MCC

Materials Characterization Center

**Workshop on the Leaching
Mechanisms of Nuclear Waste
Forms, May 19-21, 1982****Summary Report**

August 1982

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute **Battelle**

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
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MATERIALS CHARACTERIZATION CENTER
WORKSHOP ON LEACHING MECHANISMS OF NUCLEAR WASTE FORMS
MAY 19-21, 1982, GAITHERSBURG, MD.
SUMMARY REPORT

J. E. Mendel, .Compiler

August 1982

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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 Gaithersburg, Maryland, May 19-21, 1982. It was the second in a series of leaching mechanisms workshops to be held at about six-month intervals. A report of the first workshop in the series, held in Seattle, has been issued (PNL-4228, Workshop on the Leaching Mechanisms of Nuclear Waste Forms, October 27-28, 1981, Summary Report, J. E. Mendel, Compiler, Pacific Northwest Laboratory, April 1982).

CONTENTS

FOREWORD	iii
1.0 INTRODUCTION	1
2.0 SUMMARY	3
3.0 SESSIONS I. PROGRESS REPORT ON LEACHING MECHANISMS	
3.1 UNIVERSITY OF FLORIDA -- L. L. Hench and D. E. Clark	5
3.2 CATHOLIC UNIVERSITY OF AMERICA -- A. Barkatt, P. B. Macedo, W. Sousanpour, M. A. Boroomand, P. Szoke and V. L. Rogers	20
3.3 PENNSYLVANIA STATE UNIVERSITY -- W. B. White	41
3.4 ROCKWELL SCIENCE CENTER -- A. B. Harker and D. R. Clarke	52
3.5 PACIFIC NORTHWEST LABORATORY -- G. L. McVay	74
3.6 LAWRENCE LIVERMORE NATIONAL LABORATORY -- D. D. Jackson	84
4.0 SESSION II. SPECIAL TOPICS IN STATIC AND LOW-FLOW RATE LEACH TESTING	
4.1 LEACH TESTING OF WASTE-FORMS: INTERRELATIONSHIP OF ISO AND MCC-TYPE TESTS -- V. M. Oversby	97
4.2 AN EXAMINATION OF THE MCC-1 LEACH TEST METHOD, PART 1: ROUND ROBIN RESULTS -- J. L. Daniel	130
4.3 AN EXAMINATION OF THE MCC-1 LEACH TEST METHOD, PART 2: EXPERIMENTAL TECHNIQUE -- H. M. Kingston, D. J. Cronin, M. S. Epstein	133
4.4 AN EXAMINATION OF THE MCC-1 LEACH TEST METHODS, PART 3: COMPARISON OF GLASS COMPOSITIONS -- D. J. Cronin, H. M. Kingston	144
4.5 A MODEL FOR LEACHING OF SRP WASTE GLASS -- R. M. Wallace and G. G. Wicks	147
4.6 EFFECT OF SOLUBILITY ON LEACHING -- B. Grambow	150
4.7 THERMODYNAMICS OF GEOCHEMICAL SYSTEMS -- S. L. Phillips	153
5.0 SESSION III: NEAR-FIELD HYDROLOGICAL, DIFFUSION AND CONVECTION PHENOMENA	
5.1 TUTORIAL ON GROUND WATER HYDROLOGY -- C. R. Faust	155

CONTENTS (contd)

5.2	INFLUENCE OF DIFFUSION THROUGH A CONCENTRATION BOUNDARY LAYER ON THE DISSOLUTION RATE OF WASTE FORMS -- W. L. Kuhn	156
5.3	STATUS REPORT ON REFERENCE FLOW REGIONS FOR GEOLOGIC REPOSITORIES	158
5.3.1	Basalt -- M. J. Apted	158
5.3.2	Tuff -- F. R. Stevens	158
5.3.3	Salt -- J. F. Kircher	158
6.0	SESSION IV. STATUS OF MULTICOMPONENT INTERACTIONS TESTING	
6.1	INTERACTIONS TESTING AT PNL -- D. G. Coles	159
6.2	OVERVIEW OF HYDROTHERMAL TESTING OF WASTE PACKAGE BARRIER MATERIALS AT BASALT WASTE ISOLATION PROJECT -- M. J. Apted	161
6.3	A SEMI-UNIFIED APPROACH TO LEACH TESTING -- K. B. Harvey	182
6.4	REPOSITORY SYSTEMS INTERACTIONS -- G. G. Wicks, B. M. Robnett, and W. D. Rankin	192
6.5	THE DIFFUSION OF LEACHED CONSTITUENTS IN BACKFILL BARRIERS -- E. J. Nowak,	194
6.6	LABORATORY ANALOG EXPERIMENT -- D. Bowers, S. Fried, T. Gerding, D. Lam, G. Vandergift, M. G. Seitz (presenter)	196
6.7	SENTINAL GAP BASALT REACTED IN A TEMPERATURE GRADIENT -- R. W. Charles and G. K. Bayhurst,	198
6.8	WASTE GLASS - SEABED SEDIMENT INTERACTIONS: OBSERVATIONS OF THE SORET EFFECT -- L. H. Brush	227
7.0	SESSION V. WHAT IS MCC-14	
7.1	SOME THOUGHTS ON MCC-14: RECOMMENDED PRACTICE FOR EXPERIMENTALLY EVALUATING WASTE FORM LEACHING IN A GEOLOGIC REPOSITORY -- J. E. Mendel	239
7.2	THE ROLE OF OXIDATION POTENTIAL, Eh, IN THE DISSOLUTION OF NUCLEAR WASTE MATERIALS -- W. B. White and W. P. Freeborn,	247
	ACKNOWLEDGEMENTS	255

CONTENTS (contd)

APPENDIX A	WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS, May 19-21, 1982 - AGENDA	A.1
APPENDIX B	WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS, May 19-21, 1982 - PARTICIPANTS	B.1

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, will serve as progress reports for the leaching mechanisms program. This is a report of the second workshop in the series, which was held at Gaithersburg, Maryland, May 19-21, 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, 5.0 and 6.0 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

The workshop was divided into five sessions:

Session I. Progress Report on Leaching Mechanisms

The principal investigators from the six laboratories participating in the leaching mechanisms program presented progress reports on their first six months activities. Many diverse activities are going on, befitting the complexity of the subject of the program. Two occurrences at the end of this first six months period will help focus the program as it continues: (1) The decision was made to phase out study of the leaching mechanisms of crystalline waste forms and to emphasize borosilicate glass only; and (2) A 30 kg batch of homogeneous simulated defense waste glass, prepared at Savannah River Laboratory (SRL), was cast into bars at Pacific Northwest Laboratory (PNL), which have been distributed to the participants so that they can all be working with a common material.

Session II. Special Topics in Static and Low-Flow-Rate Leach Testing

Seven presentations were made in this session. Most of the presentations dealt with various aspects of the MCC-1 Static Leach Test Method and the interpretation of results obtained by the method.

Session III. Near-Field Hydrological, Diffusion and Convection Phenomena

This session included a tutorial on ground water hydrology and summaries of the probable hydrological characteristics of repositories located in basalt, salt and tuff. There was also a review of an interesting recent paper by Chambers, Pigford and Zavasky on the calculated effects of diffusion in the repository near field.

Session IV. Status of Multicomponent Interactions Testing

Eight presentations were made on techniques and approaches to interactions testing that are being applied, or can potentially be applied, to the study of waste package behavior in a geologic repository.

Session V. What is MCC-14?

The final session introduced for comment the conceptual "MCC-14 - Recommended Practice for Experimentally Evaluating Waste Form Leaching in a Geologic

Repository," which would build on the existing MCC-1 through MCC-4 leach test methods. There was also a state-of-the-art discussion on Eh measurement and control, which is an important aspect of repository-relevant interactions testing.

3.0 SESSION I. PROGRESS REPORT ON LEACHING MECHANISMS

3.1 UNIVERSITY OF FLORIDA -- L. L. HENCH AND D. E. CLARK

EFFECTS OF COMPOSITION, SOLUTIONS, AND BURIAL ON NUCLEAR WASTE GLASSES

Introduction

During the last six months efforts in our laboratory have concentrated upon identifying the relative importance of a number of systems variables on the mechanisms and rates of surface attack of nuclear waste glasses. These studies have been conducted in collaboration with the Savannah River Laboratory and Pacific Northwest Laboratory in the U.S.; SKBF/Project KBS and Studsvik Nuclear Laboratory in Sweden; Marcoule Nuclear Laboratory and the University of Montpellier in France. A preliminary investigation of a nuclear waste ceramic has recently been initiated as well in collaboration with Rockwell International.

The systems variables under consideration in our studies include: 1) glass composition, 2) waste percentage, 3) waste type, 4) leachant composition, 5) cyclic corrosion, 6) flow rate, 7) simulated geologic environment, 8) in-situ burial tests, 9) effects of overpacks and backfill materials, and 10) quality control test procedures. Progress in each of these areas will be briefly reviewed with references as to the title, authors, and location of more lengthy papers on reports presenting details of the studies.

Glass Composition Effects

Several studies have been completed that investigate the effects of SiO_2 /network modifier ratios, Al_2O_3 , $\text{Fe}_2\text{O}_3/\text{ZnO}$ ratios, etc. on glass leaching (1-3). All compositions were compatible with the 1150°C low viscosity processing requirements for either the French AVM, SRL or PNL glass melters. The MCC-1 static leach test was used and both solution analyses and glass surface analysis was obtained with various spectroscopic techniques. One of the studies (2) comparing seven glasses (Table 1) for solidification of French nuclear wastes showed that glass surface attack and leach rates were strongly dependent on the concentration of network formers in the glass, Fig. 1. On the ordinate of Fig. 1 is plotted the number of days required for a glass surface to be attacked sufficiently for its IRRS spectrum at 950 cm^{-1} (Si-O-alkali region) to be decreased by 15%. The abscissa is the sum of various combinations of glass network formers. The graph shows that a critical concentration of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > \text{approximately } 55\%$ (by weight) or $\text{SiO}_2 + \text{Al}_2\text{O}_3 > 53\%$ must be present in the glass for the surface to be resistant to leaching.

The relative resistance to 90°C static leaching at SA/V = 0.1 cm⁻¹ for the seven compositions based upon three analytical criteria were:

(1) IRRS	M3 > M4 > M5 $\approx$ M6 $\approx$ M7 > M2 > M1
(2) pH	M3 > M4 > M6 $\approx$ M5 $\approx$ M7 > M1
(3) Solution Analysis	M3 > M7 > M5 > M4 $\approx$ M6 > M2 > M1

Therefore, the final ranking of the seven glasses is:

(4) Overall Resistance	M3 > M7 > M4 > M5 $\approx$ M6 > M2 > M1

Results obtained at SA/V = 1.0 cm⁻¹ are generally the same but less conclusive due to the small solution volume which makes chemical analyses less accurate. Average leach rates for the two best glasses, M3 and M7 after 28 days corrosion in 90°C water at SA/V = 0.1 cm⁻¹ were:

$$\begin{aligned}
 L_{Si}(0,28) &\approx 0.2 \text{ g.m}^{-2}.\text{d}^{-1} \\
 L_B(0,28) &\approx 0.2 \text{ g.m}^{-2}.\text{d}^{-1} \\
 L_{Na}(0,28) &\approx 0.2 \text{ g.m}^{-2}.\text{d}^{-1} \\
 L_{Fe}(0,28) &\approx 0.003 \text{ g.m}^{-2}.\text{d}^{-1}
 \end{aligned}$$

The mechanism for protection of the better glasses appeared to be development of a stabilized film on the glass surface during the first few days of leaching. A critical concentration of +3 and +4 species is necessary to stabilize the film.

Another study was conducted to investigate the relative importance of ZnO and Fe₂O₃ in stabilizing the surface film on alkali-zinc-borosilicate glasses (3). For the composition studied, replacement of half of the 60% ZnO with Fe₂O₃ degraded the leach resistance by $\approx 3X$. Both glasses appeared to be protected by dual films, one rich in SiO₂ and a second very thin film rich in multivalent species. The second film containing the mixture of ZnO and Fe₂O₃ was less stable than ZnO alone, suggesting critical concentrations of film formers are necessary to produce a film sufficiently dense and continuous to serve as an effective diffusion barrier.

An effort to generalize the composition effects of a large number of nuclear waste glasses is nearing completion (4). An HP-85 microcomputer has been programmed to calculate and store MCC-1 leach rates and compositions for 27 nuclear waste glasses from a number of labs worldwide. The computer is also programmed to search the data file and plot on a ternary chart all glasses with a specified leach rate for each element at a given time. Since the computer can easily switch the location of various compositional constituents between the 3 axes of the ternary chart it is possible to examine and generalize the influence of various constituents on leach behavior.

Figure 2 illustrates the findings. The glass compositions are divided into 3 groups; the weight percentage of oxides of Si, B, and Na are located at the top and right corners of the ternary plot. The oxides of Al, Fe and all other constituents, labeled as WP ("waste products") are added together and comprise the 3rd axis. All of the glasses in the data file are enclosed within the compositional space labelled 45.0. Thus all nuclear waste glasses stored have a leach rate for Si at 28 days of less than 45.g/m²/day. A narrower field of compositions, but still extensive, possess leach rates of 0.1 to 0.2 g/m²/day. However, only a few compositions exhibit the very low range of 0.02 g/m²/day and these all contain nearly equivalent 51-53 w/o SiO₂ and ±2% of the other constituents.

The results of Figure 2 are similar to the general findings of this study; i.e., there is a narrow compositional range where nuclear waste glasses achieve leach rates as low as 0.02 g/m²/day in a static MCC-1, 90°C leach test. However, a much broader range of glass compositions will yield leach rates of 0.1 g/m²/day. The best compositional range tends to be approximately 51-53% (SiO₂), 24-28% (Na₂O + B₂O₃), and 21-25% (Al₂O₃ + Fe₂O₃ + WP). Analysis of the time dependent changes of the compositional space for lowest leach rates leads to the conclusion that a critical concentration of Al₂O₃, Fe₂O₃, and waste product constituents are needed to produce low leach rates. This is consistent with surface analyses that show many of these species being incorporated in a surface film which apparently serves as a diffusion barrier.

Effects of Percentage and Type of Waste

Several studies in our lab (5) and by George Wicks at SRL confirm the above conclusion that the percentage and composition of waste are an important variable in nuclear waste glass leaching. Figure 3 shows that SRL 131 with 29.8% high Fe waste leaches nearly an order of magnitude more rapidly at 90°C in an MCC-1 test than SRL 131 with 29.8% high Al₂O₃ waste. The TDS-3A waste has about a 2X greater leach rate. A 15% waste loading of TDS-3A has about 10X higher leach rate than the 29.8% loading. All three types of waste show the expected decrease in leach rates with decreasing temperature. However, a differing temperature dependence may exist depending upon waste type and percentage. If this is the case it probably relates to the mechanism of leach resistance for these glasses which appears to be film formation. Figure 4 shows a SIMS depth compositional profile for a sample of SRL 131 + 29.8% TDS-3A waste corroded at 90°C for 3 weeks in DI water. Mobile Na, Li, Ca and Mg ions are depleted at the surface whereas higher valence species such as Fe, Al, Zr, and Ti are concentrated.

A recent study (6) has shown that waste loading can be increased to as much as 40% by weight with a deterioration of leach resistance (Fig. 5). This finding is significant since an increase in glass waste loading can reduce the costs of waste glass production, transportation, and storage.

Effect of Leachant Composition

Results from two recent studies of leachant composition effects (7,8) on binary alkali silicate glasses have been used to design an experiment

for SRL 131 + 29.8% TDS-3A glass. The previous work showed that Zn and Mg had a strong inhibition effect on glass corrosion due to formation of a surface film. Table 2 shows that soluble zinc and magnesium salts also inhibit the corrosion of the more complex nuclear waste glass (9). The pH increase in the soluble cation solution is very small compared with DI water and the corresponding SiO_2 dissolution is retarded by a factor of 8X.

Cyclic Corrosion Effects

There is general agreement that the MCC-1 static leach test does not model repository leaching of waste forms. One of the concerns is that repository conditions will probably involve some degree of solution replenishment. Also the possibility exists that periodic fluctuations in water content may produce alternating periods of hydration and dehydration. The effects of such sequential or cyclic periods of corrosion on glass surfaces is generally unknown. Since protection of the glass surface is related to formation of surface films, the stability of these films under cyclic corrosion conditions is especially important.

In order to understand this effect, a modification of the MCC-1 static leach test was used. Figure 6 illustrates one of the sequences used, and defines t_1 , t_2 . Three types of corrosion conditions were compared: 1) Cyclic 1 where the specimens are immersed in the original solution each cycle; 2) Cyclic 2 where the solution is replaced with fresh DI water each cycle; and 3) Static where the duration of the static test is $n \times t_1$ (cyclic).

The conclusions for a study (10) comparing a simple binary, type II, 33 mole % Li_2O -67 mole % SiO_2 (33L) glass with the type IV SRL 131 frit without waste loading were as follows:

1. The corrosion behavior of 33L glass in the Cyclic 1 test seems like the cumulative behavior of a conventional static corrosion test. A thicker film formed on the surface in the Cyclic 2 test due to more ion exchange and less network dissolution consequently, 33L glass seems to be more durable in a Cyclic 2 test.
2. SRL 131 glass corroded more severely in a Cyclic 2 test than in Cyclic 1 and static tests. This behavior is due to localized network dissolution at scratches on the surface.

