron beam as the source in AES work.

An application of the two methods which has shown great promise in the identification of chemical states is the use of the correlation of the Auger chemical shift data with that obtained from XPS. By plotting the kinetic energy of the photoelectron lines of the various chemical states of an element on the abscissa and that of the major Auger line on the ordinate a two dimensional chemical state plot is obtained. The use of known standards to produce such a plot provides a powerful tool to establish the chemical environment one observes in an unknown sample or in a complex situation such as found with leaching nuclear waste forms.

For further information see, "Handbook of X-Ray Photoelectron Spectroscopy" by C. G. Pantano, Ceramic Bulletin 60, p. 1154-1163 (1981).

4.5 APPLICATIONS OF SECONDARY ION MASS SPECTROSCOPY (SIMS) -- C. G. Pantano

4.5.1 Introduction

Secondary ion mass spectroscopy (SIMS) is carried out by sputter etching the sample surface with a beam of primary energetic ions. Some fraction of the atomic and molecular species ejected from the sample surface are ionized in the process. The detection of these sputtered secondary-ions in a mass

spectrometer is the basis of the SIMS technique. Since the primary ion beam continuously sputter etches the sample surface, changes in the intensity of any particular secondary-ion can be related to the original in-depth concentration profile for that specie in the sample surface. Thus, SIMS is inherently a depth-profiling technique. It is ideally suited to the measurement of concentration profiles at the leached surfaces of nuclear-waste glasses because the mass spectrometer can simultaneously monitor several elements as the sample surface is continuously eroded by the primary ion beam. Other particular advantages of the SIMS technique for nuclear waste form characterization include the ability to detect minor glass components present at low concentrations (<.1%), and the ability to detect hydrogen.

Figure 4.1 shows, for example, the SIMS profiles measured at the surface of formula 127^(a) glass after 1 day of Soxhlet leach testing (MCC-5). The presence of a distinct surface reaction layer is clearly evident. Some of the glass components--e.g., Zr, Cu, Sr and O--have been enriched within the surface layer while B and the alkali species--Na, Li and Cs--have been depleted at the surface. The depth scale was calibrated by assuming a sputtering rate of 18 nm/min throughout the profile; this rate was measured using a bulk soda-lime-silicate standard. Although this would suggest that the surface reaction layer is approximately 250 nm (2500 Å) in thickness, it will be pointed out later that the sputtering rate through the surface layer may be two times larger than 'bulk' oxide glass. Thus, the surface layer in Figure 4.1 may, in fact, be μ 5000 Å in thickness. It is also important to point out that the profiles in Figure 4.1 include the major glass components--e.g., SiO₂ (46.5 wt%), B₂O₃ (6.7 wt%), Na₂O (8.4 wt%)--as well as the minor components Cs₂O (0.05 wt%) and SrO (0.26 wt%). It is highly unlikely that these minor components would be within the detection limits of any other surface analysis technique.

It is worth emphasizing at this point that the profiles of Figure 4.1 typify the major advantages and contributions of a SIMS depth profiling analysis for leached nuclear waste glass. Namely, the analysis provides a

(a) Formula 127 is a borosilicate glass designed to immobilize ICPP zirconia waste calcine.

FIGURE 4.1. SIMS Depth Profiles for a Soxhlet Leached Nuclear Waste Glass. The Zr⁺ and Cs⁺ profiles were corrected assuming that the leached layer sputters two times faster than the bulk glass (7 KeV Ar⁺ @ 0.06 mA/cm²).

qualitative description of the surface reaction of 'gel' layer and distinguishes between the major and minor components which are depleted at the surface versus those which are enriched there. These profiles can be measured in a reasonable time period with SIMS; the data in Figure 4.1 was acquired in about one hour.

The other big advantage of the SIMS technique is the capability for measuring the in-depth hydrogen profile with a related technique: sputter-induced photon spectrometry (SIPS). This method is also based upon sputter-etching the specimen surface with a primary beam of ions, although here, the characteristic photons emitted by sputtered neutrals are detected rather than the sputtered secondary-ions. The Na and H profiles in Figure 4.2 were obtained with SIPS on a systematic compositional series of ternary sodium-aluminosilicate glasses. The profiles show the depletion of sodium at the surface and a corresponding enrichment in hydrogen. It is especially noteworthy that all the glasses have the same molar concentration of Na_2O . However, the preferential release of sodium--and corresponding hydration of the surface--are reduced significantly as Al_2O_3 is substituted for SiO_2 . Auger analysis of these same glasses revealed that the reduced leaching kinetics are not due to the formation of an alumina-rich surface film. On the basis of these profiles, and complementary Fourier transform infrared analyses, the leaching behavior in the glasses is most closely related to the 'bulk' glass structure. The glasses with Al_2O_3 have two sites for sodium ions (and presumably for H^+ or H_3O^+ ions): namely, non-bridging oxygen (NBO) sites $\text{jSi-O}^-\text{Na}^+$ and charge deficient aluminate sites $(\text{AlO}_4)^-\text{Na}^+$. The data indicate that the non-bridging oxygen sites (e.g., glass with x=0 has all Na at NBO sites) more readily release Na--and capture a hydrogen bearing species--than do the charge deficient aluminate sites. One seriously questions the importance of ion-exchange mechanisms during corrosion since these aluminosilicate glasses (sometimes called ion-exchange glasses) show reduced leaching kinetics. It is not unlikely that the non-bridging sites play an important role in reacting with molecular water, and thereby enhance the reaction between aqueous solutions and alkali silicate glasses.

The ability to measure sodium and hydrogen profiles such as those in Figure 4.2 is important for understanding leaching mechanisms. These profiles reveal that some of the alkali in glasses containing Al_2O_3 is not released from the surface and that this may be related to an important reaction between molecular water and the glass structure. In the more complex multicomponent nuclear waste glasses, on the other hand, it is much more difficult to attribute hydrogen penetration to interaction with any one species or molecular

FIGURE 4.2. Hydrogen and Sodium SIPS Depth Profiles at 60°C for the Leached Surfaces of Various Sodium-Aluminosilicate Glasses, all of Which Have the Same Molar Concentration of Na_2O

site. Perhaps the major advantage of measuring the hydrogen profile in waste glasses would be to show the maximum depth of reaction between the aqueous phase and the glass.

In practice, of course, there are some severe limitations associated with SIMS or SIPS depth profiling. This becomes particularly evident when one wishes to use the profiles for more than a qualitative characterization of the surface. The difficulties associated with quantitative analysis, and the potential for sputtering artifacts, are common regardless of the material under investigation. However, the problems associated with 'charging,' and its effect upon the measured depth profiles, can be especially severe in the case of multicomponent oxide glasses. The proper interpretation of hydrogen

profiles in leached and/or hydrated glass surfaces is also a point of major concern. And, the effects of a spatially nonuniform surface composition due to precipitation and surface microstructure, must be considered in the interpretation of depth profiles.

The remainder of this discussion will assume that the primary objective of a SIMS or SIPS analysis on nuclear-waste glass is the acquisition of an in-depth profile of 'gel' or other surface reaction layers. In this regard, the important instrumental features, methods of quantitative analysis and problems associated with the application of SIMS to nuclear waste glasses are addressed (see reference 1 for a general discussion of surface analysis techniques and their relative applicability for characterization of glass and ceramic materials).

4.5.2 Instrumentation

Unlike many of the other surface analysis methods, SIMS analyses and instruments are far from standardized. It cannot be emphasized enough that the quality of any SIMS analysis is very dependent upon the design and operation of the instrument (Magee et al. 1978).

The key feature of the SIMS instrument to be used for depth-profiling is an energetic, high current density primary ion beam (this is in contrast to the low energy, low current density broad, beams used for 'surface analyses'). The primary ion beam must be focused to a fine probe and rastered over the surface to produce a flat bottomed crater. The uniform erosion of the sample--that is, in the form of a flat-bottomed crater--is absolutely crucial since it determines the depth resolution of the measured concentration profile. Of equal importance is the ability to distinguish between secondary ions which originate from the bottom of the crater--and hence from some well-defined depth in the sample surface--versus secondary ions which originate from the walls and periphery of the crater. This distinction is most conveniently accomplished by 'raster-gating' wherein the detection system is synchronized with the rastered-primary ion beam. When the primary ion beam is at the periphery of the crater, the detection system is electronically 'grated-off.' Thus, the measured depth profile is constructed from only those secondary ions which originate in the central region of the crater area; typically, the region from which ions are

collected is about 9-16% of the total crater area. The ability to uniformly erode that central area--and thereby maintain a flat-bottom--requires a finely-focused, high current density primary ion beam. Ideally, the primary beam diameter should be one-tenth the diameter of the raster pattern. If the primary ion beam is 50 to 100 μm in diameter, the raster pattern need only be 1 mm on a side. These conditions not only provide a flat-bottomed crater, but offer the practical advantages of multiple analyses on the same sample. The ability to perform multiple analyses on the same sample is especially beneficial in those very common instances where unstable charging requires that the analysis be repeatedly terminated and reinitiated. Small-area depth profiling permits the maximum utilization of a specimen.

Another instrumental feature of concern in depth profiling of leached nuclear waste glass surfaces is the relationship between spectral resolution and detection sensitivity. The inability to simultaneously achieve high detection sensitivity and high spectral resolution is common to most analytical techniques. However, the problem is especially severe where quadrupole mass spectrometers--combined with electrostatic energy filters--are used to simultaneously monitor low and high mass species. Typically, the best settings of the energy filter for low mass species are different than those for high mass species. Similarly, the mass spectrometer conditions which optimize the detection sensitivity for heavy species--like Cs^{133} and U^{238} --degrade the resolution required to simultaneously monitor H^1 , Al^{27} , Si^{28} , etc. Here again, the advantages of multiple analyses on the same sample are evident. A common procedure in our laboratory is to collect one set of data optimized for the lighter elements, and then another set of data from the same specimen for the heavier elements.

Another feature of the instrument which is of importance is the vacuum level. Although routine SIMS analyses of oxide glass are not especially sensitive to the vacuum, the analysis for hydrogen is extremely sensitive to vacuum. The presence of high backgrounds due to the H_2 and H_2O can have a dramatic effect upon the measured hydrogen profile. We have found that vacuum levels of the order 1×10^{-9} torr or less are required to obtain a meaningful hydrogen depth profile.

4.5.3 Quantitative Analysis

The generation of quantitative in-depth profiles requires calibration of the sputtering rate and the secondary-ion intensities. The sputtering rate is needed to calibrate the depth scale while the secondary-ion intensities must be calibrated to obtain absolute, or relative, concentrations. Unlike many of the other depth profiling techniques, these two parameters are interdependent; i.e., the measured secondary ion intensity for a particular element, $i_{s,i}$, is a function of the sputtering rate, S , as well as the concentration C_i . This is an especially important point in the interpretation of depth-profiles for leached glass surfaces because the sputtering rate of the surface 'gel layer' can be very different from that of the bulk glass. We have used silica-gel thin films (prepared by a sol/gel technique) to show, for example, that the sputtering rate of the leached layer on 76-68 glass is about two times larger than that of the bulk 76-68 glass.

The important effect of sputtering rate upon SIMS depth profiles is shown schematically in Figure 4.3 where we consider the hypothetical profile for species i in a 'gel' layer (Case 1) with the profile for a dense glass layer of the same thickness and containing the same concentration of species i (Case 2). Qualitatively, the profiles are very different; that is, the profile for Case 1 suggests that the gel layer is thinner than the dense glass layer and contains a higher concentration species i . Of course, the profile can be corrected providing that the relative sputtering rate for the dense glass and gel glass are determined via an independent measurement. That is, the measured secondary ion intensity for species i in the gel layer can be multiplied by the ratio of sputtering rates, $S(\text{glass})/S(\text{gel})$, to correct for the sputter rate effect upon $i_{s,i}$. The x-axis can be converted directly to depth if $S(\text{glass})$ and $S(\text{gel})$ are known. In the hypothetical example of Figure 4.3, the correction makes the profile for Case 1 identical to Case 2 since the absolute concentrations of i were assumed equal in the two layers of equal thickness.

Once the effect of the 'gel' layer structure and density upon the sputtering rate have been corrected, any real differences between the concentrations of i in the 'gel' layer and bulk glass are reflected in $i_{s,i}$ (corrected). These corrected values of the secondary ion intensities can be

FIGURE 4.3. Schematic Representation of the Relationship Between the Secondary Ion Count Rate and Sputtering Time for Species i in Films Whose Sputtering Yield Changes Without a Composition Change. The films have the same thickness; species i is present in the film, but not in the substrate (e.g., H).

converted to concentrations using 'standard' calibration curves or by normalizing the measured secondary ion intensities in the 'gel' or other surface reaction layer to those measured in the bulk glass. (We assume here that the ionization probabilities in the surface layer are the same as those in the bulk glass.) We have already shown that the secondary ion intensity for minor constituents in glass is linear with the concentration (Pantano et al.) Thus, calibration of the secondary ion intensity can be accomplished using the secondary-ion intensities measured on a fresh fracture surface of the unreacted glass or after sputtering through the 'gel' or other surface reaction layers.

In an effort to demonstrate these effects, consider the 'raw' profiles for the Soxhlet leached waste glass in Figure 4.1. Since the gel layer sputters approximately twice as fast as the bulk glass, the profiles should be corrected. Here, only the Cs^+ and Zr^+ profiles have been corrected (for clarity) and are shown by the dotted lines.

One last point of concern regarding the quantitative interpretation of depth profiles is the effect of surface nonuniformity and microstructure. Of particular interest here is the nonuniform distribution of precipitates or other reaction products on the leached layer. Since these features are generally much smaller than the rastered area, their contribution to the

profiles are 'averaged in' with the profiles of species in the underlying leached layer. Moreover, they can appear to be incorporated into the leached layer since they may sputter very slowly. Thus, one must be cautious in the interpretation of profiles for surface 'enriched' species which have long 'tails' extending into, or even through, the leached layer.

4.5.4 Charge Neutralization

In a practical sense, the 'charging' of insulating glass and ceramic specimens is the most severe limitation of SIMS. Nonetheless, charge neutralization can be achieved by simultaneously directing an electron beam at the ion bombarded region. Since it is impossible to predict the exact conditions required for charge neutralization, the procedure is necessarily empirical. Thus, the neutralizing electron beam current and beam current density are adjusted to maximize the $^{28}\text{Si}^+$ secondary ion signal. The sample is then translated slightly to provide a new area of the sample surface for analysis. Most importantly, the charge neutralization is checked periodically during the acquisition of depth profiles. In the event that the secondary ion signals are not at their maximum values, the analysis is terminated and re-initiated on a new area of the specimen. While there is no reason, a priori, to believe that maximization of the signals is an indication of complete charge neutralization, it is the only procedure that has provided any measure of success. In this regard, it is significant that these maximized signals are reproducible to within 5% from sample to sample of the same composition. Routinely, a polished or fractured glass specimen is included with each loading of 'leached' glass specimens. These are used to verify the proper set up and operation of the charge neutralization system. Unfortunately, experience, trial-and-error, and perseverance are the only available approaches to 'charging' problems in SIMS.

An unfortunate consequence of the electron beam neutralization used during SIMS analysis of oxide glasses is the high background due to electron stimulated desorption (ESD). The species most susceptible to ESD is hydrogen. For example, even though the ion beam may be a sputtering material characteristic of a region 5000 Å below the original surface (i.e., the crater is 5000 Å deep), the neutralizing electron beam simultaneously desorbs hydrogen

from sample surface; very often, the desorbed hydrogen originates from the periphery of the crater. This constitutes a hydrogen background because the desorbed hydrogen is ionized and can enter the mass spectrometer. The background due to ESD at a leached glass surface often exceeds the true hydrogen signal due to secondary ion emission. This is the primary reason SIPS is used to measure hydrogen profiles at leached glass surfaces. SIPS does not require electron beam neutralization of the sample surface.

4.5.5 Hydrogen Profiling

It is clear that hydrogen can exist in glass in two forms. In one case, it is associated structurally with the glass network (Si-OH), whereas in the other case it is present as a free molecule (e.g., H₂O, H₂, etc.). Here, of course, particular attention is drawn to the distinction between SiOH,, SiOH·nH₂O, and H₂O. Molecular water may be liberated in the ultra-high vacuum required for surface analysis. In contrast, the "structural water" (SiOH) can be liberated only through a condensation reaction: $2(\text{Si}\cdot\text{OH}) \rightarrow \text{Si}-\text{O}-\text{Si} + \text{H}_2\text{O}$. Thus, it is emphasized that the quantitative, and in many cases qualitative, measurement of hydrogen depth profiles in glass can be complicated by the time-dependent release of molecular water.

Simple experiments have shown conclusively that the hydrogen profile can be a function of its time in ultra-high vacuum prior to measurement. Since the amount of water (nH₂O) incorporated into a glass, or produced in a condensation reaction, will vary with hydration conditions and the glass composition, any attempt to quantitatively measure hydrogen concentrations using surface-analysis techniques must account for this effect. In fact, molecular water may be liberated from extensively hydrated surfaces under ambient conditions (e.g., subsequent to the hydration experiment but prior to loading in the analysis system). For example, Figure 4.4 presents the changes obtained in the hydrogen profile (SIPS) during a 40-h period in vacuum. One solution to this problem is to use a cold stage to lower the temperature of the sample immediately after it is loaded into the vacuum system. Clearly, one must be cautious regarding the interpretation of hydrogen profiles in general, and in particular where

FIGURE 4.4. SIPS Depth Profiles for Hydrogen in a Glass Containing Bulk Water; the Effect in Time in Ultra-High Vacuum is Indicated

quantitative analysis is used in an attempt to distinguish the form of the protonated species (H^+ versus H_3O^+), the degree of hydration (nH_2O), and the reaction mechanism.

Nonetheless, it may be possible to use the release of water in vacuum and its influence on the measured hydrogen profile to obtain additional information about the hydration process. We found, for example, that the 'air-side' surface of weathered float glass had a much lower hydrogen concentration than the 'tin-side' surface (Pantano 1981), even though the sodium depletions were comparable. Optical spectra showed the presence of an anti-reflection film on the air-side surface. Thus, it was suggested that molecular water was liberated from the air-side surface (prior to the analysis) because of the existence of an extensively hydrated microporous surface film. In contrast, the tin-side surface film may contain only structural water since the hydrogen profile was 'stable' in vacuum.

4.5.6 Sputtering Effects

Any depth profiling technique which involves ion sputtering can introduce distortions in the measured profile. Of particular concern in the case of nuclear waste glasses are ion bombardment induced migration of glass modifiers and differential sputtering.

It has already been pointed out that 'charging' of glasses during SIMS analysis is a major source of concern. Even though the 'charging' can be sufficiently neutralized with an electron beam to permit the acquisition of depth profiles, local electric fields in the glass surface--induced by either or both the electron and ion beam--can cause mobile ions in the glass to migrate during the analysis. This can most certainly distort the true in-depth profile. This problem can also be alleviated by cooling the sample with liquid nitrogen during the analysis. This should reduce the mobility of the glass components and thereby prevent significant distortion. An alternate approach involves the utilization of 'neutral' primary beams. To this author's knowledge, neither of these precautions have been implemented in any depth-profiling analyses of nuclear waste glasses.

In multicomponent oxide glasses it is likely that the sputtering yield for the various glass components will be different. This 'differential' sputtering effect can introduce distortions in the depth profile measured by SIMS and perhaps, more so, in the profiles obtained with XPS and AES (Pantano). The sputter yield is related to the bonding configuration and to the mass of the specie of interest. Clearly, the difference in bonding between modifier species and network species in oxide glasses, as well as the multitude of atomic masses in nuclear waste glasses, makes this a problem of general concern. The effect can be investigated by examining 'clean' or 'ideal' glass surfaces. These surfaces are best created by fracturing bulk glass. Although these surfaces are best created in vacuum, we have already shown that durable glasses may be fractured in air and immediately placed in the vacuum chamber. In either case, these surfaces should exhibit featureless in-depth profiles except for the distortions introduced by the sputtering process. We have shown, however, that these ideal surfaces do, in fact, exhibit profiles--in

SIMS and AES (and probably XPS)--due to ion-bombardment induced distortions (Pantano). The use of a simple two-component glass should facilitate the explanation of these sputtering effects.

Consider, for example, the 'ideal' surface of a two-component glass consisting of SiO_2 and SnO_2 is the minor constituent. Assume further that the sputter-induced changes in surface composition are due solely to differential sputtering. That is, the sputtering yield of SnO_2 is greater than that of the SiO_2 ; a sputter rate for SnO_2 which is 4 times that of SiO_2 is a reasonable estimate. Thus, the initial flux of sputtered particles, and therefore the secondary ion signal, is enriched in SnO_2 relative to the true surface composition. At the same time, the outermost atomic layer(s) is very rapidly depleted in SnO_2 to compensate for the enhanced sputter yield of the SnO_2 ; i.e., the flux of sputtered particles is stoichiometric with the bulk composition of the material. At this point, the surface achieves the so-called steady-state (or equilibrium) sputtered surface composition. In the absence of other effects, it can be represented simply by:

$$\frac{C'_{\text{SnO}_2}}{C'_{\text{SiO}_2}} = \frac{C_{\text{SnO}_2}}{C_{\text{SiO}_2}} \cdot \frac{S_{\text{SiO}_2}}{S_{\text{SnO}_2}}$$

where C' is the steady state surface composition, C is the initial surface composition, and S is the sputtering rate. The approach to steady-state, again in the absence of other effects, will be exponential with time; the time constant for the process should be of the order $S_{\text{SiO}_2}/S_{\text{SnO}_2}$ monolayers. In the present hypothetical case, the depletion of SnO_2 , and corresponding reduction in the SIMS signal, should occur within 5.0 nm. Obviously, one could mistakenly interpret this 'distorted' profile in terms of 'enrichment' of SnO_2 at the surface. (It may be worth noting that if the sputter rate of the minor constituent is less than that of the major constituent, the minor constituent will accumulate in the sputtered surface. Here, the approach to steady state would exhibit a somewhat longer time constant and suggest 'depletion' of the component in question.)

This simplified model can also be used to interpret the ion bombardment induced surface composition changes exhibited in AES or XPS sputter profiles. In this case, the first surface composition measured by AES or XPS--prior to any sputter etching--provides the most accurate measure of composition. Upon ion sputtering, the outermost atomic layers are rapidly depleted in SnO_2 . Thus, the AES or XPS spectra acquired as a function of sputtering time are a measure of the approach to the steady-state sputtered surface composition.

One can conclude that depth profiles obtained with SIMS are valid once the steady-state sputtered surface composition has been reached. Since the range of most depth profiles in leached glass surfaces extends far beyond the 50 nm required to achieve steady state, one is seldom concerned with this effect in SIMS profiles obtained for the polished surface of Formula 127 nuclear waste glass. The distortions observed within the first 50 nm of the profile are due to those sputtering effects and the polishing process. They are distortions which would cause problems if a 'true' surface analysis were of interest. However, since an in-depth analysis of the leached layer is of primary concern in the case of nuclear waste studies, these can be ignored here. Thus, the profiles in Figure 4.5b for this same glass after a 28-day static leach extend far beyond the distorted region of the profiles. On the other hand, when the surface adsorption of solution species is of concern, the profile for the adsorbed species and the profile due to this sputtering effect may be indistinguishable.

It should also be noted that this sputtering effect can introduce severe distortions in AES or XPS sputter profiles. This is because depth profiles acquired with AES or XPS analyze the 'sputter-distorted' surface layer. For example, the enrichment of Ca often observed at lime-containing silicate glasses surfaces is most certainly a 'differential' sputtering effect (Pantano).