A recent study (11) of cyclic corrosion of SRL 131 + 29.8% TDS showed the following:

1. There was little difference between the leaching from Cyclic 1 and Cyclic 2 tests for $t_1 = 2\text{h}$, $t_2 = 22\text{h}$, 10 cycles at 90°C . However, the 20 hour static leach test showed $\sim 3\text{X}$ greater leaching than observed in either cyclic test.
2. Increasing the duration of t_1 to 1 day still resulted in less than 90°C leaching for either Cyclic 1 or Cyclic 2 tests than the static test. Leaching was greater when the solution was replenished with fresh water (Cyclic 2) and the films tended to flake off as well.

- 3) Figure 7 shows the sequence of IRRS spectral changes associated with the Cyclic 1 test. There is a gradual replacement of the dominant 980 cm^{-1} Si-O-Si stretching vibration with a new peak around 900 cm^{-1} indicating formation of a new surface composition. In contrast, Fig. 8 shows attack of the surfaces for the first 3 cycles followed by gradual development of a more SiO_2 -rich film by cycles 7-9.
- 4) At the end of a 10 day cyclic test the surface attack is less than that observed for a 10 day MCC-1 90°C DI water static test (Fig. 9).

Flow Rate

A preliminary study (12) of a 12 ml/hr. flow rate at 70°C shows that there are no detectable ions in the leachant. However, surface attack is observed in IRRS analysis with the results being somewhat less severe than the static test but more severe than the Cyclic 1 or 2 tests (Fig. 10).

Simulated and In-Situ Burial Effects

A series of studies have been done to identify which systems variables encountered in geologic burial will have a major effect on the leaching of glass waste forms. One finding from these studies is the rapid ion depletion of glass surfaces in contact with bentonite and water (13). Figure 11 shows a series of IRRS spectra after 28 days, 90°C burial of a borosilicate waste glass with glass-glass interfaces in the top half of the figure. The same glass composition and identical burial conditions but with a glass-bentonite interface shows extensive attack (bottom half of the figure). Laboratory simulations of this effect with static leaching show that bentonite accelerated leaching is a function of the amount of water present; in dry conditions it stops. The lab tests also show that static leach tests yield much higher rates of leaching than burial experiments at equivalent temperature.

SIMS analysis of the interfaces after burial provides a quantitative analysis of the ion depletion depths and surface accumulation of high valence species. A profile of the glass-bentonite surface after 3 mo., 90°C burial is shown in Fig. 12. Conclusions from this series of burial experiments include:

There are only minor differences in the ion depletion depths of glass ABS 39 and 41 during 28 day and 3 mo., 90°C or 8°C burial in STRIPA at 360 m.

Surface compositional profiles show selective ion depletions of Na, B, at up to a rate of $1.5 \cdot 10^{-7}$ m/day for glass ABS 39 and up to $2.5 \cdot 10^{-8}$ m/day for glass ABS 41.

A thin film rich in Si, Fe and Al forms on both glasses during burial.

Moist or wet bentonite accelerates the rate of ion depletion for both glasses, with glass ABS 39 the worst, in both laboratory and STRIPA burial experiments.

The bentonite effect is much less in burial environments than in lab simulations.

There is little difference in burial surface reactions between the "pineapple slice" configuration and "minicans".

Overpack and Backfill Effects

The potential negative effect of bentonite as a backfill material was summarized above. The burial experiments however have shown no negative effects of candidate overpack materials such as Pb, Ti, and Cu on glass leaching (14). Surface attack of the glass-metal interfaces after 3 mo. at 90°C burial is very limited. Pb especially seems to be protective when in contact with the borosilicate glasses.

Quality Control Tests

Results of surface analysis using IRRS after burial experiments indicate that this tool may be useful for production quality control, QC, and quality assurance, QA. A recent result that seems especially encouraging is shown in Fig. 13. The figure shows a correlation between the integrated area under the IRRS spectra obtained with a FTIR and the mass loss of the glasses in an MCC-1 90°C leach test. The differences in integrated area result from variation in % waste loading in frit SRL 131 (from 5-40%). Therefore, the IRRS analysis of the glass appears to predict the potential leach sensitivity of the glass and waste. Additional work to follow up on the correlation is in progress. Use of this method to identify variations in heterogeneities such as crystallization or other changes resulting from variations in thermal history is also possible (15), as shown in Figs. 14 and 15. Similarly, a recent preliminary study shows that the method may be used to study corrosion of nuclear ceramic waste forms also, as indicated in this FTIRRS spectrum from Synroc, supplied by Dr. Harker, Rockwell Science Center (Fig. 16).

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T A B L E 1

NUCLEAR WASTE COMPOSITIONS (Weight %)

Glass Oxide (%)	M 1	M 2	M 3	M 4	M 5	M 6	M 7
SiO ₂	47.6	42.7	51.13	45.6	50.0	48.4	46.1
Al ₂ O ₃	-	8.6	4.05	4.9	3	2.0	5.0
Na ₂ O	12.4	14.2	13.19	8.8	12.5	11.28	12.5
B ₂ O ₃	18.6	17.8	13.56	22.0	14.41	18.47	14.2
Fe ₂ O ₃	6.4	4.0	1.601	2.8	2.96	2.96	2.96
CaO	-	-	4.10	-	2	3.76	4.1
MgO	-	-	0.348	-	-	-	-
MnO ₃	2.47	2.09	1.592	2.62	1.7	1.7	1.7
Li ₂ O	-	-	-	-	2.0	-	2.0
X							
S.W.P.	15	12.7	10.9	15.9	12.22	12.22	12.22

X Simulated Waste Products

Table 2

SRL 131 + 29.8% TDS, Time = 7 Days, 90°C

Solution	SA	pH	pH	Wt (g)	Wt (g)	[SiO ₂] ppm	Wt Loss (g)
		Before Corr.	After Corr.	Before Corr	After Corr.		
D.I. Water	3.94	5.6	9.4	.7884	.7862	34.5	0.0022
Zn 100 ppm	4.12	6.3	6.8	.8430	.8424	8.75	0.0006
Mg 100 ppm	4.19	5.3	7.3	.8697	.8694	4.5	0.0003
13 Mg 250 ppm	4.11	5.5	7.2	.7905	.7906	3.75	-0.0001
Al 250 ppm	4.16	3.5	2.4	.8484	.8453	30	0.0031

Fig. 1

NUCLEAR WASTE GLASS CONSTITUENT OXIDES

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 13

Fig. 14

Fig. 15

Fig. 16

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ALUMINOSILICATE SATURATION AS A SOLUBILITY CONTROL IN LEACHING OF NUCLEAR
WASTE-FORM MATERIALS

ABSTRACT

In the slow flow region, material loss rates of nuclear waste form materials are determined by the solubilities and the flow rates. Present studies show that the solubilities of various, widely different waste forms, as well as of minerals, can be correlated with the Al_xSi concentration products. This indicates that in these cases the solubilities are controlled by a combined equimolar aluminosilicate species. This observation serves as a basis for a predictive model for the long-term stability of waste forms under slow flow conditions. This model also provides explanations of other experimental findings, such as the increases in solubility upon departure from a neutral pH in the low as well as in the high pH region, the small magnitude of the temperature dependence, and the observation that the release rate of Cs is low relative to that of Na in the slow flow region. The relative concentrations of Si and of Al, respectively, in the leachates are related to the composition of the leach solids and are shown to depend on the immersion time in different ways in the cases of high-silica solids and of high-alumina solids, respectively. In both cases, however, the dependence of the Si:Al ratio on contact time furnishes another strong indication for the formation of a solid surface with comparable contents of Al and of Si, respectively, upon prolonged immersion in water. The results are shown to form the basis for an accurate long-term prediction of material loss rates.

1. The Dependence of Material Loss Rates on Flow Conditions

In modeling the dynamics and rates of release of the various components of solid nuclear waste forms exposed to chemical corrosion in aqueous media, a fundamental distinction exists between the processes which control the overall rates of loss and transport of material away from the waste form under conditions of rapid water flow on one hand and of slow flow on the other. At high flow rates (or high dilutions) the loss, or release rates, are controlled by the leaching kinetics of the solid in water, where the composition of the water reflects the conditions prevailing in the environment of the disposal site rather than interaction with the waste form. At low flow rates the loss rates primarily depend upon the thermodynamic solubility and upon the rate at which the water in contact with the solid, which has been considerably modified as a result of extraction of components from the waste form, is replaced with fresh, unreacted water¹. Under geologic conditions, water exchange rates are likely to be low in a large number of cases, and therefore solubilities constitute a key factor in determining the long-term durability of the material. As mentioned above, water subjected to prolonged interaction with the material becomes substantially altered. This alteration of the composition affects the reactivity of the medium with respect to the dissolution of a particular component of the waste form in the following ways: (i) pH changes, e.g., increases in pH due to extraction of alkaline components from the solid, exercise large effects on solubility limits as well as on leach rates; (ii) increasing concentration levels of the component of interest may result in approaching saturation in the case of scarcely soluble species; (iii) increasing concentrations of other leach products can affect subsequent dissolution of the component of interest due to secondary interactions; (iv) increasing solute concentrations in the aqueous phase can give rise to phenomena such as re-adsorption, ion-exchange and other modifications of the solid-liquid interface which affect further material transport processes across the surface.

Silica is a major structural element of many proposed waste forms, including both glasses (e.g., borosilicate, high-silica) and crystalline ceramics (e.g., supercalcine). Under strongly interactive conditions the solubility of silica will reflect the pH excursion (unless acidic additives are introduced to

suppress the pH rise) as well as effects of other dissolved species. Possible effects of the presence of alumina are of particular interest since alumina, too, is an important component of many waste forms.

Several glassy and ceramics waste forms were tested using a dynamic method² which involves replacing a fixed fraction of the water in contact with the solid at a constant frequency a sufficient number of times (corresponding to 4-5 complete exchanges of the leach volume) to permit the concentrations of the various species in the leachate to reach practically constant levels. It has been shown^{1,2} that the results of each test can be applied to a particular residence or contact time in the repository site by means of a simple normalization of the experimental surface-to-volume ratios to the corresponding ratio expected under repository conditions. Table 1 lists the concentrations and normalized leach rates of Si, Al, Na and Cs, respectively, in leachates obtained during the final, constant-level stages of the tests carried out at 70°C on the five waste forms mentioned above as a function of residence time. The corresponding pH values are also shown.

Within the region of short residence times, an increase in residence time gives rise to a nearly proportionate increase in the concentration of leached species and the leach rates are nearly constant, or even rise with increasing residence time as a result of the increase in pH. On the other hand, in the case of long residence times a further increase in residence time leads to a decrease in leach rate due to growing saturation, and the leachate concentrations approach a constant level. This permits evaluation of the saturation limits, which completely control the leachate composition at the limit of extremely long contact times. The onset of slow-flow behavior, which depends on the leaching kinetics of the solid and cannot be assigned a single value of flow rate, is characterized by the start of a downward trend in plotting the material loss rate as a function of increasing contact time (or decreasing flow rate). Only data corresponding to the region of low flow rates, as defined by this criterion, are shown in Table 1 (except for two rapid-flow results for CU glass which are included for comparison). It should be noted that even in the slow flow region the leach rates of Si and Al progressively decrease with increasing residence time, but the corresponding leach rates in the case of Na (as well as B and Li) show little change. As a result the pH continues to grow

TABLE 1. Results of Dynamic Leach Tests on Various Waste-Form Materials in The Slow-Flow Region, 70°C

Material	Effective Residence Time, Days	pH	Leachate Concentrations mg·L ⁻¹				Normalized Concentrations g·m ⁻² ·d ⁻¹				$\log \frac{C_{Na}}{C_H}$	$\log \frac{C_{OH}}{C_H}$
			Si	Al	Na	Cs	Si	Al	Na	Cs		
PNL 76-68 ^b	110	9.8	76.8		99.4	2.55	.062		.158	.037	7.44	5.6
	385	9.9	110		120	2.73	.025		.055	.0111	7.62	5.8
SRL TDS-131	3.2	9.5	12.5	0.58	6.7	.037	.270	.118	.353	.544	5.96	5.0
	11.2	9.6	20.3	0.67	11.7	0.71	.126	.039	.176	.299	6.31	5.2
	110	10.7	112	0.56	122	1.6	.071	.003	.187	.069	8.42	7.4
	385	11.1	232	0.56	347	3.2	.042	.001	.152	.039	9.28	8.2
	905 ^c	11.3	358	0.67	872	10.3	.029	.0005	.169	.029	9.88	8.6
	3415-11100 ^d	11.9	984	0.98	3304	49.8					11.06	9.8
CU PGM	27.5	7.1	0.86	0.11	0.27	<0.06	.0020	.0015	.008	<.019	2.17	0.6
	110 ^e	7.3	3.35	0.08	0.60	<0.01	.0019	.0003	.004	<.004	2.72	0.6
	385	7.3	7.29	0.43	0.89	<0.01	.0012	.0004	.002	<.001	2.89	0.6
Rockwell TLC	3.1	9.3	2.68	1.7	3.50	0.50	.511	.033	.813	1.34	5.48	4.6
	88.2	11.1	11.2	17	60.7	1.43	.074	.011	.492	.134	8.52	8.2
Synroc-D	2.6	8.1	1.93	1.1	1.36	0.11	.417	.076	.318	.310	3.87	2.2
	22.7	8.2	2.33	1.6	1.73	0.20	.059	.013	.047	.066	4.08	2.4
	90.8	9.5	5.10	3.5	5.28	0.76	.032	.007	.036	.062	5.86	5.0

a Based on a reference surface-to-volume ratio of 60 m⁻¹ and a porosity of 16% (cf. Ref. 1).

b PNL 76-68 glass contains <0.1% Al.

c A static powder test; regular grain size (-42+60 mesh, cf. Ref. 2)

d A static powder test; fine powder (-100 mesh); maximum value for T_r based on surface area measured with a small amount of powder (Ref. 2). Stacking likely to reduce T_r - minimum value based on unchanged (0.169 g·m⁻²·d⁻¹) Na leach rate.

e Flow test in the rapid-flow region - see Text.

throughout the slow-flow region, the solubilities of Si and Al continue to drift upwards and their leach rates do not drop to zero as might be expected when saturation is attained under constant pH conditions.

2. Solubility Control by Alumina-Silica Interactions

At first sight, it is difficult to correlate the concentration levels of silica (see Table 1) and of other dissolved species in leachates obtained with different waste form materials even in cases where the residence times or stabilized pH values are similar. The solubility limit of silica originating in various solid materials as a function of temperature and pH is well-known. In the case of amorphous and vitreous solids the solubility data at a temperature T can be expressed by an equation

$$C_{\text{SiO}_2} = C_{T_1}^0 (1 + 10^{(\text{pH} - \text{pK})}) \exp \left[\frac{\Delta H}{T} \left(\frac{1}{T_1} - \frac{1}{T} \right) \right]$$

where $C_{T_1}^0$ is the solubility at a standard temperature T (e.g., 298 K) and at a near-neutral or lower-than-neutral pH, which is low with respect to pK of silicic acid.³ ΔH is the enthalpy.⁴ Median representative values for pK, C_{298}^0 and ΔH are 9.66,³ 115 mg/L⁴ and 16.1 J·mol⁻¹,⁴ respectively. Accordingly the solubility of silica at 70°C and pH levels of 7, 8, 9, 10, 11 and 12 has values of 113, 115, 137, 360, 2590, and 24880 mg/L, respectively.

According to the experimental data given in Table 1, silica concentrations in leachates obtained with increasingly long residence times indeed approach the calculated values in the case of PNL 76-68 borosilicate glass. However, in the cases of the other four materials, much lower limiting solubilities are indicated. In the cases of the two ceramic materials this might be attributed to the fact that they are largely crystalline; however, spectroscopic studies⁶ show that a large fraction of the silica is present in a more soluble vitreous phase, which is likely to control the silica concentration in the leach solution. In particular, a large difference is observed between the silica levels of the leachate in the cases of PNL 76-68 and SRL TDS-131 glasses. The findings of the flow tests are in agreement with the results of other type of tests. For instance, MCC-1 tests⁷ carried out for periods of 3, 7, 14 and

28 days at 90°C yield concentrations of 14.6, 40.9, 55.8 and 84.0 mg/L Si, respectively, in the case of PNL 76-68 glass as compared with 5.5, 23.0, 21.2 and 22.2 mg/L Si, respectively, in the case of SRL TDS-131 glass. The observation that silica concentration in PNL 76-68 glass approaches the solubility of amorphous silica while the limiting concentration in the cases of SRL TDS-131 and CU glasses do not exceed 20% of this level is also supported by the results of static solubility tests.

The consistently large differences between the dissolved silica levels in leachates obtained with PNL 76-68 and SRL TDS-131 glasses are observed despite the similarity in major element composition between the two materials. PNL 76-68 glass has 40.0% SiO₂, 9.5% B₂O₃, 12.9% Na₂O and 11.1% Fe₂O₃, while SRL TDS-131 has 44.8% SiO₂, 10.1% B₂O₃, 12.3% Na₂O and 13.9% Fe₂O₃. The only major difference between the two glasses lies in the fact that PNL 76-68 contains no alumina (except as trace impurities) while SRL TDS-131 contains 3.8% Al₂O₃. The other three materials listed in Table 1, which have higher alumina contents even compared with SRL TDS-131 glass (CU PGM - 8.1%, Synroc-D - 19.0%, and Tailored Ceramics - 51.1% Al₂O₃) are characterized by dissolved silica levels which are much lower than the ones obtained with the two borosilicates glasses under comparable conditions.