4.5.7 Summary

In view of the difficulties associated with SIMS depth profiling, it is not surprising that the technique has seen limited application for studying the leached surfaces of nuclear waste glasses (McIntyre et al. 1980; Tait and Jensen 1982; Buckwalter et al. 1982; Houser et al. 1979). Nonetheless, it is this author's opinion that SIMS and SIPS (Houser et al. 1979) depth profiles

(a)

(b)

FIGURE 4.5. SIMS Depth Profiles for Formula 127 Glass (a) Before and (b) After Static Leaching

are useful for characterization of the leached surfaces of nuclear waste glasses. In spite of the problems associated with quantitative analysis, it is possible to readily distinguish between those species which accumulate in the surface reaction layer and those which are depleted readily distinguish between those species which accumulate in the surface reaction layer and those which are depleted. This is perhaps the major advantage of SIMS depth profiling in leached glass surfaces. Moreover, it is the only method which possesses sufficient detection sensitivity for analysis of minor and trace constituents of the glass. It is also the only method capable of detecting hydrogen, although the acquisition of meaningful hydrogen profiles is more than a routine analysis. It is perhaps safe to say that since quantitative interpretation of SIMS depth profiles in leached nuclear waste glasses require a major effort, SIMS may be most useful as a qualitative complement to other analytical methods.

4.5.8 References

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4.6 APPLICATIONS OF FOURIER TRANSFORM-INFRARED REFLECTIVE SPECTROSCOPY (FT-IRRS) -- D. E. Clark and L. L. Hench

4.6.1 Introduction

The ultimate reliability of nuclear waste glasses will depend upon the rates of interaction of repository ground waters with the glass surface and other materials present in the storage system. The number of interfaces involved in storage systems is large, as is the potential range of temperatures, flow rates or residence times, and ground water chemistries. However, most data acquired to date upon which to base predictions of glass leaching mechanisms and rates involves simple static or flow experiments using D.I. H₂O in contact with small glass samples or powders. It is essential to expand these simplified leaching studies to include simulations of the interfacial interactions that will be present in a repository. The objective of this paper is to review briefly results of two general approaches being taken to understand glass surface behavior in repository like conditions.

The first approach involves laboratory simulations of glass-rock interactions. In these studies, variables that are potentially important in repository conditions are examined individually and then combined to determine whether synergistic effects occur. An advantage to the laboratory simulations of glass-rock interactions is that changes in solution chemistry as well as the glass surface can be monitored and used in modeling predictions. A disadvantage is that many factors associated with an actual repository environment are difficult, if not impossible, to be simulated in the laboratory.

The second approach is to bury glass samples with interfaces between the glass and various components of the storage system artificially created prior to burial. Comparison of reaction rates between thermal and nonthermal periods of storage are possible by use of heater rods in the experiments. An advantage of this approach is that equilibrated ground waters of the burial site provide the medium for the glass interfacial reactions. Also, a large number of interfacial combinations can be studied, all under identical conditions. Thus statistically based comparisons of the relative importance of various factors can be made. The major disadvantage of this approach is the difficulty of obtaining solution chemistry of the water after it has interacted with the

glass. Thus analyses of rates of change of the glass surface is the basis for interpreting both the kinetics and mechanisms of the interfacial reactions that occur.

Because of the inherent advantages and disadvantages of laboratory and in-situ burial experiments it is necessary to conduct both types of studies and relate their results. Either alone will be unlikely to produce the necessary confidence in long range prediction of nuclear waste glass performance in an actual repository.

4.6.2 Variables Affecting Static and Flow Glass-Water-Interactions

The majority of glass corrosion research has involved the utilization of static testing. In this test the glass samples are immersed in an aqueous solution with a constant volume of water, V , and sample surface area, SA . Although some liquid may escape, most of the original volume of water remains in contact with the glass during testing and there is no flow of solution into or out of the cell.

Under certain conditions it is possible that ground water will flow through a geological repository containing HLW and react with its contents. Although flow rates of up to several hundred L/yr have been reported for some repositories it is thought that flow rates of approximately a few L/yr are most likely. The purpose of this and the following section is to discuss the relevance of flow rates, SA/V , cell volume, temperature, and glass/rock interactions on glass corrosion based on laboratory experiments. The final section will present data obtained from several glass compositions buried in granite at the Stripa Mine in Sweden. Eventually these field tests will be expanded to include other types of repositories both in the U.S. and abroad. The major objective is to establish a correlation between corrosion observed in the field and that observed in the laboratory so that the number of costly burial experiments can be held to a minimum. In order to achieve this objective the relative importance of experimental parameters in the laboratory must be understood.

Figure 4.6 illustrates the experimental setup used in our laboratory. Deionized water with an initial pH $\approx$ 5.6 at 25°C (due to saturation with atmospheric CO₂; the pH is $\approx$ 6 at 90°C) is passed from a large reservoir via a peristaltic pump through a 60 mL teflon cell containing the glass (inside an oven) and finally into a polyethylene collection container. The flow rate through the cell may be varied from a 0.1 mL/hr ($\sim$ 1 L/yr) to several hundred mL/hr, or the pump may be removed from the system to provide a static test. The volume of the cell and the sample surface area can also be changed. These options give a wide range of Sa/V and resident times (i.e., the time required to completely replenish the solution in the corrosion cell). This test is similar to the single pass MCC-4 flow test (MCC Test Methods). Solutions are collected and analyzed for pH and composition at regular intervals depending on the flow rate. Mass loss and surface analyses are also performed on samples after they are removed from the system. For rapidly flowing conditions ($\sim$ 1 mL/hr) the temperature of the oven is increased to give the desired temperature inside the corrosion cell.

Total mass loss versus corrosion time is shown in Figure 4.7 for SRL 131-298% TDS-3A at several flow rates at both 70°C and 90°C. Each data point is an average of two samples and corresponds to the removal of those samples from the system. As expected the corrosion rate was lower at 70°C than at 90°C under both static and flowing conditions. Due to the very low release rates at 70°C the tests were halted after 14 days and our efforts were focused on the 90°C tests. Very little, if any, difference in the rate of the total mass loss was observed during the first several days of exposure regardless of the flow rate. After seven days the rate of mass loss continued to increase for the 9 L/yr (residence time = 60 h), 90 L/yr (residence time = 6 h) flow rates, but leveled off to a value of $\sim$ 9 g/m² for Si and Li, 7 g/m² for Na, and 12 g/m² for B after 7 days exposure. These values are consistent with the mass loss based on weighing and suggest saturation of the elements in solution, with the exception of B. The increased B release probably is due to a rapid increase in its solubility at a pH of about 7.5 as reported by Fox (1980). The pH of the solutions in these low flow tests was 7.8. In contrast, the normalized elemental mass loss in the rapid flow experiment (90 L/yr) increased continuously over the duration of the experiment and at the end of 28 days the

FIGURE 4.6. Flow Experiment Diagram

FIGURE 4.7. Total Mass Loss Versus Corrosion Time for SRL Glass at Several Flow Rates and Temperatures

cumulative values were Si = 49 g/m², B = 24 g/m², Na = 81 g/m², and Li = 64 g/m² indicating selective leaching for Na and Li, and a suppressed dissolution for B. In these solutions the pH remained less than 7 over the duration of the experiment and normalized elemental concentration inside the cell never exceeded 9 g/m². These data suggest that solution concentration effects which slow down corrosion processes (Clark and Hench 1982) are relatively unimportant when mass loss is less than 9 g/m². It should be emphasized that this value is both element and pH dependent. The close agreement between the total mass loss based on weighing and the normalized Si loss for all flow conditions probably is due to the large % of Si present in the glass (58 wt%) and the fact that Si does not selectively leach. Surface film formation also probably is partially responsible for the reduced rate of

corrosion observed after seven days of exposure for the low flow condition. Samples are now being analyzed by surface techniques to determine the relative importance of solution concentration and surface film formation in slowing down the corrosion process. Wicks (1982) has found that in a recirculating system films form on glass surfaces even under high flow rates. However, in such a closed system solution concentration effects and surface film formation should be relatively independent of flow rate over long times.

Figure 4.8 presents a schematic of corrosion rate versus flow rate illustrating three regions of behavior. Region I corresponds to an increase in corrosion rate with flow rate due to a reduction in solution concentration effects. As the flow rate increases the concentrations of various elements are decreased well below their solubility limits and their contribution to the corrosion rate increases. The last to contribute to the corrosion rate are those elements with extremely low solubilities such as Al and Fe (Paul and Aman 1978). At low flow rates the pH of the solution in contact with the glass may change appreciably and influence the solubility limits. Thus, at low flow rates the shape of the curve is controlled by both solution concentration effects and pH. The role of pH is expected to decrease more rapidly than solution concentration effects as the flow rate is increased. In Region II the flow rate is so large that the glass effectively is in contact with an infinitely dilute solution, so solution concentration effects and pH excursions are minimal and corrosion rate is controlled by glass corrosion reactions. Region III corresponds to a situation in which the flow rate is so high that mechanical erosion of the glass by water and/or abrasive constituents is important.

The flow rate ranges corresponding to each of the regions in the figure are based on results reported by Wicks (1982) and on data generated in our laboratory. Region I is thought to represent the most likely repository conditions. In this region the corrosion rate is dependent on SA/V, temperature, flow rate, and cell volume. Additionally, the manner in which SA/V changes are obtained must also be specified. Decreasing the SA/V while

FIGURE 4.8. Corrosion Rate Versus Flow Rate illustrating Three Regions of Behavior

maintaining constant cell volume will decrease the flow rate required to enter Region II. However, changing the cell volume while maintaining a constant SA should have no effect on the transition flow rate delineating Regions I and II. Moreover, the same SA/V can be achieved by an infinite number of combinations of SA and V. For instance, $SA/V = 0.1 \text{ cm}^{-1}$ may be obtained with $SA = 2.5 \text{ cm}^2$ and $V = 25 \text{ mL}$ or $SA = 25 \text{ cm}^2$ and $V = 250 \text{ mL}$. Under identical flow rates the residence time is a factor of 10 greater in the latter case. Thus, in a corrosion experiment it is necessary to specify cell volume in addition to SA/V, temperature and flow rate. Alternatively, SA/V, temperature and residence time can be specified.

The thickness of surface film that forms on the glass is dependent on SA/V. Increasing the SA/V will decrease the film thickness when other conditions are held constant, and under rapid flow conditions thin films may not be as protective as thick films. A series of experiments is underway in

our laboratory to evaluate the relative importance of SA/V, temperature, flow rate, and cell volume on surface film formation and corrosion rates (see Table 4.5).

4.6.3 Glass-Rock-Water Interactions (Laboratory Studies)

The experimental setup used in our laboratory for glass-rock-water interactions studies is shown in Figure 4.6. It is the same as that used for evaluating glass corrosion in deionized water, but with the addition of a rock sample to the corrosion cell. The SA/V is based only on the glass sample but the SA of the rock is the same as for the glass. Table 4.6 presents data obtained in a static test conducted at 25°C for 4 months. Rock types investigated were granite and tuff. Compacted bentonite was also investigated because of its importance in several international nuclear waste programs. Mass loss and solution data clearly indicate that the presence of bentonite accelerates the rate of corrosion. These data also suggest that tuff may slightly decrease the corrosion rate. FT-IRRS and optical microscopy confirmed an accelerated attack by bentonite but these analyses were inconclusive for the materials.

Other experiments are now being planned with tuff, granite, basalt and salt at 90°C under a variety of SA/V, flow rate and cell volume conditions. The defense waste reference glass (DWRG) will be used for these experiments. They will be initiated upon completion of the flow tests listed in Table 4.5.

A large number of waste form corrosion studies have been conducted in other laboratories but only a few of these have involved the use of real ground water or rocks immersed in the same solution as the waste form. Although the use of synthetic ground waters are specified in the MCC corrosion tests (MCC Test Methods) these may not be representative of actual repository environments where solutions effects, E_h , and multicomponent interactions may dominate. In a repository environment the waste form will most likely come into contact with ground water equilibrated with rock, overpack, backfill and canister materials. With only a few exceptions a sufficiently large data base does not exist to say conclusively what effect the presence of repository materials will

TABLE 4.5. Flow Experiment in Progress (Glass Only)

<u>Temp (°C)</u>	<u>SA/Y (cm⁻¹)</u>	<u>F.R. (mL/hr)</u>	<u>Cell (Vol mL)</u>	<u>Residence Time (hrs)</u>	<u>Extent of Experiment Total Days</u>
90	0.2	1	30	30	28
90	0.05	1	60	60	28
90	0.2	0.5	30	60	28
90	0.05	0.5	60	120	28
90	0.2	2.0	30	15	28
90	0.05	2.0	60	30	28
90	0.1	0.5	30	60	28

Flow Experiments Completed (Glass Only)

90	0.1	0.1	60	600	28
90	0.1	1.0	60	60	28
90	0.1	10.0	60	6	28
90	0.1	Static	60	28 Days	28
70	0.1	1.0	60	60	14
70	0.1	10.0	60	6	14
70	0.1	Static	60	14 Days	14

have on the corrosion performance of the waste form. Specifically, brine solutions and bentonite have been shown to respectively decrease (Wicks et al. 1982; Hermansson et al. 1982) and increase (Werme et al. 1982) the rate of glass corrosion. In the case of brine solutions, a protective magnesium chloride complex forms on the glass surface (Hermansson et al. 1982) while the presence of bentonite appears to accelerate the ion exchange mechanisms of glass corrosion (Werme et al. 1982).

Table 4.7 provides a summary of laboratory and field waste form-rock-water interaction studies that have been performed over the last few years. This table is not exhaustive and does not include many of the tests conducted with only synthetic ground water solutions. However, the significant fact is that even though effects on glass corrosion have been observed in these studies, they have not been quantified. There appear to be several contributing factors to the absence of quantitative data:

TABLE 4.6. Glass/Rock Interactions

SRL 131 + 30 wt% TDS-3A with various rocks

Temp: 25°C

Time: 4 month

Test: Modified MCC-1

	pH	Normalized Mass Loss	g/m ²			
			Si	B	Na	Li
Glass Alone	7.41	3.53	2.19	2.18	2.81	1.62
	7.48	3.48	2.45	2.18	3.11	2.15
	7.47	4.43	2.55	2.8	3.01	2.15
Average	<u>7.45</u>	<u>3.81</u>	<u>2.40</u>	<u>2.39</u>	<u>2.98</u>	<u>1.97</u>
Glass/Tuft	6.25	2.30	1.53	1.87	3.01	1.08
	7.07	3.68	1.79	2.49	3.31	1.61
	5.52	3.43	3.11	2.80	4.22	2.69
Average	<u>6.28</u>	<u>3.14</u>	<u>2.14</u>	<u>2.39</u>	<u>3.51</u>	<u>1.79</u>
Glass/Granite	7.52	4.89	3.11	3.43	3.92	2.15
	7.58	5.52	3.16	4.05	4.12	2.15
	7.55	5.21	3.14	3.74	4.02	2.15
Average	<u>7.55</u>	<u>5.21</u>	<u>3.14</u>	<u>3.74</u>	<u>4.02</u>	<u>2.15</u>
Glass/Bentonite	8.48	7.07	7.65	6.54	90.4	3.23
	8.50	6.39	7.86	6.54	77.8	2.69
	8.49	6.73	7.76	6.54	84.1	2.69
Average	<u>8.49</u>	<u>6.73</u>	<u>7.76</u>	<u>6.54</u>	<u>84.1</u>	<u>2.69</u>

1. the lack of well characterized reference rocks representative of typical potential repositories
2. the lack of standard tests specifying systems parameters
3. the lack of sufficient field tests and data to assist in the design of practical laboratory experiments
4. direct correlation of corrosion rate with solution data is difficult because species found in solution may be common to both the glass and the rock, and species may precipitate onto the rock during exposure. Thus, both the glass and rock must be analyzed in addition to the solution of the conclusion of the experiment.

TABLE 4.7. Waste Form/Rock Interactions (Laboratory)

Waste Form	Rock	Conditions	Authors	Year	Ref.	Rock Effect
Glass Ceramic Spent Fuel	Shale	100-400°C 30 MPa	Freeborn, et al.	1982	1	
76-68 Minican	Basalt Granite	250°C 200 psi	Bradley, et al.	1981	2	Yes Greatest + for Basalt
76-68	WIPP Brine (SOLN)		Chick, et al.	1979	3	Yes Element Dependent
76-68	Basalt Salt	350°C	Westsik, et al.	1978	4	Yes
Synroc	Brine	110°C	A. Solomah et al.	1980	5	-
SRL-131 +30% TDS	Shale Basalt Granite Tuff	90°C	Wicks, et al.	1982	6	Yes Greatest + for Salt
U.K. 189 Glass	Granite	60°C	Hall, et al.	1982	7	-
U.K. 209/M22 Glass	Granodiorite	100°C 50 MPa	Savage, et al.	1982	8	-
6 Belgian Glasses	Clay	40°C- 200°C	Iseghem, et al.	1982	9	Yes
Glass-Ceramic Ceramic	Granite		Hayward, et al.	1982	10	Yes +

TABLE 4.7. (contd)

Waste Form	Location Rock	Conditions	Authors	Year	Ref.	Rock Effect
SRL-21	Granite Obsidian Basalt Chert Phosphate Clay	90°C	Clark, et al.	1982	14	-
					16	-
KBS 39	Brine Soln Silicate Soln	90°C	Hermansson, et al.	1982	18	Yes Brine + Silicate +
Glass	Chalk River Sand	Ambient	Merritt, et al.	1963	11	-
HLW Glass	Sand	Ambient 15 yr	Merritt, et al.	1976	12	-
Glass	Soil England	Ambient 2 yr, 9 yr	Fletcher	1974	13	-
KBS Glass	Granite Stripa	Ambient, 90°C 1 mo, 1 yr	Werme, et al.	1982	17	Yes +
SRL 131+30% TDS SRL 164+30% TDS	Granite Stripa	Ambient 1 mo, 2 yrs	Clark, et al.	1983	In Progress	-

- Unknown

4.6.4 In-Situ Burial Experiments

Savannah River Laboratory-UF-KBS

Preliminary results from a joint SRL/KBS-Weden/U.F. burial experiment are reported in this section. These glass compositions were prepared by SRL; 131-29.8% TDS-3A, 16S-29.8% TDS-3A, and 165-35% TDS-3A. The sample configurations used were pineapple slices and mini-cans and are described in detail by Hench et al. (1982). Each sample was analyzed by FT-IRRS and optical microscopy prior to assembly. A typical pineapple slice assembly containing glass, granite, bentonite, and various metals prior to burial is shown in Figure 4.9. This configuration provides several types of interfaces including glass/glass, glass/rock, and glass/metal. A heating rod may be placed in a 20 mm diameter hole running lengthwise down the center and temperatures of 90°C can be maintained for long times. Both mini-can and pineapple slice assemblies were buried at the STRIPA mine in central Sweden in August 1982. The assemblies were placed in holes 56 mm in diameter and approximately 7 m deep at a depth of 345 m below the surface. The holes were filled with ground equilibrated mine water (initial pH = 8.1) before inserting the samples. Flow rates through similar holes located elsewhere in the mine were approximately 1 L/yr. Some of the samples were heated to 90°C. The increase in pH of the water in the hole after sample removal was less than 1 unit. Water was also collected for analysis after the samples were removed from the hole.

Preliminary FT-IRRS data are shown in Figure 4.10 for the 1 month-90°C mini-can samples containing SRL 165-29.8% TDS-3A waste. These data show that the greatest corrosion rate occurred at the glass/bentonite interface. Optical micrographs confirmed this result. Other data suggest that the corrosion rate was greater on SRL 131-29.8% TDS-3A than on SRL 165-29.8% TDS-3A. Analysis of the 1 month samples will be completed in January 1983. The remaining assemblies will be removed at 3, 6, 12 and 24 month intervals. Samples of these same glasses will be corroded in the laboratory under controlled conditions simulating the granite repository in order to obtain the correlation between laboratory and field data.

FIGURE 4.9. The Pineapple Slice Assembly Used for the One Month 90°C Test. Pre-Burial.

FIGURE 4.10. Preliminary FT-IRRS DATA for Samples Buried of One-Month at 90°C

4.6.5 In-Situ Burial Experiments: KBS-UF Project

Two configurations of samples are being used in the Swedish project KBS to examine glass-repository interactions in an in-situ STRIPA burial experiment. One involves use of minicans where the glass is cast into stainless steel and the second is the so-called "pineapple slices." Both are described in previous publications. A center hole is provided in the samples in order to accommodate a heater rod. Two compositions of glass are compared in the experiments (Table 4.8).

Assemblies of minicans and pineapple slices are inserted into 56 mm diameter boreholes at the 350 m level in the granite STRIPA mine. Half of the assemblies are maintained at 90°C and the other half are allowed to equilibrate

TABLE 4.8. Glass Composition (wt%)

Oxide	Glass	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Na ₂ O	Fe ₂ O ₃	ZnO	Li ₂ O	UO ₂	Simulated fission products
ABS 39		48.5	19.1	3.1	1239	5.7	0	0	1.7	9
ABS 41		52.0	15.9	2.5	9.9	3.0	3.0	3.0	1.7	9

at the 9°C-10°C ambient temperature of the granite. Removal of a pineapple slice assembly after 14 days showed that all interfaces were in contact with water.

Surface analyses of the following interfaces have been performed after 1 mo, 3 mo, and 12 mo burials: glass-glass, glass-bentonite, glass-granite, glass-Cu, glass-Ti, and glass-Pb. Analysis methods include: IRRS, optical microscopy, and SIMS with ion beam profiling. (Data for the 12 mo burials with SIMS is not completed.) The same methods have been used for comparison of the in-situ burial with laboratory simulations using glass-water; glass-granite-water, and glass-granite-bentonite-water mixtures.

The results to date lead to the following conclusions:

- Lab simulations show ABS 39 to be less leach resistant than ABS 41. This difference is also observed in the in-situ burial experiments at 90°C. No compositional effects appear during 8°C burial.
- Surface compositional profiles show selective ion depletions of Na and B at a rate of 1.5×10^{-7} m/day for glass ABS 39 and 2.5×10^{-8} m/day for glass BAS 41 (based upon 3 mo burial at 90°C).
- FTIRRS analysis of 1 yr burial samples indicate that rates of ion, depletion depths of both glasses are no greater than at 3 mo. This would correspond to 90°C depletion rate of $\sim 4 \times 10^{-8}$ m/day for glass ABS 39 and $\sim 6 \times 10^{-9}$ m/day for glass ABS 41. Rates at 8°C are too low to measure using FTIRRS.
- A thin (<1 μ m) film rich in Si, Fe, and Al forms on both glasses during burial.

- Moist or wet bentonite accelerates by ~10X, rate of ion depletion for both glasses, with ABS 39 the worst, in both lab and STRIPA burial experiments.
- The bentonite effect is much less in burial environments than in lab simulations and tends to stabilize after the first month of burial at both 9°C and 90°C.
- There is little difference in burial surface reactions between "pineapple slices" and minicans (by 3 mo) and no evidence of attack at the glass-steel interface.
- Reaction layers of both glasses exposed to Cu, Ti and Pb overpacks are generally thinner than for glass-glass interfaces. No deleterious effects of glass-metal interfaces have been observed.

4.6.6 References

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4.7 BONDING OF URANIUM, NEPTUNIUM, AND PLUTONIUM IN SILICATE-BASED GLASSES --

D. Lam

No summary review available.