The fact that the solubility of silica in aqueous media is lower when alumina is present in the system has been reported in the literature.^{8,9} The reverse effect, i.e., lowering of alumina solubility in the presence of silica, is also known,^{9,10}. The reduced solubility may result from re-adsorption of the species in solution (e.g., Si) on a site of the other oxide (e.g., Al₂O₃) on the solid surface.¹¹ However, dissolution and precipitation processes in the silica-alumina system may also be controlled by diffusion of ions in solution.¹² Recent studies of aluminosilicate minerals¹³ showed that in many cases the solubilities can be expressed in terms of definite equilibrium constants involving complex entities of the general form

where R is K or Na. These studies show that when the alkali-to-proton ratio is low (i.e., in neutral or mildly acidic aqueous media) the most stable or least soluble solid in the system is gibbsite ($\text{Al}(\text{OH})_3$), provided that dissolved silica levels are below $1.2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$; when the silica content increases beyond this limit, clay-type aluminosilicates, viz. kaolinite and pyrophyllite, control the solid-liquid equilibrium (see Ref. 13, Fig. 6). The solubility product of both these species is expressed in terms of $a_{\text{Al}}^2 a_{\text{Si}}^x$, where $x=2$ (kaolinite) or $x=4$ (pyrophyllite). At high alkali-to-proton ratios (high pH) the solid phase in equilibrium becomes dominated by feldspar-type minerals, with solubility products which also include a dependence on the activity of the alkali ion. The findings also show that while gibbsite is stable even in the presence of moderate concentrations of dissolved silica, complex aluminosilicates rather than quartz are stable in natural water systems whenever Al is present.

The question now arises whether these findings apply to the results obtained with synthetic glasses and ceramic materials in laboratory tests. In this case, it is necessary to consider amorphous forms of silica and alumina as well as crystalline forms. Amorphous silica can exist in meta-stable equilibrium with water over prolonged periods of time, making it possible to consider materials which contain silica predominantly in this form to immobilize wastes. On the other hand, amorphous alumina is probably the first species to precipitate out of solution, but is very unstable and is rapidly converted to gibbsite.¹³

According to Table 1, observed silica solubilities are considerably lower than those calculated for amorphous silica in all the cases where alumina is present. It has also been observed that in the cases of data points corresponding to widely divergent samples with respect to both solid and leachate composition, and in particular in cases where large differences are observed between the dissolved Al and Si concentrations obtained with two different materials at similar pH values, the products of dissolved Al and Si concentrations are nearly the same. For instance, at pH 11.1 the concentration of Si observed in a flow test on SRL TDS-131 glass in the saturation region, 232 mg/L, is much higher than the concentration of Al, 0.56 mg/L, while the reverse is true in the case of Tailored Ceramics (11.2 mg/L Si, 17 mg/L Al).

However, the $Al \times Si$ concentration product in the second case, 190 (mg/L)^2 , is close to the one observed with SRL TDS-131, 130 (mg/L)^2 . Similarly, at pH 9.5-9.6 the Si, Al and $Si \times Al$ levels obtained with SRL glass are 20.3 mg/L, 0.67 mg/L and 14 (mg/L)^2 , respectively, while the corresponding levels obtained with Synroc-D are 5.10 mg/L, 3.5 mg/L and 18 (mg/L)^2 , respectively.

In general, when the $Al \times Si$ concentration products obtained in slow-flow tests on all glassy and ceramic waste forms are plotted as a function of pH, it is observed that all the data fall within a narrow band around a general curve which is independent of the pH in the range between pH 7 and pH 8.5, and then rises with increasing slope as the pH increases from 8.5 to at least 12. This uniform dependence is in marked contrast with the wide scatter obtained when it is attempted to correlate the various Si or Al concentration readings.

In addition to the measurements on the five synthetic waste forms, flow tests have also been carried out on two natural rocks, Pomona formation basalt from the Columbia Plateau and Swedish granite from the Stripa mine. The results are shown in Table 2. It can be seen that the Si-to-Al ratios are very different for the two materials. Basalt leachates contain much higher Si levels and much lower Al levels than granite extracts, in similarity to the case of SRL glass leachates which contain much more Si and much less Al than leachates of Synroc-D or Tailored Ceramics. However, the combined $Al \times Si$ or $(Al \times Si)^2$ concentration products again follow the general behavior illustrated in Figure 1. In the case of basalt, data for both Si and Al concentrations are available for two basaltic ground-water compositions. one composition, corresponding to the Priest Rapids member of the Upper Wanapum basalt formation,¹⁴ has a similar pH value to that of the flow test leachate corresponding to the test with the longest residence time. In this case the Si level in the ground water is higher than the one observed in the basalt leachate, the Al level is lower in the ground water (see Table 3), but the $Al \times Si$ concentration products in the two cases are similar (see Figure 1). A second data point, corresponding to the basaltic ground water of the Mabton Interbed of the Saddle Mountains formation at the Hanford site,^{14,15} where the pH has a higher value of 8.5, is characterized by a lower Si content and a higher Al content relative to the Upper Wanapum water, but this data point too fits quite closely to the plot

TABLE 2. Silica and Alumina Content of Various Nuclear Waste Solids and Rock Specimens, wt.%

<u>Material</u>	<u>%SiO₂</u>	<u>%Al₂O₃</u>
PNL 76-68	40.0	0.0
SRL TDS-131	44.8	3.8
CU PGM	57.3	8.1
Rockwell TLC	5.7	51.1
Synroc-D	6.75	19.0
Pomona basalt	51.1	14.7
Stripa Granite	73.0	12.2
Kaolinite phase of nepheline	46.55	39.50
Upper Wanapum Basalt	51.65	13.53
Mabton Interbed Basalt	52.22	14.44

shown in Figure 1. It should be noted that the data points for basaltic ground water correspond to a lower temperature than 70°C. However, the temperature dependence of kaolinite solubility in the near-neutral region appears to be quite small¹³(see below).

The last data point in Figure 1, which corresponds to the Al and Si concentrations in a saturated solution of the kaolinite phase of nepheline, is interpolated from the results of rigorous solubility measurements at 60°C and at 80°C reported in Reference 13.

3. Quantitative Analysis of the Saturation Levels

As shown in the previous section, the limiting leachate concentrations obtained in leach tests carried out on glassy and ceramic waste-form materials as well as on minerals in the saturation region can be fitted with a single curve when the AlxSi concentration products are plotted as a function of pH. This indicates that the solubilities are controlled by a combined equimolar aluminosilicate species. The commonest simple compound of this type, kaolinite, can undergo various dissociation processes, and the relative importance of these processes is pH-dependent. The major probable processes are as follows:

TABLE 3. Composition of Rock Leachates in Laboratory Tests and in Nature

Material and Formation	Effective ^a Residence Time days	pH	Solute Concentrations mg·L ⁻¹			$\log \frac{C_{Na}}{C_H}$	$\log \frac{C_{OH}}{C_H}$	Ref.
			Si	Al	Na			
Leach Test Results, 70°C								
Pomona basalt	63d	7.9	9.85	0.406	0.338	3.07	1.8	This work
Pomona basalt	1480d	8.0	34.0	0.124	2.304	4.00	2.0	This work
Stripa granite	1577d	8.7	5.81	0.971	0.959	4.32	3.4	This work
Kaolinite phase of nepheline	50d	7.0	2.57	1.12			0.0	12
Ground-Water Analysis, 25°C								
Upper Wanapum basalt	18000y	8.1	26.7	0.086	34	5.27	2.2	13
Mabton Interbed basalt	15000y	8.5	14.0	0.298	107	6.17	3.0	14

^a Based on a reference surface-to-volume ratio of 60m⁻¹ and a porosity of 16% (see Table 1).

FIGURE 1. $\text{Al} \times \text{Si}$ and $(\text{Al} \times \text{Si})^2$ Concentration Products in Saturated Leachates of Nuclear Waste-Form Materials and of Rock Materials at 70°C and in Basaltic Ground Water as a Function of pH

Following the accepted model for the solubility of amorphous silica,^{3,16} it is assumed that the neutral species ($\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$ or a similar equimolar aluminosilicate compound) has a constant, limited solubility in water, which is not affected by the pH. The pH level, however, controls the dissociation of this species into ionic species which are assumed to be very soluble in water. The concentration of the neutral compound in the aqueous phase remains constant even when the pH is changed since increased dissociation is counter-balanced by further dissolution of the solid phase and vice versa.

According to this model, the solubility product corresponding to the total Al and Si concentrations in solution should be given by

$$(\Sigma\text{Si}) (\Sigma\text{Al}) = K_1 [\text{H}^+]^3 + K_2 [\text{H}^+] + K_3 + K_4 / [\text{H}^+] + K_5 / [\text{H}^+]^2$$

However, when it is attempted to use this equation to fit the data shown in Figure 1 over the entire pH range between 7 and 12, it is concluded that the best fit is obtained when a value of 0 is assigned to the three parameters K_1 , K_2 and K_5 . An excellent fit, represented by the solid curve in Figure 1, is obtained with the simple expression

$$(\Sigma \text{Si}) (\Sigma \text{Al}) = a + b/[\text{H}^+]$$

where a (or K_3) is $4.07 \times 10^{-9} \text{ mol}^2 \cdot \text{L}^{-2}$ and b (or K_4) is $2 \times 10^{-18} \text{ mol}^3 \cdot \text{L}^{-3}$. The significance of this equation becomes more immediate when it is expressed in the form

$$(\Sigma \text{Si}) (\Sigma \text{Al}) = a(1 + 10^{\text{pH} - \text{pK}})$$

The symbol a is not a free parameter, since it corresponds to the pH-independent solubility product in the neutral region, assumed to represent the solubility of the undissociated species. The dissociation constant, pK , has a best-fit value of 9.31, corresponding to a weak acid which is, however, somewhat stronger than silicic ($\text{pK}=9.66$) and aluminic ($\text{pK}=11.2$) acids. Increase in acid strength upon complexation is a general phenomenon which results from displacement of electronic charge towards the bond between the components of the complex. Kaolinite and other clay-type minerals have been reported¹⁷ to be moderately weak ($\text{pK}<5$) acids.

The solubility products obtained in the present study are somewhat higher than those reported for pure, highly crystallized kaolinite. The values corresponding to the $(\text{C}_{\text{Al}} \text{C}_{\text{Si}})^2$ product at 70°C in the present study are 2×10^{-17} , 4×10^{-17} and $3 \times 10^{-14} \text{ mol}^2 \cdot \text{L}^{-2}$ at pH 7, 9 and 11 respectively, compared with values of 1.2×10^{-23} (25°C) at pH 7, 2×10^{-21} (25°C) at pH 11 reported for kaolinite.¹³ This discrepancy (except at pH 11) is not surprising both in view of the presence of additional components, in addition to Al and Si, in the solids included in the present study and, in particular, in view of the relatively short periods employed in the flow experiments compared with the long periods of time required for the formation of pure, highly-ordered, large-grained kaolinite. It is known that when silica is present in solution Al species appear to be initially precipitated as rather poorly crystallized, less stable clay-mineral species.¹⁸

4. Other Experimental Findings

The model postulating solubility control in waste-form leachates by a kaolinite-type, weakly acidic aluminosilicate can be shown to agree with other results of leach tests on waste-form materials. For instance, preliminary

dynamic leach tests carried out on SRL TDS-131 glass at 90°C in the slow-flow region indicate that leachate concentrations are not higher, and are probably even lower, than the concentrations measured in parallel experiments at 70°C. This agrees with the small positive or even negative temperature dependence of the solubility of kaolinite,¹³ as well as pyrophyllite and gibbsite, in the near-neutral pH region. The solubility of silica, on the other hand, increases considerably whenever the temperature is raised, exhibiting an enthalpy of 16.1 J·mol⁻¹.⁴

A very important observation is that leachate concentrations in tests on SRL TDS-131 glass¹⁹, as well as other waste-form materials²⁰, rise not only when the pH increases beyond the neutral range but, even more steeply, when the pH is lowered, either by the addition of acid¹⁹ or as the result of irradiation.²⁰ This effect does not appear in the case of amorphous³ or fused¹⁶ silica, but it is very pronounced in the cases of kaolinite as well as feldspar, nepheline and gibbsite.¹³

In the case of SRL TDS-131 glass it is observed that the Cs/Na ratio in the leachate is 1.6±0.1 in the case of the two shortest residence times, but thereafter this ratio falls off sharply and reaches 0.17 at the longest contact time employed (see Table 1). Studies of aluminosilicate minerals¹³ show that K-feldspar, which incorporates K as well as Al and Si, has a much larger stability field at the expense of the fields of kaolinite and pyrophyllite in the K-Al-Si-O-H diagram than albite in the corresponding Na-based diagram.¹³ The present studies indicate that Cs resembles K in having a higher tendency than Na towards incorporation and retention in the solid phase through bulk precipitation. Selective surface adsorption may be important, but in fact bulk reprecipitation and surface adsorption may be two representations of the same physical property, i.e., the composition of the solid surface upon prolonged contact with water. The same effect is observed in the case of Tailored Ceramics (see Table 1), but not in the case of Synroc-D, where alkali concentrations in all leachates are lower than those observed at the shortest contact times in the case of SRL glass, which appear to be too low for feldspar precipitation (see above).

A very similar effect, i.e., a drastic decrease in K/Na ratios with increasing pH and increasing alkali/proton concentration ratios, is observed

upon examining different ground-water compositions obtained from the same rock type, i.e., Pasco Basin basalt.¹⁴ While in the cases of the Wanapum, Saddle Mountain and Grande Ronde basalt formations the molar K/Na ratio is always 0.36 ± 0.03 , the K/Na mole ratios in the corresponding ground-water compositions are 0.190, 0.078 and 0.004, respectively. The corresponding pH values are 8.1, 8.5 and 9.9, respectively, showing very extensive relative enrichment of the solid surfaces with respect to K. In general, as will be described in a later paper, rock leachate compositions extrapolated to very long residence times generally show agreement with observed ground-water concentrations, taking into account early saturation with respect to Si and Al (see above) as well as sulfate. However, this agreement is observed only when the pH values of the leachate and of the ground water are similar, otherwise depletions with respect to K (see above) as well as polyvalent ions (e.g., Ca) are observed in the medium with the higher pH.

While material loss rates in the slow flow region are determined almost exclusively by the solubility limits and the flow rates, specific leach rates of various solid waste forms become important in the intermediate flow rates. At very slow flow rates, the results obtained in all cases are expected to lie along a curve such as the one shown in Figure 1, while at higher flow rates saturation is not approached and the AlxSi concentration products fall considerably below the curve. The greater kinetic durability of CU high-silica glass with respect to SRL borosilicate glass can be inferred from the fact that in the latter case the experimental data lies on the curve even with a residence time as short as 3 days (see Table 1 and Figure 1) while in the case of CU glass the only data point which exhibits saturation (i.e., a considerable fall-off in Si leach rate) and which falls on the AlxSi curve in Figure 1 occurs at a contact time of 385 days. A considerable departure from the curve occurs even at the second slowest residence time of 110 days, where the observed AlxS concentration product is only $3.5 \times 10^{-10} \text{ mol}^2 \cdot \text{L}^{-2}$, compared with a value of $4.1 \times 10^{-9} \text{ mol}^2 \cdot \text{L}^{-2}$ expected on the basis of the curve in Figure 1. At a residence time of 28 days the corresponding concentration product drops to $1.2 \times 10^{-10} \text{ mol}^2 \cdot \text{L}^{-2}$. The silica concentrations in these last two cases are lower than those required for kaolinite precipitation according to Ref. 13. In the case of the ceramic waste forms, where kinetic leach rates are close to

those of SRL glass, saturation is observed with contact times higher than 1 day. The superior durability of CU high-silica glass in the slow flow region is due to a reason other than low leaching rate constants, viz. the suppression of a pH rise beyond 7.5 and the resulting prevention of increase in aluminosilicate solubility levels.

5. Al:Si Ratios in the Leachates and Surface Composition

The observations described so far show that the solubility controls involve combined aluminosilicate species. However, the individual dissolution characteristics of Al and of Si have not yet been discussed. The Al:Si mole ratios in the various leachates corresponding to the slow-flow region, based on the data in Table 1, are shown in Table 4 along with the Al:Si ratios obtained from the composition of the leached solids. It can be seen that generally the C_{Al}/C_{Si} ratios in the leachate are higher the larger the corresponding ratios in the solid material. However, the change in (C_{Al}/C_{Si}) leachate with increasing contact time shows a different type of behavior in the case of high-alumina solids compared with the case of high-silica solids. In the case of high-silica solids such as SRL borosilicate glass or basalt the Al:Si ratio in the leachate decreases with increasing contact time, while in the case of high-alumina solids such as Synroc-D and Tailored Ceramics the opposite effect is observed. It is impossible to explain this phenomenon in terms of changes in pH, since the pH always rises with increasing contact time. As mentioned above, dissolution rate-controlling mechanisms involve in many cases surface reactions rather than diffusion control.^{12,13} The surface adsorption of dissolved silica on alumina surfaces⁸ and vice versa²¹ has been observed. It is therefore probable that in the case of high-silica a relatively rapid process of dissolution of both silica and alumina takes place until the concentration reaches the solubility product. Since the exposed surface of the solid contains more silica sites than alumina sites, further immersion leads to preferential readsorption of Al on the surface of the solid, accompanied by further dissolution of Si so that the concentration product in the leachate is maintained unchanged. A similar mechanism involving long-term readsorption of Si on an Al-rich surface is postulated in the case of high-alumina solids.

TABLE 4. Al:Si Mole Ratios in Solid and Leachate Compositions

Material	Effective ^a Residence Time days	pH	(C _{Al} /C _{Si}) Leachate	(C _{Al} /C _{Si}) Solid
SRL TDS-131	3.2	9.5	0.048	0.11
	11.2	9.6	0.034	
	110	10.7	0.005	
	385	11.1	0.003	
	905 ^b	11.3	0.002	
	3415-11100 ^c	11.9	0.001	
CU PGM	385	7.3	0.061	0.17
Stripa granite	1577	8.7	0.17	0.20
Pomona basalt	63	7.9	0.043	0.34
	1480	8.0	0.004	
Mabton basalt	15000y	8.5	0.022	0.33
Wanapum basalt	18000y	8.1	0.003	0.31
Kaolinite phase of nepheline	50	7.0	0.45	1.00
Synroc-D	2.6	8.1	0.59	3.30
	22.7	8.2	0.71	
	90.8	9.5	0.71	
Rockwell TLC	3.1	9.3	0.66	10.5
	88.2	11.1	1.58	

^a See Footnote a, Table 1

^b See Footnote c, Table 1

^c See Footnote d, Table 1

6. Conclusions and Implications to Nuclear Waste Disposal

Based on a broad range of experimental data, the concentrations of aqueous solutions in contact with widely different solids (glassy and ceramic waste-form materials, minerals) in the saturation region follow a general solubility law which corresponds to the formation of a combined equimolar aluminosilicate species as the solubility-controlling species. At a given temperature, the dependence of the solubility of the various solids on the pH can be expressed in terms of a simple, single-stage acid dissociation equilibrium of this aluminosilicate species.

These findings indicate that at slow flow rates the solubility and the resulting material loss rate of nuclear waste form material at a given temperature will be determined by the $Al \times Si$ concentration product at the pH level of the leachate; accordingly, accurate long-term loss predictions can be made provided the limiting pH is known. For instance, in the case of CU glass the pH level approached upon prolonged exposure does not exceed 7.5 (see Table 1) since the glass contains a sufficiently high phosphate content (4-5% P_2O_5) to buffer the leachate and prevent the leaching of alkalis from causing a pH run-away. In this case the solubility remains within the minimum plateau region of the pH-dependence curve and its value can be accurately defined. On the other hand, rapid selective alkali leaching which is observed in the case of SRL TDS-141 glass, for instance, even in the slow-flow saturation region causes the pH to continue rising with increasing contact time to a value of at least 12 without exhibiting an approach to a limiting level. As a result, the solubility continues to grow exponentially with rising pH and it is very difficult to specify an upper limiting value for the solubility of the glass matrix. A reliable prediction of the safe upper limits on the release of minor components can still be made, however, in the case of SRL TDS-131 glass, assuming that the Na (or B, Li) leach rate throughout the saturation region has a constant value (cf. Table 1) and that this value represents the limiting rate of the alteration of the matrix into a more stable aluminosilicate form and of the release of non-precipitating minor components into the surrounding solution. In other words, in the saturation region the concentrations of minor elements will become constant and the maximum release rates of minor waste-form components over long periods of contact time will be limited by the alteration rate of

the waste-form into recrystallized and reprecipitated species. However, release rates of minor components into the saturated leachate, which may occur at the interface, may be much slower than the net alteration rate due to readsorption on the altered surface or on clay-like precipitates, which may also be viewed as reincorporation into the composition of reformed aluminosilicate. Such an effect has been demonstrated in the present paper even in the case of the highly mobile Cs^+ ion. On the other hand, anionic species such as the ones formed by Mo, Tc, Np etc. may be expected to resist readsorption and to leach out at high rates, close to the limiting Na leach rate. The general conclusion that in the case of materials which do not form a permanently protective surface layer the limiting release rates will be determined by the limiting leach rates of Na rather than of Si has been derived previously²² on the basis of layer stability considerations.

It can be concluded, in addition, that as long as the pH of the surrounding ground water is lower than the pH of the waste form leachate in pure water, material loss rates in ground water will always be limited by the Al_2Si product in the saturated leachate in pure water. If the pH of the waste-form leachate is much higher than that of the ground water, the former will completely dominate the loss rates. However, when the two pH values are similar, or when both lie between pH 7 and 8.5, ground water which is already saturated with respect to aluminosilicate (e.g., basaltic or granitic water) can be expected to give rise to substantially lower material loss rates. This does not apply to salt brines and to ground water with relatively high fluoride levels.

In order to test the conclusions of the present paper more experimental data are required, in particular results of comprehensive analyzes of leachates corresponding to very long contact times of waste form with water and of aged ground water from various geologic formations. The roles of scarcely soluble components other than Al and Si, e.g., Fe^{19} and Zr^{13} , in placing additional constraints on leachate saturation levels should also be explored in more detail.

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THE DISSOLUTION OF CRYSTALLINE CERAMICS

INTRODUCTION

The present program objectives are to lay out the fundamentals of crystalline waste form dissolution. Nuclear waste ceramics are polycrystalline. An assumption of the work is that to the first order, the release rate of a particular radionuclide is the surface-weighted sum of the release rates of the radionuclide from each crystalline form that contains it. In the second order, of course, there will be synergistic effects. For example, the dissolution of one component may change the chemistry of the solution which will then alter the dissolution rate of other components. There will be also grain boundary and other microstructural influences.

As a first approximation, we have selected crystalline phases one at a time. The sequence of investigations and measurements is:

- (i) Identification of the actual chemical reactions of dissolution including identification of the solid reaction products if such occur.
- (ii) The rates of these reactions are then determined empirically to give what may be called macroscopic kinetics. These kinetics are expressed as empirical rate equations which take into account both forward and back reactions thereby including saturation effects and also take into account the explicit rate dependency on various solutional parameters such as pH and silica activity.
- (iii) Determination of the rate-controlling mechanisms. Mass transport, surface reaction, diffusion through gel layers or reaction product layers on the surface are possibilities.
- (iv) If the rate is controlled by surface reactions, the final step would be to determine the atomic kinetics, that is the specific atomic reactions that occur at the dissolving interface. These

kinetics have not been determined for any phases of interest to nuclear waste forms and it seems unlikely that one could justify this final and rather difficult step, although it is the scientific bottom line.

Our concern with the crystalline forms are in two areas: The crystalline components of the reference ceramic waste form and related ceramics and the alumino-silicate phases that appear in some experimental waste forms and as waste-rock interaction products. Specific compounds are:

Reference Ceramic Phases

zirconolite

magnetoplumbite

spinel

Tc-bearing spinel and perovskite

Aluminosilicate phases

nepheline

pollucite

$\text{CsAlSi}_5\text{O}_{12}$

Sr-feldspar

REFERENCE CERAMIC PHASES

Zirconolite

Zirconolite ceramics with the compositions $\text{CaZrTi}_2\text{O}_7$ and $\text{CaZr}_{0.9}\text{U}_{0.1}\text{Ti}_2\text{O}_7$ were synthesized by direct sintering of the component oxides.

One-gram solid pellets of zirconolite were immersed in 200 ml of 0.1 N HCl (pH = 1), deionized water, and 0.1 N NaOH (pH = 13) for times from two days to four weeks. The concentrations of zirconium and titanium in the leachates were below limits of analytical detection for all runs. The uptake of calcium and uranium as a function of time was measured. Calcium saturates very quickly and is essentially time-independent throughout the range of the experiments. Uranium is continuously extracted in what appears to be linear in time. The initial extraction of calcium is the same in acid and in deionized water and is below limits of detection in base. Uranium is extracted by acid and by base but is little attacked by deionized water.

One explanation for the resistance of titanium and zirconium ceramics to solution is that a passivating film of ZrO_2 or TiO_2 quickly builds up on the crystal surface which protects the material from further attack. Some preliminary Auger spectroscopy experiments do not support this hypothesis. Figure 1 shows a depth profile on a zirconolite ceramic leached at $90^\circ C$ for one day and for 14 days. To the accuracy of these measurements, zirconium is, if anything, depleted on the surface.

Magnetoplumbite

Magnetoplumbites with compositions $CaAl_{12}O_{19}$ and $CaLa_{0.05}Al_{12}O_{19}$ were synthesized. It proved difficult to retain cesium in these structures under ceramic sintering conditions and it was also difficult to obtain material free of $CaAl_4O_7$ and Al_2O_3 . The dissolution of the calcium phase was followed by reacting crushed 200 to 300 μm particles in 0.1 N HCl (pH = 1), deionized water (pH = 6) and 0.1 N NaOH (pH = 13). The uptake of calcium and aluminum into solution can be easily followed. Determination of reactions and filling of rate equations is underway.

Spinel

Spinel phases appear in most of the ceramic waste forms that have been proposed, including both the high alumina and high titania ceramics, as well as precipitates in some of the waste glasses. Spinel shows an amazing range of chemical composition with extensive solid solution among most of the intermediate size cations including the transition metals and smaller noble gas core ions. A ternary system that contains some of the spinels of interest is $NiAl_2O_4 - NiFe_2O_4 - Fe_3O_4$. As a starting point, the end members $NiAl_2O_4$ and $NiFe_2O_4$ were selected. These spinels have been synthesized and formed into sintered ceramics. The leachabilities are very low at $25^\circ C$ except in acid (pH = 1) solutions.

Technetium-Bearing Phases

The objective here is to obtain information on the extraction of technetium from ceramic and possibly glass waste forms. The tentative host phases for technetium are spinel solid solutions between Mg_2TiO_4 and Mg_2TcO_4 and perovskite solid solutions between $CaTiO_3$ and $CaTcO_3$. Synthesis of these

FIGURE 1. Depth Profiles Into Zirconolite ($\text{CaZr}_{0.9}\text{U}_{0.1}\text{Ti}_2\text{O}_7$) Obtained by Auger Spectroscopy.

materials is underway. It appears that 0.1 mole fraction of the technetium phase will be the one used for dissolution measurements.

ALUMINOSILICATE PHASES

Most of the aluminosilicate work is a matter of tidying up studies began earlier or of fitting in some additional detail in the behavior of aluminum and silicon in dissolution processes. As an example, a minimum in the solubility curve near neutral pH is observed in the dissolution behavior of all compounds investigated, due to the common speciation pattern of aluminum in acid and basic solution.

Nepheline

A fairly complete model for the dissolution kinetics of natural crystals of $(\text{Na},\text{K})\text{AlSiO}_4$ was completed as the Ph.D. thesis of Mwakio Tole under a previous cooperative project with Rockwell. Copies have been distributed to several members of the present team.

Pollucite

A fairly detailed investigation of the dissolution kinetics of $\text{CsAlSi}_2\text{O}_6$ has been completed. Both surface analysis methods and analyses of leach solutions have been used. A summary of the results is given in the separate presentation by Dr. C. G. Pantano. (A text of Pantano's presentation immediately follows this article).

CsAlSi₅O₁₂

This phase apparently does not occur in nature but seems to be a cesium host of even greater stability than pollucite. Figure 2 shows some dissolution data for cesium. This compound appears to follow the parabolic kinetics law common to many glasses and silicate crystals. There is a pronounced pH dependence which is shown in Figure 3.

Sr-Feldspar

SrAl₂Si₂O₈ was originally selected because it was a possible strontium host for a high silicate ceramic. Although ceramic waste form formulations drifted off into other directions, the investigation of Sr-feldspar dissolution was continued because it seems a good model for the behavior of aluminosilicates in the presence of alkaline earth ions. The work was completed under the present project and is the Ph.D. thesis of Ms. Varda N. Fleer.

Figure 4 shows a typical dissolution run. After an initial phase which is believed to be the establishment of a pitted surface, the kinetics are linear in time, that is of zero order, with respect to all dissolving species. Finally, at long times, there is a break in slope and the dissolution curves have zero slope. This final stage represents the saturation and precipitation of secondary phases which then control the level of dissolved silica, alumina, and strontium in solution. However, the dissolution of the feldspar itself is essentially congruent. There is the usual minimum in the solubility curve near neutral pH (Figure. 5).

Table 1 summarizes some of the results. The various factors can be compiled into a macroscopic rate equation which has the form

$$\frac{dc}{dt} = \frac{A}{V} a_H^n + k_0 e^{-\frac{E_a}{RT}}$$

FIGURE 2. Dissolution of $\text{CsAlSi}_5\text{O}_{12}$ at 70°C

FIGURE 3. Characteristic cesium dissolution rate at 30 days and 70°C as a function of pH

FIGURE 4. Dissolution of $\text{SrAl}_2\text{Si}_2\text{O}_8$

FIGURE 5. Solubility of $\text{SrAl}_2\text{Si}_2\text{O}_8$ as a function of pH

TABLE 1. Dissolution of $\text{SrAl}_2\text{Si}_2\text{O}_8$

Dissolution:	congruent
Kinetics:	linear
Mechanism:	surface reaction - controlled
Dissolution etch pits:	rectangular
Generalized rate expression:	

$$k_{\text{net}} = \frac{dc}{dt} = \frac{A}{V} a_{\text{H}}^n + k_o e^{-E_a/RT}$$

where:

C = concentration in solution

t = time

A = surface area of solid

$k_o = A(T) a_{\text{H}}^{n+}$

$n = \begin{cases} 1, & \text{acidic solutions} \\ -0.14 & \text{at } 25^\circ\text{C, basic solutions} \\ -0.28 & \text{at } 70^\circ\text{C, basic solutions} \end{cases}$

and

<u>pH</u>	<u>$A(T)(\text{mole ml cm}^{-2}\text{sec}^{-1})$</u>	<u>$E_a(\text{kcal mole}^{-1})$</u>
2	4.5×10^{-12}	7.67
5.6	2.9×10^{-9}	8.06
10.5	2.0×10^{-4}	13.86

DISSOLUTION OF POLLUCITE

T. Henderson, T. Vezza, W. B. White and C. G. Pantano

The dissolution of single crystal and polycrystalline pollucite ($\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) has been investigated under static and Soxhlet conditions. Polycrystalline ceramics were prepared from a commercial pollucite powder by sintering at 1100°C, 1200°C and 1300°C, and also by hot isostatic pressing (hip) at 1200°C. The static tests were run at 40°C and 90°C in water (for up to 183 days) and in brine and silicate solutions (for 28 days). The solutions were analyzed with DC-plasma emission and the leached surfaces were examined with scanning electron microscopy (SEM) and other surface analysis techniques.

The single crystal surfaces were very resistant to preferential leaching of Cs. Ion-scattering spectroscopy (ISS) showed only a partial depletion of Cs from the outermost monolayer after one hour in water at 120°C. An acid treatment (24 hours at 25°C and pH=2) was necessary to completely remove Cs from the outermost monolayer.

In contrast, the dissolution behavior of the polycrystalline ceramics showed a strong dependence upon the processing used to prepare the materials. This was found to be due to the formation of a glassy Cs-aluminosilicate phase during sintering. The most important variable was the sintering temperature. In particular, ceramics prepared at 1100°C vs 1200°C showed radically different behaviors. The ceramics sintered and/or hip'd at 1200°C were, of course, more dense than ceramics sintered at 1100°C. Nonetheless, the Cs leach rates were about three times greater for the denser ceramics. The glassy phase was analyzed in the electron microprobe and was found to be richer in Cs_2O for ceramics processed at the higher temperatures. The 1200°C hip'd ceramic exhibited the same leach rate for Cs as the 1200°C sintered ceramic. This is consistent with the interpretation of glassy phase dissolution since the glassy phase in the hip'd material had a comparable Cs_2O concentration to the ceramic sintered at 1200°C. In contrast, the Al and Si leach rates were observed to decrease with densification. This 'apparent' reduction in the leach rates for

Al and Si was found to be due to concomitant precipitation; this was shown conclusively via surface analyses by AES, SIMS and SEM.

The static leach data obtained in H_2O @ $90^\circ C$ exhibited the best fit to a parabolic rate law; the parabolic rate constants are given in Table 1. The fit was quite good for the Cs, and less so for the Al and Si. It is not surprising that the Al and Si data do not fit a simple kinetic law since two phases are dissolving simultaneously; moreover the surface analyses showed that precipitation of $Al(OH)_3$ and to some extent SiO_2 , accompany the dissolution. Under Soxhlet leaching conditions, the Cs release exhibited linear kinetics (Table 1). In addition, the release rate was higher for the less-dense ceramics. Thus, the leaching mechanism for these materials is affected significantly by the solution replenishment.