4.8 RUTHERFORD BACK SCATTERING -- G. Arnold

4.8.1 Summary

The RBS technique consists of bombarding the surface of a polished and conductively coated sample with a monoenergetic beam of positive He ions of about 2 MeV. The ions elastically scatter from the nuclei of the elements composing the surface with an energy characteristic of the element involved in the scattering process. The amplitude of the RBS signal is proportional to the ion energy, the scattering angle, the scattering cross section, the fraction of the element present in the surface being analyzed and the square of the atomic number. This enhanced sensitivity to the high Z elements makes the technique very powerful for studying trace quantities of heavy elements in a glass matrix. The RBS technique also integrates the scattered ions produced over the full penetration depth of the helium ions. Hence deconvolution of the spectra provides a depth profile of the material being analyzed, with depth resolution determined by the energy resolution of the detection system and the scattering geometry. The technique is quantitative and in principle provides a depth profiling capability over a layer thickness of about 2 microns. The technique cannot, however, resolve scattering from individual elements of mass greater

than 40 and density variations in the material can obviously affect results. The technique offers another means of defining depth profiles and has unique advantages for trace high Z elements.

For more details see L. C. Feldman, "CRC Reviews in Solid State Materials Science" (May 1981, pp. 142-167) and B. C. Scales et al., "Rutherford Backscattering Investigation of the Corrosion of Borosilicate Nuclear Waste Glass," to be published in J. Non-Crystalline Solids (1983).

5.0 SESSION III. IN SITU CHARACTERIZATION OF LEACHING SURFACES

5.1 LASER RAMAN SPECTROSCOPY -- G. J. Exarhos and W. E. Conaway

5.1.1 Introduction

Molecular information including the nature of localized chemical bonding and structure of materials is afforded by this inelastic light scattering technique. In situ measurements are possible for a wide variety of materials including crystals, glasses, polymers, and polycrystalline ceramics. Specie identification, concentration, and localized temperature are discernable from measured vibrational spectra. This technique is particularly useful for studies of surface coatings with thicknesses ranging from microns to tens of Angstroms. Studies requiring both time and spatially resolved information can be performed on commercially available instrumentation.

Raman spectra are excited by directing the focused output from a pulsed or CW ion laser or the emission from a turnable dye laser onto the sample; scattered light is collected by an efficient optical system designed for that particular scattering geometry. A double or triple monochromator equipped with a sensitive photomultiplier tube and photon counting electronics is used to analyze the scattered light. Recent advances in detector technology have led to the development of gated optical multichannel detectors which significantly reduce the time required to acquire a spectrum. This time resolved mode of data collection offers additional advantages including improved rejection of non-Raman scattered light, and maximization of the signal to noise ratio during in situ measurements.

A preliminary experiment was conducted in order to demonstrate the feasibility of applying Raman vibrational measurements to in situ studies of glass/water interactions. Yttrium metaphosphate, $Y(PO_3)_3$, glass fibers (25 microns in diameter) were immersed in boiling water for two hours and analyzed by Raman spectroscopy. The intensity ratio, I_{690}/I_{1200} , of two strong features at 1200 cm^{-1} and 690 cm^{-1} assigned respectively to nonbridging oxygen $>PO_2$ and bridging oxygen O-P-O symmetric stretching interactions increases following high temperature leaching. Results indicate selective attack at the non-bridging oxygen site accompanied by metal cation dissolution. This experiment demonstrates that molecular information can be extracted from vibrational spectra and suggests the application of this technique to leaching studies of glasses.

5.1.2 Silicate Glass Leaching Studies

Extensive investigations designed to understand mechanisms responsible for glass dissolution in aqueous media rely on quantitative solution for leached species (Tait and Jensen 1982) in addition to substrate analyses using surface-sensitive probes (XPS, SEM, SIMS) (Buckwalter et al. 1982). Microstructural and surface atom distribution information afforded by these techniques require that the substrate be transferred to a high vacuum environment for the analysis. Such conditions may lead to alteration of the surface structure and bonding associated with the water/substrate interaction. In situ vibrational Raman measurements are reported for binary silicate glass fibers in contact with deionized water. Surface-induced bonding changes resulting from ion exchange reactions with the glass and subsequent hydration of the structure were followed by means of the observed Raman spectra.

Glass of composition $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ was obtained by melting frit, prepared from a soluble ammonium silicate (Ludox AS40) and sodium carbonate, in a Pt crucible for 1 hour at 1500°C . Thin fibers (25 μ dia) were drawn from the melt and the glass stoichiometry was verified through its Raman spectrum (Brauer and White 1977). Sectioned fibers 1 cm in length were mounted in teflon holders and inserted into Spectrosil grade fluorescence cells filled with deionized water. Raman spectra of fibers in and out of leachant were excited in both 90° forward and 180° backscattering configurations using 150 mW of 514.5 nm excitation from an Ar^+ laser. Scattered light was analyzed using a Spex 1403 double monochromator equipped with photon counting electronics. Measurements were obtained daily for samples leached at 25°C and 90°C . Raman spectra of vitreous SiO_2 and a powdered form of silicic acid having the composition $0.8(\text{H}_2\text{O}) \cdot \text{SiO}_2$ were also measured.

Observed changes in the Raman spectrum of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ during leaching can be explained by ion exchange reactions between sodium cations localized in ionic glass sites and hydrogen ions from the solution. Total exchange of sodium cations for these thin fibers occurs for leaching times approaching 1 week; hydrogen ions become localized at nonbridging oxygen sites in the glass. Owing to the small mass of glass fiber and large solution volume, no significant change in solution pH was recorded during leaching.

Figure 5.1 depicts 180° backscattered Raman spectra measured in air of pristine $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass (a) and the same fiber following 1 week of 25°C aqueous leaching (b). Spectrum (a) is representative of the trisilicate composition (Brauer and White 1977) and exhibits two strong features at 1100 cm^{-1} and 540 cm^{-1} assigned to symmetric stretching vibrations involving

FIGURE 5.1. Raman Spectra Obtained from Samples Measured in Air at 180° Backscattering Geometry

silicon/nonbridging oxygen and silicon/bridging oxygen motions, respectively. Observed features for the leached glass spectrum may be interpreted in terms of measured spectra of vitreous silica and silicic acid.

Vibrational features exhibited by vitreous SiO_2 at 450 cm^{-1} , 800 cm^{-1} , and 1200 cm^{-1} can quantitatively be understood in terms of a continuous random network model (Sen and Thorpe 1977) incorporating four-fold coordinated silicon and two-fold coordinated oxygen. The remaining two sharp lines observed have previously been ascribed to localized "defect" modes in the glass represented by broken bonds or an alternate atom coordination number (Stolen et al. 1970). Galeener (1982) has recently suggested that the 606 cm^{-1} feature could be explained by the existence of planar three-fold rings in the structure. Assignment of the 495 cm^{-1} band is still under discussion.

The Raman spectrum of a stable silicic acid approaching the meta-composition is depicted in Figure 5.1(d). The relatively low nonbridging oxygen stretching frequency, 971 cm^{-1} , is indicative of a significant number of nonbridging oxygen atoms in the structure (Furukawa et al 1981). Particle size effects lead to increased scattering at higher frequencies and therefore a rising baseline results.

Incorporation of H^+ into glass fibers of composition $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ is manifested by dramatic changes in the Raman spectrum. The leached fiber spectrum (b) appears to be a linear combination of the vitreous SiO_2 (c) and silicic acid (d) spectra. However, features assigned to "defect modes" in vitreous SiO_2 are not apparent in the leached fiber spectrum. Either such localized features were not present in the starting material or bonding defects (broken bonds, unsatisfied coordination) are susceptible to attack by aqueous species. These ideas are consistent with results presented by Pantano and Kerey (1982) on alkali aluminosilicate glasses where glass durability decreases with increasing alkali (more nonbridging oxygens) in the structure. Experiments on fibers leached at 90°C for 2 days gave identical results.

Freshly drawn fibers react rapidly with water. This effect is manifested on the OH stretching region of the Raman spectrum by the appearance of four broad bands at 3250 cm^{-1} , 3425 cm^{-1} , 3600 cm^{-1} , and 3650 cm^{-1} . Such features intensity and broaden during leaching into a diffuse band centered at ca. 3450 cm^{-1} which is comparable to the broad band exhibited by silicic acid.

Attempts to measure OH Raman active vibrations of fibers in H_2O are precluded by strong solvent Raman scattering in this region.

In situ acquired Raman spectra during leaching of $Na_2O \cdot 3SiO_2$ glass fibers are depicted in Figure 5.2. Vibrational bands decrease in intensity as a function of time and broaden to the low frequency side. This observation suggests formation of an increasing number of nonbridging oxygen sites caused by aqueous

FIGURE 5.2. In Situ Raman Spectra of $Na_2O \cdot 3SiO_2$ Fiber in Water Measured in a 90° Forward Scattering Geometry

attack of the silicon-bridging oxygen network. The feature at 1640 cm^{-1} is intrinsic to water. As sodium cations are replaced in the structure, the features assigned to silicic acid and vitreous silica begin to appear. The very weak Raman spectrum (d) is comparable to the Raman spectrum in the fiber removed from solution [Figure 5.1(b)].

In this study, Raman spectroscopy has been successfully used as an in situ structural probe to follow glass leaching in aqueous solutions. Leaching glass fibers in water does lead to formation of a surface graded refractive index which tends to minimize the amount of Raman scattered radiation thereby degrading the signal. Though not discussed here, removing the fiber from solution minimizes this loss of scattering power and reduces background noise without significantly altering bonding interactions within the leached layer.

5.1.3 Acknowledgments

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5.1.4 References

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5.2 ZETA POTENTIAL AND ZERO POINT OF CHARGE/ -- C. Jantzen

Since glass dissolution occurs at a solid-solution (electrolyte) interface, electrochemical concepts such as zeta potential and zero point of charge can be applied to leaching of radioactive waste glasses. Solids^(a) in an aqueous environment are electrically charged (Parks 1965). Upon immersion this charge is balanced by oppositely charged counterions in the solution. The innermost layer of counterions are more tightly bound while a smaller additional contribution to the neutralization of the surface charge comes from a diffuse ionic distribution in an outer layer. Together these form the electric double layer. The zeta potential is the measured electrokinetic potential between the fixed layer and the outermost layer boundary (Figure 5.3).

Two types of electric or diffuse double layers can be defined. For convenience they will be referred to as Type I and Type II. The first type can be considered to be due to imperfections or substitutions within the body of a solid hence producing an electrical charge on the solid surface. The charge is balanced by an excess concentration of ions of opposite charge called counterions. These counterions are attracted to the surface from the surrounding solution. The charged surface of the solid is then considered to be the fixed layer and the balancing counterions are the mobile or diffuse layer. Together these form the electrical double layer (Figure 5.4). The second type of diffuse double layer can be considered to be due to specific chemical forces, e.g., ions that are adsorbed at the surface causing it to become charged. These adsorbed ions are potential-determining ions and they constitute the fixed layer. The mobile or diffuse layer is made up of oppositely-charged counterions as in Type I. Type II diffuse layers are the type most commonly associated with colloids. Since Gouy and Chapman were the first to recognize that the mobile layer was diffuse due to the electrostatic repulsion of the similarly-charged ions composing the layer, the diffuse layer is commonly referred to as the Gouy layer. Theoretical treatment of surface charge

(a) Solids are used in the broad sense including glasses, oxides, hydroxides, and hydrous oxides.

FIGURE 5.3. Schematic Representation of the Electrokinetic Potential of a Colloid with Negative Charges on the Surface of the Particles. T Particles surface; F Firmly adhering inner layer; C Loosely adhering outer layer with diffuse ionic distribution; d Electric double layer which also corresponds to the interior solution (J); A Exterior solution; E Distance from the particle surface; P_e Electrokinetic (zeta) potential; P_t Thermodynamic potential (adapted from Rosler and Lange, 16).

balancing as a function of the ionic strength of the solution and ionic charge and size is referred to as the Gouy theory (Parks 1962 for example).

The Gouy diffuse double layer model predicts (Stumm and Morgan 1970) the following:

1. A preferential concentration of highly charged ions near an oppositely-charged surface, e.g., $\text{Ca}^{+2}/\text{Na}^{+}$, concentrations, will be high near a negatively-charged surface.

FIGURE 5.4. Electrical Double Layers. Type I is due to an interior lattice charge; Type II to the adsorption of Potential Determining ions. Positive and negative ions are denoted by + and -, respectively [adapted from Berner 1971].

2. Increases in ionic strength or concentration of the electrolyte decrease the concentration of highly-charged ions in close proximity to the charged surfaces.
3. The ion exchange capacity of a surface comes about from an excess of counterions in the double layer which can be exchanged for other ions.
4. Adsorption of counterions can cause a charge reversal of the surface.

The counterions in the electric double layer can be H^+ or OH^- and, hence, the zeta potential is a pH-dependent parameter. There are several mechanisms by which H^+ and OH^- , or hydroxo-complexes can determine the surface charge on immersed solid materials. An anhydrous solid can become hydrated by 1) physical adsorption of water molecules (including hydrogen bonding to surface oxygen

ions but not dissociation), 2) chemisorption of water which subsequently dissociates resulting in surface MOH groups, or 3) reaction with the solid forming an oxyhydroxide, hydroxide, or other metal-electrolyte complex (Parks 1962). These mechanisms explain the pH dependence of the surface charge and the existence of a pH which results in zero net surface charge. This pH value is the pH of the zero point of charge (ZPC) of the isoelectric point of the solid (IEPS).^(a) Technically, the pH_{IEPS} represents the pH at which an immersed solid surface has zero net charge while the pH_{IEP} represents a pH resulting in electrically equivalent concentrations of positive and negative metal hydroxo-complexes in solution (Parks 1965). The isoelectric points of known solids (IEPS) correlate with the isoelectric points of the metal hydroxo-complexes (IEP) in solution (Parks 1965; Parks 1962).

Previous research (Jantzen 1982) has shown that the leachability of the individual species from a composite waste form is a function of the surface characteristics of the solid monolith. Since the isoelectric point of a solid (ZPC) reflects the chemical composition of the solid and the electrolyte in which it is immersed, then these principles are applicable to glass waste form leaching. The early stages of glass leaching can be envisaged as a process of ion exchange and matrix dissolution. These processes release charged cationic or anionic species at the glass surface, e.g., from the reaction front. Whether these species form hydroxo-complexes which are cationic ($pH < ZPC$) or anionic ($pH > ZPC$) depends on the pH of the electrolyte (leachant).

The ZPC of a simple solid is related to its cationic charge, and the radius of the central ion and is affected by its state of hydration, crystallinity, and impurity concentrations (Parks 1965). The ionic potential of an ionic species (ionic charge/ionic radius), has been correlated directly with the ZPC for a wide range of solids (Parks 1965) and indeed the ionic potential

(a) IEPS is defined by Parks (Parks 1965) as a ZPC arising from the interaction of H^+ and OH^- in the solution with the solid while the ZPC is the zero point of charge of the surface of the solid. Most authors do not distinguish between the ZPC and the IEPS. Hereafter, only the term ZPC will be used.

of aqueous hydroxo-complexes is the parameter responsible for geochemical distribution of elements observed in natural environments (Mason 1966; Langmuir 1979). However, it is the structure of the electric double layer, which is absent or collapsed at the ZPC which controls the behavior of near colloidal suspensions or adsorption of the material dissolved from the solid, e.g., surface reprecipitation.

The Gouy model can be used to explain the results of leaching experiments. For example, one observes preferential adsorption of ions with a high charge to radius ratio, e.g., Zr, U, Fe, in the surface gel layers (Table 5.1). These elements are enriched in the surface layer according to their ionic potential (Winter 1965; Barkatt et al. 1981) regardless of the type of leaching test carried out (Table 5.1). Relations between ionic strength of the electrolyte and surface elemental concentrations should be an expression of the SA/V parameter of a particular leaching experiment while the ion exchange capacity should be an expression of the kinetics of diffusion of the ions through the gel layer and through the diffused double layer (reaction layer). Lastly, adsorption counterions has been found to cause charge reversals of leached waste glass surfaces and will be discussed in more detail below.

At or near the zero point of charge, when the zeta potential is reduced or ion pair formation occurs, complexes of colloidal dimensions can form. The electrochemical models of the solid-solution interface, therefore, emphasize the physical model of counterion adsorption or a colloid destabilization as the surface charge neutralization mechanism. In terms of a leaching model or mechanism, the formation of the charged hydroxo-complexes or colloids could account for the dissolution mechanism while readsorption of these complexes accounts for surface reprecipitation (back reactions) and subsequent passivation of the leached surface.

The charge on a colloid or hydroxo-complex determines its stability. At the pH of deionized water or natural waters (pH about 7), the complexes listed in Table 5.2 have the associated charges while the solid surfaces have the charges indicated in Table 5.3. Oppositely charged surfaces and hydroxo-complexes or colloids can, and probably do, attract for surface charge neutralization.

TABLE 5.1. Preferential Concentration of Multivalent Ions in Leached Glass Surface Layers

Glass	Elements Enriched in Surface Layers	Leach Test Description
Silica gel (Kepak 1981)	$Zr^{IV} > U^{IV}$ $Pu^{VI} > U^{VI} > Gd^{III} > Ca^{II}$ $\approx Ba^{II} \approx Na^{I}$	Order of ion sorbability
SRL 131 (Wicks et al. 1982)	Fe, Al, Mn, Mg	MCC-1
SRL 131 (Rankin et al. 1982)	U	MCC-1
European (Lanza and Parnisare 1978)	U, Ce, Fe	IAEA
Roman (Winters 1965)	$Mg > Fe^{II} > Ca^{II}(a)$	IAEA
Borosilicate and high silica (Barkatt et al 1981)	$Fe^{III} > Ln^{III} > Zn^{II} > Sr^{II}(a)$ at 70°C	Powdered sample
PNL full radioactive (Mendel et al 1978)	$Ce > Cm > Pu > Mn > Co > Sr > Ca(a)$	---
SRL 21 (Sales et al. 1983)	Fe, Ni, Mn, Ti, and U	MCC-1
Zn borosilicate (Kenna et al. 1982)	Zr, U, Re	Soxhlet, 20 mo.
PNL 76-68 (Grambow 1982)	Ca, Sr, Nd, Fe, Zn	MCC-1

(a) Given as relative retardation on leaching.

TABLE 5.2. Charged Hydroxo-Complexes in Natural Environments (pH ~ 7)

Positive	Negative
Ferric Hydroxide (Mason 1966)	Ferric Hydroxide (Mason 1966)
Aluminum Hydroxide (Mason 1966)	Silica (Mason 1966; Jednacak et al. 1974)
Chromic Hydroxide (Mason 1966)	Vanadium Pentoxide Hydrate (Mason 1966)
Titanium Dioxide Hydrate (Mason 1966)	Manganese Dioxide Hydrate (Mason 1966)
Thorium Dioxide Hydrate (Mason 1966)	Humus Colloids (Mason 1966)
Zirconium Dioxide Hydrate (Mason 1966)	Sulfide Sols (Mason 1966)
Cadmium Hydroxide (Rosler and Lange 1972)	Clays (Mason 1966)
Cerium Hydroxide (Rosler and Lange 1972)	Am(III) Colloids (Jantzen et al 1982)
Uranium Colloids (Bunker and Arnold 1983; Kepak 1981)	Po(IV) Colloids Kepak 1981)
Am(III) Colloids (Kepak 1981)	Eu(III) Colloids (Kepak 1981)
Po(IV) Colloids (Kepak 1981)	Zr(IV) Colloids (Kepak 1981)
Eu(III) Colloids (Kepak 1981)	Pu(IV) Colloids (Kepak 1981)
Y(III) Colloids (Kepak 1981)	Ce(III) Colloids (Kepak 1981)
Pu(IV) Colloids (Kepak 1981)	

TABLE 5.3. Solid Surface Charges in Natural Environments (pH ~ 7)

Positive	Negative
Al ₂ O ₃ (Hunter 1981)	Vitreous Silica (Jednacek et al 1974)
Fe(OH) ₃ (Hunter 1981; Mason 1966)	Vycor Glass (Jednacek et al 1974)
Alumina Tailored Ceramic	Borosilicate Glass (Jednacek et al. 1974)
Waste Form (Jantzen 1982)	Colloidal Silica (Jednacek et al. 1974)
Leached SRL 131(a)	Sodium Alumino-Silicate Glass (Horn and Onoda 1978)
Waste Glass (Jantzen et al 1982)	Soda Lime Silicate Glass (Mason 1966; Jednacek 1974)
	Silica (quartz) (Horn and Onoda 1978)
	TiO ₂ (Hunter 1981)
	Synroc (titania ceramic)
	Waste form (Jantzen et al. 1982)
	SRL 165 Waste Glass (Jantzen-in preparation)

(a) With hydrated layer enriched in Fe(OH)₃

Recent zeta potential measurements of SRL 165 waste glass indicate that the glass surface is strongly negative (Table 5.3) over the pH range 4-10. The important components of the reprecipitated layer, such as ferric hydroxide (Wicks et al. 1982) are known to form positive hydroxo-complexes (Tables 5.2 and 5.3). Hence, negative glass surface potentials attract and bond these complexes onto the leached glass surface. After leaching, the waste glass has a surface charge characteristic of the adsorbed ferric hydroxide (Table 5.2) and

the leachate has the pH_{ZPC} of ferric hydroxide (Jantzen et al. 1982). This mechanism explains the stability of the surface layers on waste glass.

The origin of the surface layers appears to be from the dissolution of the solid and is related to the isoelectric point of the solid (ZPC): the ZPC reflects the chemical composition of the solid monolith and the electrolyte in which it is immersed (Parks 1965). The pH of the final leachate appears to represent the pH at which the immersed solid surface or the reprecipitated layer has zero net charge. The ZPC, in turn, is related to the cationic charge, radius of the ions, crystallinity, and other properties (Stumm and Morgan 1970) of the immersed solid material. Therefore, the solids controls the ZPC which in part controls the pH through the role of the potential determining ions (H^+ and OH^-). At or near the pH_{ZPC} the electric double layer of near colloidal dimensions is absent or collapsed, and adsorption of metal hydroxo-complexes from the hydrolysis products of the materials dissolved from the solid can occur.

A qualitative picture of the dissolution behavior of nuclear waste solids can be described as dissolution controlled and modified by electrolyte-solid surface reactions. The surface reactions are controlled by the chemical composition of the solid and the concentration of positive and negative metal hydroxo-complexes in the solution which have been derived from the hydrolysis of the solid. Adsorption of the metal hydroxo-complexes (back reactions) form surface layers which can be passivating (Wallace and Wicks 1983).

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5.3 APPLICATION OF CHEMICAL ETCHING TECHNIQUES -- Aaron Barkatt, Alisa Barkatt, M. A. Boroomand and W. Sousanpour

5.3.1 Abstract

A method for the analysis of the surface structure of leached nuclear waste glasses by means of stepwise etching with dilute hydrofluoric acid has been developed. The method is simple and accurate. Enrichment and depletion factors of the various glass constituents in the surface have been calculated and are shown to be consistent with those obtained from leachate analysis. Measurements carried out on PNL 76-6B glass leached for 28 days under conditions of high dilution at 70°C show this glass to acquire a thick (20-25 μm), stable layer with the profiles of all components approaching the bulk composition at similar gradients.