It is concluded that the dissolution of polycrystalline pollucite is due largely to the preferential release of the glassy phase constituents since the single crystal studies verify the insolubility of the pollucite grains at near-neutral pH under static conditions. The dissolution behavior of polycrystalline pollucite under static and Soxhlet conditions is drastically different. Under static conditions, the pollucite grains are in equilibrium with the solution and the dissolved species originate only from the glassy phase. The glassy phase is more prevalent and has a higher Cs_2O content in the denser ceramics sintered at $1200^\circ C$; thus, the denser ceramics exhibit higher Cs leach rates. Under Soxhlet conditions the leach rates are linear and proportional to the specific surface area. Thus, the glassy phase is depleted from the surface region of the ceramics very rapidly, and the congruent dissolution of the pollucite grain continues at a linear rate. The Cs leach rates were highest in water, and lowest in the brine solution.

TABLE 1. Kinetics of Pollucite Dissolution

Normalized Parabolic Rate Constants
in $\text{g/m}^2\text{-day}^{1/2}$ at 90°C in Static H_2O

	<u>1100°C</u>	<u>1200°C</u>	<u>1200°C HIP</u>
Cs	0.11	0.27	0.28
Al	0.92	0.10	-
Si	1.21	0.68	0.39
Specific Surface Area in m^2/g	0.142	.061	-

Normalized Rate Constants
in $\text{g/m}^2\text{-Day}$ in Soxhlet

	<u>1100°C</u>	<u>1200°C</u>	<u>1200°C HIP</u>
Cs	0.46	0.15	incomplete

DISSOLUTION MECHANISMS IN HIGH-LEVEL NUCLEAR WASTE CONSOLIDATION FORMS

1. INTRODUCTION

This report summarizes the Science Center results from the first six months of study on the MCC/DOE sponsored Nuclear Waste Form Dissolution Mechanisms program. During this initial period the bulk of the Science Center effort has focused upon polycrystalline ceramic nuclear waste forms as no samples of defense waste borosilicate glass were available. The polycrystalline ceramics studied were those developed at Lawrence Livermore National Laboratory (LLNL) and the Rockwell Science Center specifically for the immobilization of Savannah River Plant nuclear defense waste. This report contains results of studies upon solution-solids interface phenomena and the role of cracking in determining the overall performance of a waste form undergoing ground water leaching.

2. SOLUTION-SOLID SURFACE STUDIES

The studies of the solution-solid interface effects occurring during leaching were conducted with static leach tests using deionized, silicate and brine waters. The two ceramic waste forms tested were a 60 wt% waste composition designated as LS04-HP4A by LLNL and a modified assemblage designated as RSC-S29 designed and fabricated at the Science Center. The simulated SRP waste composition used in the ceramics is shown in Table 1, with the ceramics phase content and fabrication conditions shown in Table 2.

As can be seen from the table, both of the ceramic forms have densities of about 4 g/cm^3 , contain spinel, nepheline and fluorite structures as well as a minor amorphous phase. The major differences are in the relative proportion of the fluorite, magnetoplumbite and perovskite phases and the elemental distribution in the spinel phases. At a microstructural level the ceramics are similar in that they are extremely fine grained ($1 \mu\text{m}$) and that the nepheline grains are associated with the intergranular amorphous material. The distribution of the waste elements among the phases of the two ceramic forms is summarized in Table 3, as determined by analytical STEM and electron microprobe.

The dissolution mechanisms associated with the ceramic forms depend upon several variables including:

1. The volume fraction of the phases
2. The nature of the ceramic microstructure, i.e., microstructurally isolated grains versus veins of individual phases
3. The ion content, pH and temperature of the leach water.

To provide insight into the manner in which these variables affect waste form dissolution, a series of experiments have been performed in which solution and surface analyses have been combined with microscopic observations.

The analytical studies have centered around static leach tests in which monoliths, ground powders, cracked specimens and ion beam thinned foils have been exposed to deionized, silicate and brine waters at temperatures ranging from 20 to 150°C. From these studies an overall mechanism can be deduced to describe the waste form performance.

The initial studies in deionized water were found to be the most aggressive towards the ceramic form and revealed that the short term static leach behavior was controlled by three principal effects.

1. Dissolution of the amorphous material exposed on the surface by preparative cutting and grinding
2. Slow continuous dissolution of the amorphous and nepheline phases along bulk material pathways defined by the grain distribution
3. Surface layer formation by precipitation of minerals specifically compatible with the exposed ceramic surface, i.e., the ceramic surface chemical state and double layer potential were involved in determining the nature of the precipitate layer.

The solution analysis of the MCC-1 type tests in deionized water demonstrate the effect of the initial dissolution of the amorphous phase. As can be seen in Table 4, the concentrations of Na, Al and Cs in the solutions shows a rapid increase to the 3-day level with a slow release of Ca, Cs, Si and Na then occurring as the nepheline ($\text{NaAlSi}_3\text{O}_8$) grains at the surface dissolve. This behavior is confirmed by the XRD patterns of the RSC-S29 ceramic as prepared and leached sample surfaces. Comparison of the patterns in Fig. 1 shows that the only crystalline phases disappearing from the surface are nepheline and a trace amount of the sodium silicate phase, hauyne.

The role of the interfacial material in the dissolution process becomes quite apparent in the leaching of ion-beam thinned foils. Figure 2 shows a TEM micrograph of a 50 nm thick foil which was exposed to 90°C deionized water for 4 hours. The light areas surrounding the nepheline grains are holes in the foil representing the location of the dissolved intergranular material. The nepheline grains themselves show only slight attack by the solution, whereas the other crystalline phases show no effects of the leaching process.

Though the solution analyses in deionized water indicate that the ceramic will leach through dissolution of its more soluble phases, the tests performed in silicate water show the waste form to be stabilized with a Si rich surface layer slowly appearing with time. Table 5 demonstrates the stability of the ceramic in the silica water, while the XPS spectra in Fig. 3 shows the enhancement of the Si on the ceramic surface after 28 days in the solution.

In the case of the salt brine, the ceramic surface acts as a preferential site for the formation of a surface phase, potentially identified by XRD and XPS as a magnesium oxychloride. Inert gold foil in the leach solution showed no such precipitate.

These phenomena are qualitatively shown in Figs. 3, 4 and 5. The XRD and XPS patterns comparing "as prepared" ceramics to the leached surfaces show the decrease in the exposed nepheline content and the buildup of the surface

precipitation products. In the D.I. and silicate waters, the silicate phases dominate, while in the brine case precipitation and passivation appears to dominate. In all cases the more inert zirconolite, spinel, magnetoplumbite and perovskite phases show no appreciable leaching. Uranium is the only element detected in the leach solutions at temperatures up to 150°C other than those associated with nepheline or glass. This is undoubtedly due to the extreme sensitivity of analysis technique for this element. However, the U analysis show leach rates that could easily be associated with traces of U in the intergranular phases.

The present results indicate that the controlling features of the ceramic dissolution process are in order of importance:

1. Solution ionic concentrations of the soluble species Si, Na, Ca, etc.
2. The presence of ions in the ground waters capable of preferentially precipitating on the ceramic surface, i.e., Mg^{+} , Cl^{-} , etc.
3. The surface area fraction made up of silica containing species in the ceramic and the degree of grain encapsulation on the microscopic scale.

In the 3 waters tested, the following short-term leach mechanisms were observed:

1. Deionized water
 - a) Initial dissolution of exposed amorphous material, followed by gradual leaching of the nepheline phase
 - b) Bulk penetration of the ceramic appeared to be less than 1 micron in 18 days at 90°C.
 - c) Higher temperatures accelerate the leaching process until saturation is achieved with respect to the surface phase (stratlingite).

2. Silicate water

- a) Silicate water stabilizes the ceramic with very little pH change, and no major dissolution occurring
- b) A silicate rich surface layer appears to form slowly.

3. Salt Brine

- a) Salt brine to preferentially precipitate "sorel cement," magnesium oxychloride on the ceramic surface.

3. INVESTIGATION OF EFFECTS OF CRACKING ON WASTE FORM LEACHING

Cracking is expected to be an inevitable characteristic of nuclear waste forms whether noncrystalline or crystalline. It is likely to occur as a result of processes as varied as thermal shock, impact damage, or swelling on irradiation (Table 6). Thus determination of the effect that the presence of cracks may have on dissolution is essential in establishing upper and lower bounds on the release rates of radionuclides from nuclear waste forms.

The presence of cracks can have a number of consequences on the dissolution of nuclear waste forms, as summarized in Table 7. The least detrimental to the overall release of radio-nuclides is that the cracks merely act to increase the effective surface area of material exposed to the leachant. At the other extreme is the possibility of pre-existing cracks growing with time of exposure under the combined action of corrosion at the crack tip and stresses generated by molar volume increases of the dissolution products forming at or near the crack tip. Residual stresses will, it is anticipated, also act to promote crack advance.

The way in which we have chosen to introduce cracks of a carefully controlled nature is by the indentation technique. A conventional Vickers hardness indenter is loaded onto a flat, highly polished surface of the material, as if a hardness measurement is being made. Above a threshold load,

short, stable cracks grown from the corner of the hardness impression reaching a length that is related to the fracture toughness of the material. The cracks propagate into the body of the material and have the characteristic shape shown schematically in Fig. 6. Typically, the extent of crack penetration into the material is commensurate with the length of the crack observed on the surface. A further advantage of the cracks induced by indentation, is that they can act as stress concentrators so that fracture can be initiated from the site of the indentation. The cracks once formed remain due to the residual stress field of the hardness impression. The materials are then in a suitable form for leaching and, in our experiments, are exposed in the standard MCC-1 test configuration.

After dissolution exposure the samples were removed and dried as prescribed in the MCC-1 test procedures and then loaded under three point bending until fracture occurred. Fracture normally originates at the indentation impression to expose the faces of the radial cracks and the cross section for examination under the scanning electron microscope. The fast-fracture technique described here for exposing a cross section has been found to be preferential to cutting a section of a leached bar and then polishing down, because in this latter method features such as cavities created by the preferential dissolution of one region tend to be filled in (hence obscured) by the polishing media. One advantage of having a polished surface on the sample is that preferential dissolution and re-precipitation phases may be more easily identified than on the as-cut surfaces specified by MCC. The other advantage is that the position of the original surface can be readily distinguished when examining the fractured cross section.

The preliminary results of a microstructural characterization of cracked samples of a ceramic waste form exposed to deionized water for 28 days are presented here. The ceramic was the LS04-HP4A material produced by Lawrence Livermore National Laboratory from the Savannah River Laboratory simulated waste. The material is a polyphase ceramic containing the phase and elemental distribution as given in Table 3.

Figure 7 is a high magnification view of the vicinity of the tip of one of the radial cracks after leaching but prior to fracture. Two features stand out. The small, white particles on the surface that are a phase believed to have precipitated out from the leaching solution when the solubility limit was reached. The other feature is the surface pits (the regions in dark contrast) where preferential dissolution appears to have occurred. The crack tip region itself is unaffected.

The depth of dissolution is revealed by examination of the cross section produced by fracture as shown in Fig. 8. The original, polished surface exposed to the leachate intersects the cross section at the line AA. Columnar cavities extending into the material from the surface indicate that dissolution of the material has penetrated to an average depth of $\sim 1 \mu\text{m}$ within the 28-day exposure. Clearly, on the basis of this micrograph, the dissolution process is inhomogeneous and some of the material is unaffected. Also, as may be seen, the depth of dissolution varies from one location to another.

The cross section in the vicinity of the indentation produced radial cracks is shown in the scanning micrographs of Fig. 9. The top left-micrograph is of the general area and the radial cracks can be delineated by comparison with the schematic diagram of Fig. 6. The micrograph at top-right is a higher magnification view of part of the right-hand radial crack and the adjacent region. The radial crack front is indicated by the dashed line FF. The region to the left of the line FF was exposed to the leachant during the leach test whereas the region to the right was only revealed by the post-leach fracture event. The higher magnification micrographs at the bottom left and bottom right were recorded from either side of the radial crack front in the regions A and B, respectively. The region within the crack exposed to the leachate (bottom left) is distinctly different to that shown in the bottom right; pits have been created by the leachant, such as those arrowed, and a white, particulate precipitation phase can be identified. Neither feature is seen in the area away from the crack, indicating that the leachant is able to enter the cracks and attack the material at the crack faces.

The origin of the pits and the preferential regions of dissolution can be understood with reference to the concurrent observations by transmission electron microscopy and X-ray diffraction. X-ray diffraction analysis of the surfaces of the leached samples indicates that on dissolution the nepheline phase disappears, whereas the other crystalline phases appear unaffected. (XRD of hydrothermally exposed samples suggest that a stratlingite phase forms on the surface by precipitation from the leachate; it is believed that the bright, small particles seen in Figs. 7 and 9 are the same phase). Transmission electron microscopy results of thin electron microscope samples exposed to leachant for 4 hours clearly show that both the intergranular glass phase and the nepheline phase dissolve much more rapidly than the other phases present, with the intergranular glass phase etching out fastest. An example of the observed dissolution microstructure is reproduced in Fig. 2.

Although the experiments described here are not very sophisticated in nature, they simply demonstrate the role that cracks may play during the initial stages of dissolution exposure.

The microstructural results obtained to date indicate that at short term exposures

- cracks act to increase the net surface area
- leachant is able to enter narrow cracks
- dissolution of phases exposed by the crack can occur with mass transport of the dissolved species out of the crack and into the main body of leachant.

With particular reference to the improved Synroc D composites, LS04-HP4A, the noncrystalline intergranular phase and the crystalline nepheline phase dissolve preferentially and thereby control the depth of penetration and dissolution of the crystalline waste-form. In these particularly resistant materials to dissolution no evidence has been seen (after 28 days) of corrosion dissolution assisted crack growth.

Table 1

CHEMICAL COMPOSITION OF SIMULATED SAVANNAH RIVER PLANT COMPOSITE DEFENSE WASTE

<u>COMPONENT OXIDE</u>	<u>wt %</u>	<u>COMPONENT OXIDE</u>	<u>wt %</u>
Fe_2O_3	30.5	Na_3PO_4	1.18
MnO_2	6.9	SiO_2	10.20
U_3O_8	4.2	ThO_2	0.77
Al_2O_3	30.0	Ce_2O_3	0.64
CaO	4.2	Cs_2O	0.34
NiO	2.1	SrO	0.38
Na_2O	7.2	ZrO_2	0.53
Na_2SO_4	0.96		

TABLE 2.

FABRICATION CONDITIONS AND PHASE CONTENT OF TEST CERAMICS

RSC-S29

Waste Loading - 59.8%

Additives: TiO_2 , ZrO_2 , CaO , SiO_2 , La_2O_3 Redox Control: $\text{U}^{6+} \rightarrow \text{U}^{4+}$ Consolidation: HIP, 1040°C , 10,000 PSIDensity: 3.97 g/cm^3 PHASES

Nepheline	21.9 volume %
Zirconolite	20.5
Murataite-type	19.8
Spinel (Magnetite-type)	13.0
Magnetoplumbite	12.1
Perovskite	7.7
Amorphous	
Trace: Pseudobrookite, Hematite, Unknown	} < 5

Approx. Calculated Density 4.0 g/cm^3 LS04-HP4A

Waste Loading - 62.7 wt%

Additives: TiO_2 , ZrO_2 , CaO , SiO_2 Redox Control: $\text{U}^{6+} \rightarrow \text{U}^{4+}$ $\text{Fe}^{2+}/\text{Fe}^{3+} \approx 1$ Consolidation: HUP, 1100°C , 3000 PSIDensity: 4.0 g/cm^3 PHASES

Nepheline	26 volume %
Zirconolite	17
Perovskite	14
Spinel 1 (Hercynite-type)	38
Spinel 2 (Ulvo-type)	
Amorphous	
Minor Phases: Murtaite- type	} ~5
γ -Iron Alloy, α -Iron Alloy	
Trace: Unknowns	

Approx. Calculated Density 4.0 g/cm^3

TABLE 3.