5.3.2 Introduction

The interaction between nuclear waste glasses and aqueous media is likely to be controlled in most cases by the composition, structure and chemical properties (in particular, solubilities) of the surface regions of the glass, which have been modified upon prolonged exposure to water, rather than by the composition and properties of the original bulk glass. The character of the

surface depends on the leach conditions (leachant composition, temperature, flow/dilution parameters) as well as on the glass composition.

Many sophisticated spectroscopic methods have become available in recent years for the study of the structure of leached glass surfaces (Hench 1977). These methods can provide structural information for depths ranging from a few nm to tens of microns, but quantitative analysis of all important components of the glass, including light elements and those present at low levels (<20%) is often hard to accomplish. Moreover, most of these physical methods require post-leaching treatment of the samples prior to surface analysis, and this treatment generally includes intense drying of the samples under high vacuum. In view of the high sensitivity of leached surfaces of defense waste-forms, especially borosilicate glass, to rupture under chemical and mechanical stresses, in particular upon drying (Walton and Meritt 1980), such procedures can cause severe problems in relating the spectroscopic findings to the as-leached surface. Sputtering and ion-milling procedures can cause further changes in the surface structure, since heavier species are less susceptible to sputtering (McVay and Pederson 1981).

Chemical methods based on progressive etching with hydrofluoric acid were used in the study of surface composition of weathered minerals (White 1979). This method is simple, inexpensive, highly sensitive and accurate, and does not require any pretreatment of the leached sample before the analysis. It can be easily adapted to studies of radioactive samples. The depth resolution, i.e., thickness of the analyzed surface regions, can be controlled simply by varying the concentration of HF or the duration of each etching period. The drawbacks of this technique include the fact that it does not permit a direct measurement of the density or the amount of water absorbed into the surface layers, and that the thickness of the etched slices of the layer is evaluated on the basis of the chemical analysis rather than measured directly. Another problem which has been cited with respect to the use of HF for surface profiling is selective leaching (McVay and Pederson 1981). In the case of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass, for instance, it was found that HF solutions selectively remove Na^+ ions from glass, and that the effect is larger when more dilute HF solutions are used. As a result, the observed concentration profiles of the various elements are

dependent on HF concentration to a depth of $\sim 0.15 \mu\text{m}$. However, in the cases of borosilicate nuclear waste glass (PNL 76-68 and MCC Reference Defense glass) studies carried out at present show that the observed elemental profiles between $0.2\text{--}25 \mu\text{m}$ are independent of HF concentration over the range of at least $0.1\text{--}5\%$.

5.3.3 Experimental

The procedure described below was intended to ensure that the leached sample would not be at any time exposed to drying, and it supplemented the surface analysis with quantitative analysis of the leachate.

A sample of the test glass was cut, ground and cleaned (using ethanol in an ultrasonic bath) following the specifications of the MCC-1 leach test procedure (Mendel 1981). The surface area of the sample was $400 \pm 20 \text{ mm}^2$, the usual dimensions being $12.7 \times 12.7 \times 1.5 \text{ mm}$, although cubic samples with an edge dimension of 8.2 mm were also used. The samples were securely tied with a long polytetrafluoroethylene (PTFE) fiber and suspended in the center of a volume of 100 or 150 mL of deionized water in a 240-mL PTFE jar. The jar was tightly sealed with the wire protruding out of the leachant. At the end of a leaching period of 28 days at a temperature of $70 \pm 1^\circ\text{C}$ a series of 25 mL polystyrene vials were filled each with a volume of 20 mL of dilute high-purity hydrofluoric acid (such as Merck supra-pur grade) at a desired concentration. The sample was removed from the leach vessel using the PTFE wire, rinsed at once with running cold deionized water for 20 seconds, then immersed in the first HF vial for 60 ± 1 seconds, transferred into the second vial, and the procedure was repeated until the sample has been successively immersed in each of the vials (usually numbering between 20 and 35). With a little practice it proved easy to ensure that the transfer from one vial to another took no longer than 2 seconds, that the sample was gently lowered without striking either the sides or the bottom of the vial, and that the sample remained covered with solution even during the transfer and is not exposed to drying during any stage of the procedure. The resulting solutions were shaken to ensure homogeneity and analyzed within a few hours by means of DC plasma spectroscopy and atomic absorption/flame emission using blanks and standards made up with the same concentration of HF. Adsorption spectrophotometric determinations (e.g., in the

case of uranium) were carried out following evaporation and redissolution in dilute HNO_3 or HCl . All the major components present in the glass at concentrations above 0.5% and, whenever possible, even minor components were determined.

After removing the sample the pH of the aqueous leachate in the original PTFE container was determined. A volume of 5 mL of concentrated HNO_3 (e.g., Baker Ultrex grade) and 1 mL of concentrated HF (e.g., Merck Supra-pur grade) was added to each 100 mL of leachate, and the leachate was returned to the 70°C oven and allowed to stand overnight, and then quantitatively analyzed as detailed above using blanks and standard solutions with the same levels of acid concentration.

In parallel with the gradual etching experiment on the leached sample, a control experiment was carried out using an identical procedure on a sample of glass of the same composition, prepared and cleaned under the same conditions, which had been placed in a dessicator containing a drying agent immediately after preparation and left in the dessicator for the entire 28-day period. This made it possible to verify that the changes in the composition of the surface layer which were observed in the case of the leached sample indeed reflected the results of the leaching process.

5.3.4 Calculations

Since the density of the leached surface layer cannot be assumed to be the same as that of the original glass (Boult et al 1979), and since this method does not provide direct means of determining the concentration of water present in the leached layer, the observed concentration profiles are reported in terms of relative concentrations rather than of absolute weight fractions. Since silica is the major matrix element of silicate and borosilicate glasses, and since it is not expected to undergo a very large extent of either selective leaching or sorption during the formation of a stable surface layer, the results of the analysis of each of the consecutive etch solutions are given for each element M in terms of the M:Si ratio. This ratio (in the case of the solution obtained in the n-th etch interval) is then normalized to the corresponding ratio in the case of the bulk glass, determined from the results of HF dissolution of the dry glass, to give the value of

$$R_M(n) = \frac{(M/Si)_n}{(M/Si)_{bulk}} = \frac{C_M(n)/C_{Si}(n)}{f_M/f_{Si}} \quad (1)$$

where $C_M(n)$ and $C_{Si}(n)$ are the concentrations of the element M and of Si, respectively, in the n-th etch solution, and f_M and f_{Si} are the corresponding weight fractions in the bulk glass. Elements for which $R_M(n)$ is smaller than unity can be considered to undergo selective leaching, while elements for which this value exceeds a value of one exhibit retarded dissolution as a result of resorption or reprecipitation.

The relative concentrations of the various elements in successive etch solutions given the composition profiles of the surface layer. A more quantitative representation can be obtained in terms of the equivalent thickness based on silica content. Since silica is the major matrix element and is not very susceptible to either selective leaching or conspicuous, selective resorption (see above) it is the most suitable component to serve as an indicator of the etched depth. Moreover, classical models of glass corrosion (Rana and Douglas 1961; Holland 1966; Barkatt et al 1981) are based on findings that indicate that the leaching process is characterized by selective migration of highly soluble species, such as alkalis and boron, out of the glass to leave behind vacant sites which become occupied by the aqueous leachant and by the reincorporation of polyvalent metal ions from dissolved regions of the glass. The amount of dissolved silica, on the other hand, reflects the thickness of the region which has been completely dissolved. According to this model the concentration of silica per unit volume throughout the surface layer, unlike those of other elements, is not very different from its original value in the bulk, although the density of the layer and the resulting weight fraction of Si may be considerably different from those observed in the glass. This does not require the concentration of Si in the successive HF etch solutions to be constant; it is likely that the altered structure of the outermost layers will change the rate at which these layers dissolve in HF. (Considerable depletion of silica from the surface can be expected to give rise to a layer characterized by low density and low stability; in that case thickness calculated on the basis of constant silica density will be much smaller than the actual etched thicknesses.)

More quantitatively, this model assumes that the attack of water on the glass can be expressed in terms of the thicknesses of two regions. The first is a region which has been completely dissolved, the depth of which is

$$d = \frac{C_{Si}(aq) \cdot V_{aq}}{\rho f_{Si} A} \quad (2)$$

where $C_{Si}(aq)$ is the concentration of Si in the aqueous leachate, V_{aq} is the volume of the leachate, ρ is the density of the glass, A is the surface area of the sample and f_{Si} is the weight fraction of Si in the glass. The second is the leached, dealkalinized, hydrated surface region. The thickness of the n -th fraction of the zone, i.e., the fraction dissolved in the n -th volume v of dilute HF, where the final concentration of Si is C_{Si} , is given by

$$t_n = \frac{C_{Si}(n) \cdot v}{\rho f_{Si} A} \quad (3)$$

Accordingly, the composition profiles reported below are given in terms of the normalized concentration ratio $R_M(n)$ of each element M with respect to Si in the n -th etched slice of the glass surface [eq. (1)] as a function of the equivalent depth of the corresponding etched slice based on Si, i.e., the distance T_n between its mid-point and the surface of the leached surface at the start of the etching process, where

$$T_n = \sum_{i=1}^{n-e} t_i + 1/2 t_n \quad (4)$$

As detailed above, the actual thicknesses of the etched surface layers may be somewhat different from the corresponding values of t_n due to variations in the density of Si in the leached surface layer; these deviations are not likely to be very large as long as the layer is dense and stable. Such deviations will result in some staggering of the T_n scale of the $R_M(n)$ versus T_n diagrams relative to the actual concentration profiles.

It is now possible to correlate the findings of the gradual etching procedure with the analysis of the leachate. The correlated results refer to a layer of thickness L_S . While it should be possible (provided the assumption of constant Si concentration is approximately valid) to obtain a good agreement

between the two sets of data regardless of the value of L_s used in the calculations, it is desirable to use a realistic value of this parameter. Sodium is the most typical and usually the most abundant of the elements which undergo selective depletion, giving rise to the formation of a distinct selective layer. Accordingly, the total thickness of the layer L_s can be evaluated by calculating the leach of total depletion of the $R_n(\text{Na})$ versus T_n plot, i.e.,

$$L_s = \int (1 - R_{\text{Na}}(n)) dt_n \quad (5)$$

where the integration is performed over the entire thickness of the sample which is analyzed by HF etching. The experiment should continue long enough to ensure that the entire layer has been traversed and that a region where $R_{\text{Na}} = 1$ (and, in general, $R_M = 1$ for all the monitored elements M) has been reached. Since the depletion of Na in the outermost layers is in most cases almost complete while the inner surface-bulk boundary is characterized by a nearly symmetric sigmoid curve, L_s can be usually approximated by evaluating T_n at the point on the $R_{\text{Na}}(n)$ versus T_n plot where $R_n(\text{Na})$ reaches a value of one-half.

$$L_s = T_n (R_{\text{Na}}(n) = 1/2) \quad (6)$$

Next, the relative surface abundance factor $R_M(n)$ [eq. (1)] for each of the glass components is averaged over the entire thickness of the layer by integration over the corresponding $R_M(n)$ versus T_n curve:

$$R_M(S) = \frac{C_M(S)/C_{\text{Si}}(S)}{r_M/r_{\text{Si}}} = (1/L_s) \int_0^{L_s} R_M(n) dt_n \quad (7)$$

where $C_M(S)$ and $C_{\text{Si}}(S)$ are the average concentrations of the element M and of Si, respectively, in the surface layer of thickness L_s . If $R_M(S) < 1$, the layer as a whole is depleted with respect to M compared with the bulk; if $R_M(S) > 1$, the layer is enriched with respect to M.