PHASE DISTRIBUTION OF SRP WASTE ELEMENTS IN CERAMIC WASTE FORMS

<u>WASTE COMPONENTS</u>	<u>LS04-HP4A</u>	<u>RSC-S29</u>
Fe, Al, Mn, Ni	Spinel (Hercynite + Ulvo)	Spinel (Magnetite)
Ca, Ba, Sr	Perovskite, Amorphous	Magnetoplumbite, Perovskite
Na, K, Cs	Nepheline, Amorphous	Nepheline, Magnetoplumbite, Amorphous
Si	Nepheline, Perovskite, Amorphous	Nepheline, Magnetoplumbite, Perovskite, Amorphous
U, Th	Zirconolite, Perovskite	Zirconolite, Murataite-type, Perovskite
Trace Elements Pb, Zr, Co, Mg, Cr	—	Magnetoplumbite

Table 4

MCC-1 LEACH PERFORMANCE OF RSC-S29 CERAMIC

90° C STATIC LEACH TEST

NORMALIZED RELEASE g/m^2

	3 Day	7 Day	14 Day	28 Day	56 Day	112 Day
pH 90° C	7.11	7.17	7.17	7.18	7.50	7.80
Cs	8.5	12.8	7.5	8.0	8.5	8.2
Sr	1.0	1.0	1.1	1.2	1.0	<1.1
U	$<2 \times 10^{-2}$	$<2 \times 10^{-2}$	$<2 \times 10^{-2}$	4.4×10^{-3}	$<2 \times 10^{-2}$	2.4×10^{-3}
RZ	<0.6	<0.6	<0.6	<0.6	<0.6	<0.6
Na	7.1	9.1	10.9	11.3	12.1	18.7
Al	3.7	5.3	6.0	6.0	5.8	7.2
Si	15.5	13.9	15.5	16.9	16.8	20.7
Ti	-	-	-	-	$<1.5 \times 10^{-2}$	$<1.5 \times 10^{-2}$

Table 5

NORMALIZED RELEASE (g/m ²)							28 DAY LEACH RATE (g/m ² -d)	
DAY	MCC-1			DAY	MCC-2		MCC-1	MCC-2
	14	21	28		14	28	90°C	150°C
Na	<3	<3	<3	Na	<3	13	<0.1	0.5
Ca	0.4	0.9	0.8	Ca	2.5	3.3	3×10^{-2}	0.1
Al	1.7	2.5	2.6	Al	10.1	9.6	9×10^{-2}	0.3
Si	<3	<3	<3	Si	<3	13	<0.1	0.5
Cs	<2	<2	<2	Cs	7	6	$<9 \times 10^{-2}$	0.2
Sr	<1	<1	<1	SR	<1	<1	$<4 \times 10^{-2}$	$<4 \times 10^{-2}$
U	1.9×10^{-2}	2.5×10^{-2}	2.3×10^{-2}	U	2.0×10^{-2}	2.6×10^{-2}	8×10^{-4}	9×10^{-4}
La	<0.7	<0.07	<0.7	La	<0.7	<0.7	$<3 \times 10^{-2}$	$<3 \times 10^{-2}$
Ti	2.2×10^{-2}	2.4×10^{-2}	2.3×10^{-2}	Ti	1.5×10^{-2}	1.5×10^{-2}	8×10^{-4}	5×10^{-4}
Fe	$<2 \times 10^{-2}$	$<2 \times 10^{-2}$	$<2 \times 10^{-2}$	Fe	4.8×10^{-2}	3.2×10^{-2}	$<6 \times 10^{-4}$	1.1×10^{-3}
Mn	$<8 \times 10^{-2}$	$<8 \times 10^{-2}$	$<8 \times 10^{-2}$	Mn	8×10^{-2}	$<8 \times 10^{-2}$	$<3 \times 10^{-3}$	$<3 \times 10^{-3}$
Ni	<0.2	<0.2	<0.2	Ni	<0.2	<0.2	$<6 \times 10^{-3}$	$<6 \times 10^{-3}$
Zr	$<3 \times 10^{-2}$	$<3 \times 10^{-2}$	$<3 \times 10^{-2}$	Zr	$<3 \times 10^{-2}$	$<3 \times 10^{-2}$	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$

TABLE 6
SOURCES OF CRACKING IN NUCLEAR WASTE MATERIALS

- Differential Thermal Contraction
- Anisotropic Thermal Contraction
- Differential Swelling
- Anisotropic Swelling
- Devitrification Stresses
- Thermal Shock
- Exfoliation

TABLE 7
POSSIBLE CONSEQUENCES OF PRESENCE OF CRACKS

- Increases effective area exposed to leachant
- May provide a short-circuit transport path into and out of microstructure
- Narrow cracks might be clogged with corrosion product
- Molar volume increase of corrosion product may accelerate crack growth - symbiotic corrosion cracking
- Exfoliation

Fig. 1 A comparison of the X-ray diffraction patterns recorded from the surface of the RSC-S29 ceramic in its as-fabricated condition (top), after exposure to DI water for 28 days (center) and after 56 days exposure (bottom). The only change detectable is the progressive dissolution of the nepheline phase (shaded).

FIG. 2 Transmission Electron Micrograph of A Thin (~50 nm) Microscope Sample of LS04HP4A Material After Being Immersed In DI Water For 4 Hours at 90°C. The amorphous intergranular phase has dissolved preferentially leaving the holes in the foil that appear light. The nepheline grains also show some attack.

Fig. 3 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.

Fig. 4 Comparison of the X-ray diffractograms obtained from the surfaces of the RSC-S29 ceramic after 28 days in silicate water (top), brine (center) and DI water (bottom).

Fig. 5 The X-ray diffraction patterns recorded from the surfaces of the RSC-S29 ceramic after 28 days at 90°C and 150°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.

SC82-17208

PLAN VIEW

MEDIAN
CRACKS

SIDE VIEW

Fig. 6 Schematic diagram illustrating the morphology of the median (radial) cracks introduced by indentation fracture.

FIG. 7 Scanning Electron Micrographs of the Vickers Indentation (Left) and At Higher Magnification Part of the Indentation Induced Crack (Right) After Exposure To DI Water For 28 Days at 90°C. White surface precipitates and pits (appearing dark) produced by the dissolution exposure can be discerned in the higher magnification view.

FIG. 8 Cross Section of the Ceramic After Immersion In DI Water For 28 Days at 90°C. Two magnifications are shown. The intersection of the room temperature fracture with the polished surface in contact with the leachant is indicated By the Line A-A. columnar cavities produced by dissolution are seen to a depth of $\sim 1 \mu\text{m}$ below the original surface.

FIG. 9 Low Magnification View of the Indentation Radial Fractures After Dissolution Immersion and Subsequent Exposure By Breaking of the Sample (Top Left). Higher magnification of the boundary, FF, of one of the sectors of a radial crack (top right). The region A formed the face of the the radial crack and was exposed to the leachant whereas region B was only exposed by subsequent fracture. The regions A and B are shown at high magnification in the micrographs of bottom left and bottom right, respectively. Pitting caused by the preferential dissolutions of one of the phases (nepheline) and the precipitation of a reaction product (white features) characterize the crack face open to the leachant, whereas the region B is unaffected.

3.5 PACIFIC NORTHWEST LABORATORY -- G. L. McVay

A REVIEW OF RECENT PNL RESEARCH ACTIVITIES RELATED TO GLASS LEACHING MECHANISMS

Development of a defensible predictive model for elemental removal from the repository necessitates the understanding, on a mechanistic level, of waste form leaching characteristics in a realistic repository environment. Borosilicate glass is the primary candidate for a high-level waste form and thus has received the largest amount of leaching mechanism-related research activity. Research areas which are important to the understanding of glass-water interactions are given in Table 1. The topics are separated into general areas and areas specific to nuclear waste. All of the research areas are being investigated to some degree by nuclear waste-related programs, and those marked with an asterick are being investigated in a more fundamental way by DOE/BES programs. The areas to be discussed in this presentation/writeup are glass-metal interactions and surface-area-to-solution-volume-ratio effects. All of this research was conducted on PNL 76-68 glass which has the composition given in Table 2.

GLASS-METAL INTERACTIONS

All waste package concepts include metallic barriers as canister and over-pack materials. It is thus important to determine if the various candidate metals have an effect on glass leaching behavior. The interactive effects of several metals (Cu, Sn, Al, Pb and Ti) on PNL 76-68 glass leaching in distilled water have been previously investigated. General conclusions were that the more reactive metals retarded leaching while the more inert metals had little effect. The interactive effects of lead were particularly noteworthy since glass leaching was essentially stopped. This particular effect was attributable to a lead hydroxide coating that rapidly covered the glass surface. Although the previous glass-metal interactive studies were informative, they did not include iron, which is a potentially important constituent of the waste package. In addition, the experiments were conducted in deionized water rather than groundwaters.

TABLE 1. Important Areas of Research For Understanding Glass-Water Interactions

General		Nuclear Waste	
*	● Identification of Water Reaction Species	●	Radiation/Radiolysis
*	● pH	●	Interactions
	● Temperature	●	Alteration Products
*	● Surface Charge	●	Accelerated Testing
	● Solubility		
	● Back Reactions		
*	● SA/V		

TABLE 2. Composition of PNL 76-68 Glass

Oxide	Amount (Wt%)	Oxide	Amount (Wt%)	Oxide	Amount (Wt%)
Rb ₂ O	0.13	TeO ₂	0.28	Fe ₂ O ₃	10.34
SrO	0.40	Cs ₂ O	1.09	Cr ₂ O ₃	0.44
Y ₂ O ₃	0.23	BaO	0.59	NiO	0.21
ZrO ₃	1.88	La ₂ O ₃	0.56	P ₂ O ₅	0.51
MoO ₃	2.42	CeO ₂	1.26	Na ₂ O	12.80
RuO ₂	1.13	Pr ₆ O ₁₁	0.56	SiO ₂	39.80
Rh ₂ O ₃	0.18	Nd ₂ O ₃	4.67	B ₂ O ₃	9.47
PdO	0.56	Sm ₂ O ₃	0.35	CaO	2.00
Ag ₂ O	0.03	Eu ₂ O ₃	0.08	ZnO	4.97
CdO	0.04	Gd ₂ O ₃	0.05	TiO ₂	2.97

The present study was undertaken to evaluate the effects of iron on the leaching characteristics of PNL 76-68 glass in realistic groundwaters. Experiments were conducted with ductile iron in contact with deionized water, tuff and basalt groundwater leachants that contained glass samples. The iron and glass samples each had the same surface area and were not in contact with each other but were both in the same Teflon container. Groundwater compositions are given in Table 3 and the sample surface area to solution volume ratio used was 10 m⁻¹.

TABLE 3. Groundwater Compositions(a)

	<u>Tuff Water</u>	<u>Basalt Water</u>
Ca	13.2	1.3
K	5.0	1.9
Mg	2.1	0.04
Na	47.0	263.0
Sr	0.04	0.0
Si	30.2	56.0
F ⁻	2.1	37.0
Cl ⁻	7.4	148.0
CO ₃ ⁼	0.0	27.0
HCO ₃ ⁻	120.0	70.0
SO ₄ ⁼	18.3	109.0
NO ₃ ⁻	8.0	1-3
pH	7.5	9.8

(a) ppm by wt.

Time-dependent leaching results for PNL 76-68 glass in D.I., tuff, and basalt waters are shown in Figure 1 by the 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 in Figure 1, the leaching characteristics of the glass are quite different in the various leachates. The D.I. water results show the characteristic initial rapid release rate that decreases with leach time. Tuff water, which has more elements than D.I. 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 least 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 solution composition

FIGURE 1. An Illustration of Two Effects On The Leaching Characteristics of PNL 76-68 Glass: The Effect of Groundwater Composition Without Iron Present and the Effect of Having Iron Present During Leaching.

controls the leaching characteristics; and as elemental concentrations increase in the leachate, elemental release rates decrease.

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 occurs. The starting solution composition has little effect on the leaching characteristics of the glass samples. These results are illustrated by the cross-hatched region in Figure 1. This cross-hatched region includes the boron and cesium leaching results from D.I., tuff, and basalt waters. Elemental removal rates in all of the leachates are initially similar to those observed for early time leaching in D.I. 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 D.I. water alone. Consequently, more elemental removal occurs from the glass samples.

The results presented in Figure 1 are from solution analyses. Solid state analyses of the glass samples from the same experiments show consistent behavior. Cross sections of glass samples that have been exposed to 90°C D.I., basalt, and tuff waters for 28 days at a SA/V ratio of 10 m^{-1} are shown in Figure 2. The top row had only glass and leachate while the bottom row had ductile iron included. Reaction layer depths of glasses exposed only to the various leachates are quite different as can be seen from the top row of Figure 2.

The average depths of reaction are 9, 5 and 1 microns for D.I., tuff, and basalt water leachates, respectively. However, when iron is present during leaching, the reaction layer that develops on the glass is thicker and

FIGURE 2. SEM Micrographs (3000 X) of Cross Sections of PNL 76-68 Glass Reaction Layers after 28-day Exposures to 90°C D.I., Basalt, and Tuff Waters with (Bottom Row) and Without (Top Row) Ductile Iron Present. As in Figure 1, the SA/V ratios were 10 m^{-1} .

essentially the same in all three leachates. These results are shown in the bottom row of Figure 2 where the average layer thickness is 14, 13, and 13 microns for D.I., tuff, and basalt water, respectively. Elemental depth profiles of these depletion layers using EDAX and SIMS analyses show that although some differences exist in samples exposed only to the solutions, essentially no difference could be detected in the samples that had iron included in the leachate.

The effect of iron is opposite to the effects observed for the previously evaluated metals. An enhancement in the glass leaching in the presence of iron cannot be attributed to pH effects since only 1/2 pH unit increase is measured due to the influence of iron.

In addition to a small pH increase, the presence of ductile iron also causes formation of precipitates – at least part of which are colloidal in nature. These precipitates are essentially x-ray amorphous. However, EDAX and XRF analyses of the filtered precipitates show them to contain primarily iron and silicon, with many other elements present in lesser quantities.

Placing ductile iron in basalt or tuff groundwater, without glass present, tends to remove many of the elements and make the two groundwaters more nearly equal in composition, as shown in Figures 3 and 4 for Si and Ca. In Figure 3 the time dependence for removal of silicon from both basalt and tuff groundwaters by ductile iron at 90°C with an SA/V ratio of 10 m^{-1} is illustrated. The results show a rapid removal of silicon from both groundwaters by the iron. The total amount of silicon in solution, including colloids, is shown by the dashed lines. After filtration of the leachate through 200-nanometer filters, the amount of silicon in solution decreased, due to removal of the colloids, as shown by the solid lines. Further filtration through 100-nanometer and 1.8-nanometer filters removed no additional silicon. Basalt and tuff groundwaters have initial silicon concentrations of 56 and 30 ppm, respectively. Yet after a short time exposure to iron, the silicon concentrations are equal. Most of the silicon forms a precipitate on the iron coupon. However, some colloidal precipitates are also formed as can be seen from Figure 3. Essentially identical results are found for calcium removal from basalt and tuff groundwaters by iron, as shown in Figure 4.

FIGURE 3. Time-Dependent Changes in the Si Concentrations of 90°C Basalt and Tuff Groundwater When Exposed to Ductile Iron at an SA/V Ratio of 10 m^{-1} .

FIGURE 4. Time-Dependent Changes in the Ca Concentrations of 90°C Basalt and Tuff Groundwaters When Exposed to Ductile Iron at an SA/V Ratio of 10 m^{-1} .

When ductile iron is placed in the leachates along with PNL 76-68 glass, the effect of groundwater composition on leaching is essentially eliminated (Figure 1). Furthermore, because iron silicate precipitates are formed as silicon is leached from the glass and these precipitates effectively remove many of the other leached elements from solution, the relatively high initial leach rates observed in D.I. water are maintained for longer periods of time as illustrated by the cross-hatched region of Figure 1. This results in enhanced leaching and larger depletion layer depths as shown in Figure 2.

SURFACE AREA TO SOLUTION VOLUME RATIO EFFECTS

The effect of variations in the ratio of glass surface area solution to solution volume (SA/V) is important to understand for data interpretation and predictive capabilities for various repository accident scenarios. Additionally, it can be used as a means of time compression or accelerated testing.

Variations of SA/V for monolithic samples ranged from 1 to $1.6 \times 10^{-4} \text{ m}^{-1}$. The reaction layer thickness formed on leached 76-68 glass decreased with increasing SA/V values, as given for representative elements in the SIMS depth profiles of Figure 5. The smallest reaction layers were found for the highest SA/V values. This occurs because of solubility constraints. If a small volume of solution is in contact with the sample, then only a small amount of leaching must occur before the solution starts to saturate with certain elements and leach rates slow. With larger amounts of solution, more leaching must occur before saturation, which results in higher sustained leach rates and larger depletion layers. The depletion depth results shown in Figure 5 indicate that the gel layers formed for different SA/V ratios are similar in nature, only varying in thickness.

If larger solution volumes result in longer times to reach the same elemental concentration in solution, then it should be possible to utilize this relationship for time-scale expansion or compression of leaching. Comparisons of the time dependence of the leachate concentration for different SA/V ratios are shown in Figure 6 for silicon. Similar plots exist for other elements leached from PNL 76-68 glass. As shown in Figure 6, an increase by an order of magnitude in the SA/V ratio results in one order of magnitude decrease in

FIGURE 5. Effect of SA/V Ratio on Elemental Depletion Depths in PNL 76-68 Glass Leached 14 Days at 90°C in D.I. Water.

FIGURE 6. Silicon Release From PNL 76-68---The Relationship of Time Versus SA/V Ratio.

the time required to reach the same concentration of silicon in solution. Since this relationship was followed by all elements evaluated, it seems reasonable to assume that the basic mechanism of glass corrosion has not been altered by varying the SA/V ratio. Rather, the implication is that solubility constraints limit glass corrosion under these conditions. For example, 4000 days at $1 m^{-1}$, 400 days at $10 m^{-1}$ and 40 days at $100 m^{-1}$ are expected to result in identical solution concentrations and identical rates of release from the glass per unit surface area at the specified times. However, SIMS analyses of the reaction layers has shown that the thicknesses of these layers for these different conditions are markedly different. Very thin reaction layers are found at $100 m^{-1}$ compared to $10 m^{-1}$ when glasses are leached at these SA/V values until solution concentrations are identical. The fact that leaching per unit surface area proceeds at the same rate under the above specified conditions, when reaction layer thicknesses vary widely, stresses the importance of solubility constraints, and down plays the moderating effects of the reaction layer for this particular glass. Additionally, the fact that leach rates can be the same with varying gel layer thicknesses cast serious doubt on any diffusion controlled model for leaching.

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

HLW LEACHING MECHANISMS PROGRAM, SEMIANNUAL STATUS REPORT, MAY 1982

INTRODUCTION

Development has been undertaken of a general-purpose numerical model (PROTOCOL) for the dissolution reactions of nuclear waste forms in water. It is intended to improve our predictive capability for leach rates by bringing together and applying all the known factors that affect them, including especially chemical properties and processes.

The initial assembly of this computer model coincided approximately with the inception of the leaching mechanisms program. This was possible because it is a composite code, and some of its component parts were already available. Its capabilities were at first quite limited, but it functioned well enough to indicate that the approach was feasible. Inasmuch as there appear to be no other models of similar design, the following discussion of its origin, structure and intended uses may be appropriate.

CONCEPT AND ORIGIN

The kinetic section of PROTOCOL was derived in part from an earlier and much simpler dissolution model⁽¹⁾, which can be characterized as essentially a rate/mass converter. In this previous concept, experimental rate functions and waste form geometry entirely defined the mass release from a repository-scale solid, without a treatment of the possibility that the functions might actually contain chemistry-dependent terms that would not transfer to a different system. Solubility constraints and groundwater compositional effects could not be considered in detail, although it was recognized that they could control release in some systems. No quantitative treatment of alteration or precipitation of solid phases could be made, although the maximum release of silica was computed on the basis of water volume flow and a saturation concentration, and was tabulated for comparison with the results of release rates computed for the solid. Such an entirely rate-based analysis could perhaps be valid for elements with relatively simple chemistry, which undergo no significant chemical interactions in the dissolution process and even hand

calculations would be of value. In a multicomponent system, however, these requirements are unlikely to be met for all important elements.

When it became necessary to develop a more advanced model, it was recognized that it might be possible to make an arbitrary division of a dissolution system into two quasi-independent systems that are coupled at the interface, and that could be treated by existing techniques. That is, most reactions in aqueous solutions should be very fast relative to mass fluxes from solid phases as durable as nuclear waste forms. Therefore, it seemed reasonable to attempt to treat the water as an equilibrium system, whose composition is being continuously modified by dissolving species, and by flow. (Some exceptions: polymerization kinetics and the deposition of poorly ordered solid phases.)

IMPLEMENTATION

Kinetic-equilibrium coupling was achieved by the attachment of a chemical equilibrium code (MINEQL)⁽²⁾ as sets of subroutines and data files. In this configuration, the MINEQL section of the model is unaware in a formal sense of any solid phases that it has not precipitated. Their presence is registered only by transfers of mass into a MINEQL array. This allows phases to be considered that are not thermodynamically stable in water.

The problem of considering the potentially very complex interactions in a dynamic system was approached by the simple expedient of running the simulations as a sequence of discrete time increments, during each of which both kinetic and equilibrium redistributions of component masses are calculated. This approach requires a very large number of calculations, but has in fact been found to be well within the capabilities of existing computers.

These activities are sufficiently complex that some constraints are suggested: The model does not attempt to explain or predict some processes on a molecular scale for which the theoretical basis is not well developed, but assumes that these phenomena can at this time best be described by experimental-based dissolution rate functions. However, there is considerable activity in the area of understanding and modeling reactions at and near the interface,⁽³⁻⁵⁾ and their inclusion in overall dissolution models should eventually be possible. In the PROTOCOL definition, rate functions are

empirical, are treated as submodels, and are used to generate mass fluxes of species from the solid phase(s). All the values for parameters that they may contain are to be provided by PROTOCOL, either from its data files and arrays, or by computation.

Elsewhere in the dissolution system, the model does not, as might a geochemical code, attempt to predict an inflowing groundwater chemical composition that would result from reaction with host rocks and other repository materials, such as containers and backfill. Such properties of the repository system are at present assumed to be available as input data. It also does not address the fate of dissolved species after they leave the resident water volume, or immediate vicinity of the waste form. At the same time, there is enough flexibility that features can be added to the model where sufficient information is available.

PROTOCOL is still in a state of more or less continuous revision, as improvements are incorporated, but its current sequence of operations is shown in Figure 1.

The primary use of the model in the near future will be to act as an interpreter for experimental information, inasmuch as leaching mechanisms are to some degree system-specific, and their understanding and application require a physico-chemical context. The other function of the model is to serve as an interface between the experiment and the chemical performance of a waste form in a geologic repository.

In the following sections are discussed model development during the first half of FY 1982, including the following tasks: data base extensions, modifications of PROTOCOL to consider reactions in laboratory environments, preliminary checkout of functioning, and beginning simulations of other experimental data as capabilities were added. The main emphasis has been on the acquisition and processing of thermochemical data, as essential elements of more realistic chemical reaction modeling.

FIGURE 1. Protocol Sequence

DATA BASE DEVELOPMENT

A major upgrade has been completed in the model data base to meet the needs of the high level waste leaching mechanisms program. The first priority was to equip PROTOCOL with an elevated temperature capability. The two necessary features that have been added are an expanded data file and an upgraded file manager program.

The publicly-available MINEQL data file contains component identification numbers, stoichiometric coefficients and logarithms of the equilibrium constants for reactions. These reactions are for the formation of species from a set of basis species, or components at 298K. Their origins are unspecified, but are probably NBS Circular 500 or equivalent handbooks.

THE MINEQL that has been used in this project is an expanded in-house version. In addition to increases in the numbers of components and other

species, it contains for each species S^0 , ΔH_f^0 , ΔG_f^0 , a literature reference number, chemical formula, and mineral name, if any. Because of the size of this file, most of its maintenance is done by a file manager program, which computes log K values from free energies of formation and generates new, revised files as needed.

The free energy table for the basis species set was extended to 723K (450°C), although most data at the higher temperatures are necessarily estimates, and not to be relied upon for precise calculations. A master thermodynamic file was created for other species, into which available stability information as a function of temperature is being stored. The file for data at 298K was expanded linearly: each entry for a species is followed by similar line entries for higher temperatures. Data at any temperature is acceptable, and thermochemical properties can be entered in either kcal or kJ.

The file manager program has been extended to process this new data. The following facilities are now operational: on request, ready-to-use isothermal data files for PROTOCOL are generated for any temperature from 298K to 700K. Interpolations in free energy are performed wherever required. The master thermodynamic file is also revised on request. New equilibrium constant values are computed for species when additions or changes have been made.

The result is that data revisions for any species at any temperature can be immediately propagated throughout the entire system. Manual calculations and data editing are minimal: species formation reactions can be balanced semiautomatically.

EXTENSIONS IN SCOPE

As mentioned above, PROTOCOL was evolved from a program that considered only the leaching of waste forms in a repository environment. Some extensions were necessary to simulate experimental leaching reactions under considerably different conditions, but these have so far proved to be fairly straightforward. The modifications already completed include the way resident water volume and volume flow rate are specified. No difficulties were encountered when the water flow rate was set to zero, so that no logical modifications were necessary to accommodate static leach experiments.

Several other technical improvements were made: the kinetic data file has been made smaller and simpler. Instructions were made easier and more flexible. A modest reorganization has speeded up the run time by a factor of five. A few hundred time increments can be run in four to five seconds, depending on the complexity of the system and the amount of detailed output requested.

An effort has been made to make available more of the data that will be used in reaction simulations. Most of the kinetic information is already tabulated with the output. However, the results of simulations by PROTOCOL depend in part on equilibrium thermochemical calculations. These data are compiled from a variety of sources, and are continuously revised as new or more accurate values become available.

I believe that in the interests of quality assurance, and of making the workings of the model more transparent, it is very desirable to attach to every computation a record of the value and origin of every datum that was used. The intent is to provide enough information in the output file that a meaningful independent evaluation or even recalculation could be carried out.

To achieve this, I have made PROTOCOL self-referencing: two additional output tables are automatically generated for every run. The first table lists every species that had been selected from the isothermal data file and considered in the computation. For each species are tabulated its chemical formula, serial number, free energy of formation, mineral name, if any, and reference number. The second table is a list of references for the free energy values, or for the information that was used to derive them. The effort is about 95% complete: only the basis species reference numbers remain to be retrieved and inserted. I believe that this self-documentation will help to clarify the meaning of model results. In some sense, it will address the difficult question of validation of a model that is in a continuous state of flux, and that selects for each problem a potentially unique set of input data.

INITIAL CHECKOUT

PROTOCOL was taken through numerous exercises to examine its operation, using tabulated rate functions for silica. The purpose of these simulations was to assure that we can show any effects on release of solubility, water composition, temperature, flow rate, SA/V ratio, and the accuracy of thermochemical data.

Because of the sluggish kinetics of crystallization of silica at low temperatures, I have removed the crystalline forms from the active file, and propose to replace them only for systems where they are specifically recognized to appear.

Some earlier computations were repeated with this assumption. Variations were run on a leaching problem in which a 10 gram sample of amorphous silica was dissolved into 100 ml of neutral water. Some results of these computations are shown in the accompanying figures. Note that concentrations in the resident water volume have been plotted, not the total mass of silica lost by leaching.

Values for parameters were varied in the following ranges:

- Temperature, 40–90°C (Figure 2). Rates increase appropriately with increasing temperature, and precipitation and constant molality are achieved at correspondingly earlier times.
- Water flow rate, 0–1 ml/day. Only minor effects of flow rate on solution concentration of H_4SiO_4 were found. Changes in molality as a function of time and flow rate are plotted in Figure 3.
- Surface area. Inasmuch as the solid surface area is no longer tied to a specific geometry, I have varied it from 10^{-1} to $10^3 \text{ m}^2/\text{g}$. Concentrations and changes in saturation time appear to vary in a reasonable way (Figure 4).
- Initial concentration of silica, 10^{-4} to 10^{-20} molal. (Figure 5). The inhibiting effect of an initial concentration of a leached species in the water is shown clearly. It is also clear that the magnitude of the effect very much depends on when measurements are taken.

FIGURE 2. Computed Aqueous Silica Concentrations as a Function of Temperature

FIGURE 3. Computed Changes in Dissolved Silica Concentrations as a Function of Flow Rate

FIGURE 4. Computed Effects of Surface Area on Dissolved Silica Concentrations

- Sensitivity to thermochemical stability data. The ΔG_f , 313K for H_4SiO_4 was used as a variable, and decreased by 100 cal steps (Figure 6). This was done, not because of actual uncertainty in this value, but to simulate a reaction in which the stability of a species that might be formed is not well known. The result shows that care must be taken to use the most accurate and self-consistent data available.

The result of these exercises is an increased confidence that the composite model approach to dissolution is feasible. The primary concern at this time is the reasonableness of results as far as trends in corrosion depth, release rates, aqueous molalities, and new phases are concerned, rather than precision of numerical values. For example, there is internal consistency between kinetic and equilibrium functions; that is, between mass changes in solid and solution. The aqueous silica concentration rises to the saturation value, then remains constant. At the same time, mass release and depth of

FIGURE 5. Computed Effects of Initial Silica Concentration on Dissolved Concentrations

FIGURE 6. Computed Effects of Changes in ΔG_f^0 of H_4SiO_4 on Time to Saturate ($T = 313K$)

corrosion continue to increase, corresponding to a solid state phase conversion. When the masses and depths of new phases are printed out, other comparisons will be possible.

OTHER SIMULATION EXERCISES

Another set of problems being analyzed contains dissolution rate data for natural nepheline (Mwakio Tole thesis, Penn State, 1981). This set consists of 11 runs at 3 temperatures and 4 pH values. A feature that is new to PROTOCOL is that rate data are reported for 4 components, Na, K, Si and Al. This exercises parts of the logic that have not been previously tested, and brings multicomponent solids into the array. The data were fairly easily adapted for PROTOCOL.

Most of the simulations were run out to one year. Detailed analysis of the output tables has not been completed, but the leached elements form new phases at various times during the reaction. These are summarized in Figure 7.

WORKS IN PROGRESS

The elevated temperature files are still somewhat sparse, and their expansion will be an ongoing activity. Redox reactions at elevated have not yet

	T = 298K	333K	353K
pH = 3	K	D, K	D, A
5	D	D, K	D
7	D	D	D
11	D	D, M	-

D = Diaspore M = Muscovite
K = Kaolinite A = Amorphous Silica

FIGURE 7. Computed Phases Precipitated During the Dissolution of Nepheline

temperatures have not yet been added, and have a high priority. I surmise that the limitations of the approach we are taking may well be in the existence and accuracy of the required thermochemical data. For this reason, I will try to include, wherever possible, an analysis of the effects of uncertain data. At the same time, it should be recognized that data constraints are not permanent.

Aside from the data base, numerous extensions and improvements are to be made as time permits. Some revisions will be designed to make the model smaller, faster and more convenient, and will not necessarily be visible. For example, logic can be added to automatically convert any units in reported data to PROTOCOL format. No restrictions on reporting and possibly no manual conversions should therefore be required. Options for various other solid configurations will be added, including powders.

Additional improvements that will be added as soon as possible include the capability for handling arbitrary changes in water volume, composition and flow rate during a run. Success in prediction depends a great deal on knowing what external changes are imposed on a dissolving system, and when they occur.

Currently, as new phases are precipitated during a run, their identities are simply reported to the user's terminal and written to the output files. I propose to add them formally to the set of solid phases, including tabulation of the appropriate information on their deposition rates and physical dimensions.

In order to further illustrate model operations and capabilities, I propose to begin writing an informal users manual. It would contain definitions of variables, file formats, creation of submodels, conversions of experimental data and construction of data files, file manager operations, instruction files and run options, sequences of subroutine calls.

SUMMARY

PROTOCOL is evolving into an integrated software package. It has been provided with an elevated temperature capability, including an expanded data file and a more sophisticated file manager program.

Checkout of PROTOCOL functioning was continued with dissolution exercises for amorphous silica. So far, the results seem very reasonable, and it is

concluded that the major functions are working as intended. Predictions of chemical events can be made as a result of the interactions of both kinetic and equilibrium processes.

Modeling exercises are in progress with experimental dissolution data. It is expected that this will be very effective in identifying areas where improvements are desirable. An analysis of data on the leaching of natural nepheline as a function of both pH and temperature predicts the formation of several solid phases, especially of aluminous materials.

PROTOCOL is still under intensive development, and many extensions are planned or considered. It promises to be a very useful device for the interpretation and extrapolation of leaching data for nuclear waste form materials.

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4.0 SESSION II. SPECIAL TOPICS IN STATIC AND LOW-FLOW-RATE LEACH TESTING

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4.1 LEACH TESTING OF WASTE FORMS: INTERRELATIONSHIP OF ISO AND MCC TYPE TESTS -- V. M. Oversby, Lawrence Livermore Laboratory^(a)

Abstract

Leach testing experiments were conducted on SYNROC-D material to examine the parameters which affect leaching results and to measure the activation energy for leaching of elements from SYNROC-D. Measured leach rates were found to be controlled by precipitation of insoluble phases for those tests where the sample surface area to volume of leachant (SA/V) multiplied by leaching time (t) exceeded $0.3 \text{ cm}^{-1}\text{d}$ for leach tests at 90°C . In these cases the apparent activation energy for leaching was approximately 10 kcal/mole based on Na and Si data. For leach tests at 90°C with $(\frac{SA}{V})(t)$ less than $0.2 \text{ cm}^{-1}\text{d}$, the activation energy for Na and Si dissolution was 18.5 kcal/mole for sample S29 and 14.5 kcal/mole for sample LS04. These activation energies are in agreement with values reported by Tole and Lasaga (1981) for nepheline dissolution.

The effect of sample geometry was investigated by leaching a series of crushed samples of different grain size. The results support the view that geometric surface area should be used in leach rate calculations rather than gas adsorption BET surface area.

Comparison of results on S29 leaching of crushed samples and monoliths show that data from MCC-1 and ISO type leach tests may be directly compared when the data are examined at constant $(\frac{SA}{V})(t)$.

(a) Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract No. W-7405-ENG-48.

Introduction

Leach testing of radioactive waste forms is done to satisfy a number of information needs in waste management programs. Manufacturers of waste forms need simple tests which can be conducted under hot cell conditions to provide quality control during fabrication. Standardized tests such as the MCC-1 leach test developed by the Materials Characterization Center of Battelle Pacific Northwest Laboratories can be very useful for this type of quality control application. The MCC-1 test is also useful for comparing different waste forms under a fixed set of conditions and for providing means of interlaboratory comparison.

Persons involved with the design of geologic repositories for high level nuclear waste need a different type of information. In this case extrapolation of data to long times is needed and data on variation of durability with temperature, solution composition, geometry of the waste form and water to solid volume are needed. The draft ISO (1979) leach testing procedure involves variation of temperature; duration of leaching is altered by changing leach solutions at specified intervals. Variation of solution to solid volumes is allowed within the test framework. The ISO test can provide data which will yield activation energies for leaching if care is taken to measure initial leach rates. Slight modification of the ISO test procedure will provide information relevant to leaching mechanisms.

This paper reports a study of the leaching behavior of SYNROC-D, a titanate ceramic waste form developed for immobilization of Savannah River defense high level wastes. Details of preparation methods and sample properties are given in Campbell et al., (1982). The chemical composition of the sample used in the leach testing studies is given in Table 1.

There were four main objectives to this work.

- (1) Determine the activation energy for leaching from, or dissolution of, SYNROC-D.
- (2) Determine the effect of solubility limitations on leaching of SYNROC-D.
- (3) Examine the relationship between sample geometry and leaching behavior (crushed sample vs monoliths).
- (4) Determine whether BET or geometric surface area should be used in leach rate calculations.