On the other hand, the total depletion or enrichment of each element relative to Si during the leaching process can also be evaluated from the analysis of the leachate. It has been assumed above that the presence of an amount of $C_{\text{Si}}(\text{aq})V_{\text{aq}}$ of Si in the leachate is due only to the complete dissolution of a

thickness d of the original glass [cf. eq. (2)] and not to layer formation. Accordingly, a corresponding amount of each element M as indicated by the abundance of M relative to Si in the bulk, $C_{Si}(aq)V_{aq}f_M/f_{Si}$, can be expected to be present of the aqueous leachate as a result of the total dissolution of the region corresponding to d . However, in the case of soluble elements such as alkalis or boron, the actual concentration in the leachate $C_M(aq)$ is higher due to preferential leaching from the surface layer. The thickness of the layer has been defined as L_S . The actual amount of M in the aqueous leachate is $C_M(aq)V_{aq}$. The amount of M remaining in the surface layer, $AL_S C_M(S)$ is smaller than the initial amount prior to leaching $AL_{S\rho} f_M$ by a quantity which is equal to the excess of M transferred into the aqueous medium. These material balance consideration accordingly yield

$$AL_{S\rho} f_M - AL_S C_M(S) = C_M(aq)V_{aq} - C_{Si}(aq)V_{aq}f_M/f_{Si} \quad (8)$$

$$C_M(S) = \frac{AL_{S\rho} f_M + C_{Si}(aq)V_{aq}f_M/f_{Si} - C_M(aq)V_{aq}}{AL_S} \quad (9)$$

According to the definition of $R_M(S)$ in eq. (7) and to the definition of $C_{Si}(S) = \rho f_{Si}$,

$$\begin{aligned} R_M(S) &= \frac{C_M(S)/C_{Si}(S)}{f_M/f_{Si}} = \frac{AL_{S\rho} f_M + C_{Si}(aq)V_{aq}f_M/f_{Si} - C_M(aq)V_{aq}}{AL_{S\rho} f_M} \\ &= 1 + \frac{V_{aq}[C_{Si}(aq)f_M/f_{Si}] - C_M(aq)}{AL_{S\rho} f_M} \end{aligned} \quad (10)$$

The same result is obtained in the case of an element such as Fe or Mg which is expected to undergo enrichment in the surface layer, since eq. (8) is still valid although the differences which appear in its left-hand and right-hand terms are now negative.

Consequently, the average normalized relative enrichment (or depletion) factor $R_M(S)$ which characterizes each element M in the leached surface layer can be independently calculated from the etching results [eq. (7)] on one hand and from leachate analysis [eq. (10)] on the other. Discrepancies between the

two results which exceed the analytical error would reflect inaccuracies in the basic assumption of considering the leach process as a combination of a complete dissolution of an outer region of thickness d and alteration of the composition of an inner region of a thickness L_S without changing the density of Si atoms in the latter region.

5.3.5 Results and Discussion

The method detailed above was recently applied to several glasses, including Corning Pyrex® and Vycor® as well as the simulated waste-form glasses SR1 TDS-131, PNL 76-68 and MCC Reference Defense Waste Glass. In the present paper we discuss the results obtained with PNL 76-68 glass. In this case leaching was carried out for 28 days in deionized water at 70°C in PTFE vessels which permitted some water loss (10-30%) during the test period; at the same time, leakage of atmospheric CO₂ into the vessels prevented a pH excursion from taking place in the solution remained near-neutral (pH 6.7). Each experiment was duplicated in its entirety and the results of duplicate experiments were observed to agree within 10%. In all cases, the analysis of all the HF etching solutions obtained upon treating glass samples which were placed in dessicator immediately after cutting, grinding and cleaning and stored under dry conditions for 28 days agreed within experimental error with bulk analysis, indicating that no significant changes in surface composition had taken place during the storage period. Similar analysis of the leached samples, however, showed very marked changes in the nature of the surface layers as compared with the bulk glass.

The concentrations of HF used in the two etching experiments carried out on PNL 76-68 glass were 1.5% and 1%, respectively, and the leached sample was immersed for 1 minute in each of a series of 25 HF vials. No flaking and no surface separation were visually observed throughout the leaching and etching periods. In addition, the leached layer did not exhibit enrichment is evident in the outermost 5 μ m of the surface. The results can be interpreted in terms of selective leaching of the soluble elements (specific alkali diffusion is not indicated, since the profile for B is identical with the one for Na) and precipitation or resorption of the other species (Holland 1966). Cs and Sr leach out easily because of the high solubility of their compounds in water at

neutral pH, and their enrichment in the outermost, highly altered layer is an indication of sorption or ion-exchange on the resulting surface, which contains large fractions of known sorbing oxides such as iron and cerium oxides in addition to silica.

The total equivalent thickness of the altered surface layer was evaluated according to eqs. (5) and (6) by calculating the equivalent depth corresponding to the total extent of Na depletion. The result (see Figure 5.5) is 15.4 μm . Integration and averaging of $R_M(n)$ over this thickness yields the values of $R_M(S)$ given in Table 5.4. Independent evaluation of this quantity on the basis of analysis of the concentrations $C_M(\text{aq})$ in the original leachate leads to values of $R_M(S)$ which are, in most cases, quite close to those obtained using the etching method. This shows that the calculations based on the model assuming the existence of a completely dissolved zone and an altered zone with unchanged C_{Si} are, to a large extent, self-consistent. In the case of elements such as Fe, Ti, Zn, Cr, Ca and Zr, for instance, practically the entire quantity which has been present in the dissolved zone is located at the end of the leach period in the outer layer of the leached zone.

In addition, the results of the HF etching surface studies agree with observations made using solid-state spectroscopic methods such as x-ray diffraction. Such observations (Strachan and Barnes 1981) show that the surface layers of PNL 76-68 glass are enriched with respect to Zn, Fe, Ti, Ca and the rare earths and depleted with respect to B, Na and Mo, while Cs is depleted in the inner gel layer and is enriched in the outer precipitation zone.

5.3.6 Conclusions

The gradual HF etching technique of analyzing surface structure is generally consistent both with leachate analysis and with other available information on the composition of leached glass surfaces. In the case of PNL 76-68 glass leached for 28 days at 70°C (high dilution) the layer is thick (about 20-25 μm), shows similarly gradual gradients in the case of all monitored species. The results indicate that the assumption that silica concentrations in the layer are not very different from the bulk level is apparently valid. This is in agreement with the observations that the layer is mechanically and chemically stable, indicating that the silica network in this case remains largely intact upon leaching.

FIGURE 5.5. Concentration Profiles of PNL 76-68 Glass Leached at 70°C for 28 Days, S/A = 6.9 m⁻¹; Etching with 1.5% HF at 1 Minute Intervals

TABLE 5.4. Surface Structure of PNL 76-68 Glass Leached at 70°C. (a)
Average enrichment (depletion) factors in surface layer,
 $R_M(s)$

Element, M	Percentage in Glass, $f_M \times 100$	Concentration from Leachate, C (aq), mg/L	$R_M(s)$ in Leachate Analysis	$R_M(s)$ From HF Etching
Fe	7.74	0.043	2.3	3.84
Ti	1.80	0.006	2.36	2.22
Zn	4.02	0.094	2.35	2.18
Cr	0.30	0.013	2.35	2.16
Ca	1.43	0.092	2.34	2.09
Zr	1.40	<0.05	2.36	1.90
Sr	0.34	<0.01	2.36	1.59
Ce	3.17	0.018	2.36	
Nd	1.13	<0.01	2.36	
Si	18.70	80.8	(1.0)	(1.0)
Cs	1.04	4.03	0.07	0.58
B	2.95	18.7	0.36	0.16
Na	2.54	129.0	0.00	0.11

(a) $V_{aq} = 62.5$ mL; $A = 429$ mm²; 28 days.

5.3.7 Acknowledgment

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5.3.8 References

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APPENDIX A

AGENDA
WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS
DECEMBER 7-8, 1982

APPENDIX A

AGENDA THIRD ANNUAL WORKSHOP ON THE LEACHING MECHANISMS OF DEFENSE HIGH-LEVEL WASTE FORMS DECEMBER 7-8, 1982

DECEMBER 6, 1982

8:00 - 10:00 p.m. Welcome Get Together (Beer, Wine, Cheese, etc.)
 Hospitality Room, Westlake Inn

DECEMBER 7, 1982

Executive Conference Room, Rockwell Science Center, Thousand Oaks, CA

8:00 - 8:05 a.m. Welcome Alan Harker

8:05 - 8:15 Opening Remarks Ed Hennelly

SESSION I - PROGRESS REPORT ON LEACHING MECHANISMS PROGRAM

8:15 - 8:45 Overview and Discussion of John Mendel
 Future

8:45 - 9:45 Catholic University Pete Macedo

Coffee Break

10:00 - 11:00 University of Florida Larry Hench

11:00 - 12:00 Pennsylvania State University Will White

Lunch

1:00 - 2:00 p.m. Rockwell Science Center Alan Harker

2:00 - 3:00 Pacific Northwest Laboratory Gary McVay

Coffee Break

3:15 - 4:15 Lawrence Livermore National Don Jackson
 Laboratory

6:00 - 7:00 No-host social hour - Westlake Inn Cocktail Lounge

7:00 Dinner - "The 94th Aero Squadron" - Van Nuys, CA

AGENDA
Page 2

Executive Conference Room, Rockwell Science Center, Thousand Oaks, CA

SESSION II - CHARACTERIZATION OF LEACHED SURFACES

8:00 - 8:20 a.m.	Introduction of Surface Characterization Techniques	Alan Harker
8:20 - 8:50	Application of Scanning Electron Microscope/ Microprobe Analysis	Lee Daniel
8:50 - 9:15	Applications of Analytical Transmission Microscopy	David Clarke
9:15 - 9:45	Applications of Auger Spectroscopy and XPS	Larry Pederson
Coffee Break		
10:00 - 10:30	Applications of SIMS	Carlo Pantano
10:30 - 11:00	Applications of FTIR	Larry Hench
11:00 - 11:30	Bonding of Uranium, Neptunium, and Plutonium in Silicate-Based Glasses	Dan Lam
11:30 - 12:00	Rutherford Back Scattering	George Arnold

Lunch

SESSION III - IN SITU CHARACTERIZATION OF LEACHING SURFACES

1:00 - 1:30 p.m.	Laser Raman Spectroscopy	Greg Exharos/Tom Shaw
1:30 - 2:00	Zeta Potential and Zero Point of charge	Carol Jantzen
2:00 - 2:15	Application of Chemical Etching Techniques	Ronnie Barkatt

Coffee Break

AGENDA
Page 3

SESSION IV - DESIGN OF GROUP EXPERIMENTS

2:30 - 4:30 Open discussion led by
 Alan Harker

4:30 Closing Remarks John Mendel

LATER - EXECUTIVE SESSION: MEETING OF THE STEERING COMMITTEE OF THE
 LEACHING MECHANISMS PROGRAM AT ALAN HARKER'S
 HOME

APPENDIX B

PARTICIPANTS

WORKSHOP ON THE LEACHING OF NUCLEAR WASTE FORMS
DECEMBER 7-8, 1982

APPENDIX B

PARTICIPANTS
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Arnold, George W.	Sandia National Laboratories Albuquerque, NM 87185	FTS-844-3848
Barkatt, Aaron	Catholic University of America Keane Hall Washington, DC 20064	202-635-5522
Clark, David E.	University of Florida College of Engineering Department of Materials Science & Engineering Ceramics Division Gainesville, FL 32611	904-392-1497
Daniel, J. Lee	Battelle Pacific Northwest Laboratory P.O. Box 999 Richland, WA 99352	FTS-509-375-2338
Exharos, Gregory	Battelle Pacific Northwest Laboratory P.O. Box 999 Richland, WA 99352	FTS-509-375-2440
Flintoff, John	Rockwell International Science Center 1049 Camino Dos Rios P.O. Box 1085 Thousand Oaks, CA 91360	805-495-4545
Gause, Evelyn	Brookhaven National Laboratory Upton, NY 11973	FTS-666-3451
Gray, Peter L.	E. I. du Pont de Nemours & Co. Savannah River Laboratory Aiken, SC 29808	FTS-239-3771
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