Experimental Method

Leach testing described in this paper was carried out in Parr acid digestion bombs, 23 ml size, which consisted of an inner TFE teflon capsule containing the test sample and leach solution and an outer stainless steel casing. New teflon capsules were cleaned prior to use by rinsing with deionized water three times. The bombs were then filled with 16 ml of deionized water and placed in an oven held at 150°C. After three days, the cleaning water was discarded and new water was placed in the bombs. This water was used to determine whether any element of interest in our leaching work could be detected after heating at 150°C for one day. No element of interest could be detected by ICP analysis, so it was concluded that the cleaning procedure was adequate. Use of this cleaning procedure eliminates the use of acid in the teflon capsules. When acid is used in the capsules, some acid diffuses into the teflon and is not completely removed until after several stages of heating with pure water. Consequently, it is possible to obtain spurious leach results when using acid cleaned teflon capsules if the capsule walls still contain some acid which diffuses into the solution during the leach test. When leach testing is carried out in deionized water the

change in pH can be large due to this effect, and leaching is actually taking place in dilute acid solution.

Leach tests were carried out on crushed and sized samples of SYNROC-D using a modified version of the ISO leaching procedure (ISO, DIS/6961, 1979). The modifications include use of crushed samples rather than monoliths and variations in the schedule for changing leach solutions. Most of the testing used the grain size fraction 177 to 246 μm . Surface area was calculated assuming cubic geometry with all particles 212 μm size. Sample weights and duration of leaching were varied to investigate the effects of solution composition on leach rate.

At the start of each test a portion of crushed and sieved sample was weighed into a clean teflon capsule. Approximately 16 grams of deionized water was added, the capsule placed inside the stainless steel casing and then placed in an oven maintained at the desired leaching temperature. Temperatures were maintained to within $\pm 2\text{ }^{\circ}\text{C}$ of the nominal temperature. After the desired leaching time the bombs were removed from the oven, cooled on a steel plate and opened as soon as they could be handled with bare hands. Solutions were decanted without filtration into plastic tubes and stored at room temperature until analysed. If leaching was to continue, fresh deionized water was then added to the sample and the bomb returned to the oven. Because of the storage of solutions before analysis, it was not possible to obtain valid data on Ti. All other elements were shown to be stable in solution at the concentrations relevant to these experiments without acidification over a period of at least three weeks. The longest that samples were normally stored before analysis was two weeks.

Solutions were analyzed for Na, Al, Si, Ca and Sr by inductively coupled plasma spectrometry (ICP). The detection limits were set at 4 times the standard deviation of an acidified water blank. The detection limits varied

with the time when analyses were performed, but were generally better than Na = 0.008 ppm, Al = 0.015 ppm, Si = 0.022 ppm, Ca = 0.003 ppm and Sr = 0.008 ppm. In no case were measurable amounts of these elements found in control blanks run in teflon capsules in parallel with the leaching experiments.

Results and Discussion

The first series of experiments conducted using S29 SYNROC-D material were designed to measure the activation energy for leaching for Na, Al, Si, Ca and Sr. Samples were leached in deionized water at 50°C, 90°C, 120°C and 150°C. Solutions were decanted and fresh water added after leaching times of 1 day, 3 days ($\Delta t = 2$ days), 6 days ($\Delta t = 3$ days) and 10 days ($\Delta t = 4$ days). The concentrations of Na, Al, Si, Ca and Sr in the solutions were used to calculate normalized elemental leach rates for each element using the formula

$$\text{normalized elemental leach rate} = \left(\frac{\text{grams x in solution}}{\text{grams x in solid}} \right) \left(\frac{\text{weight of solid}}{\text{surface area of solid}} \right) \left(\frac{1}{\text{leaching time}} \right)$$

Leach rates calculated by this formula are those which would apply to the bulk sample if the whole sample dissolved at the same rate as element x. Leach rates for crushed samples reported in this paper are based on surface areas which are calculated assuming cubic geometry with the linear dimension being the mean value of the sieve fraction used.

Results for the first set of experiments are labeled Nov. '81 and are given in Tables 2, 4, 5 and 6. Data for the second leach period (Day 2-3) are plotted in Figure 1 as $\ln(\text{leach rate})$ vs $\frac{1}{T}$ ($^{\circ}\text{K}^{-1}$). If the leaching process were controlled by an activation energy, the leach rate would follow the empirical Arrhenius law

$$\text{rate} = A \exp(-E_A/RT)$$

where A = experimental constant, $\text{g/m}^2\text{d}$

E_A = activation energy for leaching, cal/mole

R = gas constant, $\text{cal/mole } ^\circ\text{K}$

T = temperature in $^\circ\text{K}$

For a single forward reaction, a plot of $\ln(\text{rate})$ vs $\frac{1}{T}$ will give a straight line whose slope is $-E_A/R$.

Leach data for 50, 90 and 120°C shown in Figure 1 do form quite good linear arrays in the Arrhenius plot. However, data for 150°C show rates which are the same or less than those for 120°C . Since assumption of a negative activation energy or a drastic change in leaching mechanism between 120°C and 150°C seems unreasonable, we have our first indication that the experimental conditions do not satisfy the restrictions necessary to obtain the activation energy for leaching. A second indication that something other than simple leaching or dissolution is occurring is provided by the value of E_A calculated from the 50 to 120°C data. The leaching of Na and Si from SYNROC-D should be controlled by the dissolution of nepheline. Tole and Lasaga (1981) reported activation energies of about 15 kcal/mole for Na and Si dissolution from nepheline wafers at near neutral pH. Since the pH of the leach solutions reported in this paper was usually between 6 and 7, we should expect an E_A close to 15 kcal/mole. The low value of about 10 kcal/mole suggests that precipitation reactions are occurring, and that the apparent leach rate is the result of two competing processes.

To test this hypothesis a series of leach tests were run at 70, 90, 120 and 138°C using the same water volume as in the November tests, but a smaller amount of sample at each temperature. Results from these tests are given in Tables 3 through 6 and are labeled Dec. '81A. The data are plotted as $\ln(\text{leach rate})$ vs $\frac{1}{T} (^\circ\text{K}^{-1})$ in Figure 2. Again, a three point linear array can be defined with an apparent activation energy of about 10 kcal/mole,

but the data for 90°C plots above the line in all cases. Tie lines connecting the 70°C and 90°C data indicate a higher activation energy which is similar to the Tole and Lasaga (1981) nepheline value. Comparison of the leach rates at 90 and 120°C for the Nov. '81 and Dec. '81A data show that for all elements except Al, the leach rates had increased roughly in proportion to the decrease in sample size. This was interpreted as confirmation of control of the apparent leach rate by a precipitation reaction.

If apparent leach rate is determined by precipitation of new phases rather than by kinetic control of the dissolution process, we would expect to find constant concentrations of elements in the leach solutions at a given temperature regardless of the sample size or the length of the leaching period. Examination of the solution concentration data for 90°C leaches (Table 7) shows that this is the case for all elements except Al in the Nov. '81 and Dec. '81A data sets. The concentrations of Si, Na, Ca and Sr in these solutions should represent the solubility limits of the new phases which are formed by precipitation. To determine the activation energy for leaching in the absence of precipitation, we must have final leach solutions whose concentrations are lower than these solubility limits.

A third set of experiments were conducted at 70, 90, 120 and 150°C where the sample size was again reduced and the duration of leaching was shortened. Examination of the solution concentration data labeled Dec. '81B in Table 7 shows that concentrations of all elements at 90°C for the single day leach samples were less than in the previous two leaching experiments. Thus, we should expect that these samples are not saturated with respect to phases which had previously been precipitating from solution. The final leach test of this series was conducted for 3 days in an attempt to produce saturation. Despite the three times longer leach time, the solution concentrations increased only by 20 to 50% indicating that the single day samples were close

to the solubility limits of phases which had previously precipitated from solution.

The Dec. '81B data for days 1 through 3 are listed as normalized elemental leach rates in Tables 3 through 6. The data for Day 3 is plotted in Figure 3 along with the 50°C data for Day 2-3 for the November experiments. The slope of the line defined by the 50, 70 and 90°C data now gives an activation energy of 19.3 kcal/mole for Na dissolution from SYNROC-D. A similar plot for the Day 2 data gives 17.7 kcal/mole. The average activation energy for the two data sets is 18.5 kcal/mole for both Na and Si leaching. Substitution of this activation energy and the average measured leach rate at 90°C into the Arrhenius equation gives values of $A_{Na} = 5.8 \times 10^{11} \text{ g/m}^2\text{d}$ and $A_{Si} = 7.6 \times 10^{11} \text{ g/m}^2\text{d}$.

The data for leaching at 120°C and 150°C do not lie on the line defined by the 50 to 90°C data for the Dec. '81B experiments. This is interpreted to be due to precipitation of some insoluble materials from the higher temperature solutions.

Leaching data for Al did not follow the pattern set by Na and Si. At 50°C, the concentration of Al in solution was only slightly above the ICP detection limits, and the calculated leach rate was about $3 \times 10^{-3} \text{ g/m}^2\text{d}$. At 70°C the average Al leach rate was $6 \times 10^{-2} \text{ g/m}^2\text{d}$ which represents a factor of 20 increase in leach rate for 20°C increase in temperature. The Na and Si leach rates increased by a factor of 10 over this temperature range. At 90°C, the Al leach rate was about $1 \text{ g/m}^2\text{d}$ which represented nearly a 20 fold increase again for 20°C temperature rise, while Na and Si leach rates increased only by a factor of about 4. Nepheline is the only crystalline phase which contains Na and Si in SYNROC-D. Al occurs in nepheline which makes up 18% by weight of S29 and in spinel which constitutes 48% by weight of the S29 sample (Campbell et al., 1982). Assuming an average

of 36% Al_2O_3 in both phases, about 30% of the Al is present in nepheline and 70% is in the nearly insoluble spinel. The lower leach rate for Al at 90°C as compared to Na and Si can then be explained by assuming no Al is leached from the spinel phase. This is a reasonable assumption since Fe, a major component in the spinels, is not found in leach solutions in measureable amounts.

While the presence of Al in spinel can explain the 90°C leaching data, the low leach rates at 70 and 50°C must be due to another cause. Tole and Lasaga (1981) found that Al precipitated from solutions which were near neutral in pH as $\text{Al}(\text{OH})_3$, bayerite. They identified this product in a nepheline dissolution experiment run at pH = 5, T = 80°C. Precipitation of this material would explain the low apparent leaching of Al from SYNROC-D at 50 and 70°C.

A second fabricated sample of SYNROC-D was also tested for leaching characteristics at 70, 90 and 120°C. This sample, LS04, had the same chemical composition as S29 but during early testing by F. Bazan showed lower Ca and Sr leach rates (personal communication). Leach data for crushed material (177-246 μm) of LS04 are given in Tables 3, 4 and 5. Solution concentration data at 90°C are given in Table 7. Solution concentrations at all three temperatures were low enough that precipitation of insoluble phases from the leach solutions should not be a problem. Leach rates for Al, Si and Na are in good agreement for LS04 and S29 (Dec. '81B data set), while the Ca and Sr leach rates are substantially lower for the LS04 sample. This suggests that the perovskite phase in LS04 was better formed during the hot-pressing fabrication step than was the case for S29.

The leach data for LS04 are plotted in Figure 4 as $\ln(\text{leach rate})$ vs $\frac{1}{T}$ ($^\circ\text{K}^{-1}$). The activation energy for Na dissolution from this sample is 14.5 kcal/mole. This is slightly lower than the activation energy found for the

S29 sample. Tole and Lasaga (1981) reported activation energies of 14.5 kcal/mole for Na at pH = 5.0 and 16.0 kcal/mole for Na at pH = 7.0. The pH value of leach solutions reported in this paper was approximately 5.5 at the start of leaching and increased slightly as leaching progressed. For samples leached at 90°C or less the final pH was approximately 6. The highest pH values were 7 for samples leached for several days at 150°C.

The solution data given by Tole and Lasaga (1981) can be recalculated to normalized elemental leach rates by using the relationship

$$\text{leach rate} = ([x]) \left(\frac{1}{f_x t} \right) \left(\frac{V}{SA} \right)$$

where $[x]$ = concentration of element x in solution, g/cm³

f_x = fraction of x in the solid

t = leaching time, d

V = volume of leach solution, cm³

SA = surface area of solid, m²

The nepheline sample used by Tole and Lasaga (1981) had $f_{Na} = 0.12$ and $f_{Si} = 0.205$. Their (1981) data for dissolution of natural (Na_{0.76}K_{0.19}) nepheline are compared with the SYNROC-D data from this paper in Table 8. The values used for SYNROC-D are the average of several separate leaches from solutions thought to be unaffected by precipitation reactions. The data from Table 8 are plotted in Figure 5; data points at pH 5 and 7 were averaged to provide a single value for the 60 and 80°C temperatures. There is excellent agreement between the leach rates for Na and Si from nepheline dissolution and SYNROC-D leaching. It is interesting to note that the Tole and Lasaga (1981) samples were 1 mm thick wafers (i.e., monoliths) and the surface area used to calculate the leach rates was "geometric" for all data in Table 8.

Shade (1981) reported data on leaching of nepheline glass and ceramics at 90°C. He noted that his ceramic nepheline contained a second crystalline phase in addition to nepheline, as well as some residual amorphous material. The samples used for leaching were "monoliths" with approximately 1 cm² of surface area. The leach rates he measured during the early stages of leaching were 11 g/m²d for Na and 7 g/m²d for Si at 90°C. After 2 days of leaching the results showed lower leach rates and appeared to be affected by precipitation of insoluble phases. The leach rate for Si is in excellent agreement with the value reported in this paper for the case where no precipitation occurs. The Shade (1981) Na leach rate is about twice that measured for SYNROC-D. The higher Na leach rate may be due to the second crystalline phase which Shade (1981) noticed in his sample. It is interesting to note that the Si concentration after 1 day of leaching nepheline ceramic was about 13 ppm (calculated from Shade (1981) Figure 3). This is far higher than the concentration of Si which can be maintained in contact with SYNROC-D at 90°C without back reaction or precipitation occurring.

There has been a great deal of discussion in the literature concerning what is the appropriate surface area to use in calculating leach rates. Measurement of the surface area of crushed materials can be done by the BET gas adsorption method using gases which do not chemically react with the sample being measured. Coles and Bazan (1982) report BET surface area data determined using N₂ and Kr for 150-300 μm size fractions of SYNROC-C and Cs-hollandite. The surface areas measured using N₂ were larger than the surface areas determined using Kr by about a factor of 2. In turn, the Kr BET surface area was about 15 times larger than the geometric surface area which can be calculated assuming cubic geometry for the grains.

To investigate the effect of surface area on leaching of crushed samples a series of samples were prepared by crushing and sieving a specimen of S29 SYNROC-D into several grain size fractions. Surface area of these samples was measured using Kr BET. Geometric surface area was calculated assuming all grains were cubic with linear dimensions equal to the midpoint of the sieve range. The data are given in Table 9. The ratio of BET to geometric surface area increased systematically as the grain size of the particles increased. Thus, it seemed possible that a series of leach tests on these samples might answer the question of whether BET or geometric surface area was the appropriate area to use in leach test calculations.

Four size fractions were investigated - 177-246 μm (Dec. '81B data set), 246-417 μm , 417-840 μm and 840-1650 μm . The leach tests were carried out at 90°C, and sample sizes were chosen so that precipitation reactions would be eliminated or minimized. Data for concentrations in the leach solutions are given in Table 7 and calculated normalized elemental leach rates are given in Table 10. Note that the data contained in column 2 of Table 10 includes sample weights, calculated geometric surface area, BET surface area and the average volume of leach solution divided by geometric surface area of the samples. Leach rates for Days 1, 2 and 3 are given based on geometric surface area. Leach rates for all elements show a decrease which is proportional to the decrease in leaching volume/surface area. This suggests that precipitation reactions were taking place despite the attempts to eliminate them.

The last column of Table 10 shows leach rates for Day 3 calculated using the measured BET surface areas. Use of BET surface area causes a further spreading of the data. During the early stages of leaching, sample dissolution should be independent of grain size. Since use of BET surface

area causes the leach rates to spread, BET surface area does not appear to be measuring the surface area which is appropriate to leaching.

The geometric surface area used in this paper is based on cubic geometry where the cubes are all assumed to be the same size, namely the middle of the sieve fraction size. This is obviously a simplistic model, especially for SYNROC-D where the grain shape is more like rectangular prisms than cubes. For coarse grain size fractions the number of cubes per gram is about twice that calculated assuming cubic geometry. Thus, "real" geometric surface areas would be about 1 1/2 times greater than that which was calculated.

Table 11 shows a comparison of results for S29 leaching at 90°C using the MCC-1 test on a monolith sample after leaching for 3 days under static conditions with data for crushed material (177-246 μm) where the leach solutions were changed daily. The surface area used for the MCC-1 test is the measured geometric surface area and the leach volume to surface area of sample is fixed at 10 cm. From the experience gained in this study concerning precipitation from S29 leach solutions we would expect that the MCC-1 test would be little affected by precipitation at 3 days leaching, but would be seriously affected thereafter.

The average leach rate over the first three days by the MCC-1 method is in good agreement with that measured on crushed material using the modified ISO test and geometric surface area based on cubic geometry. The agreement is improved if our estimate of "real" geometry surface area is used. Leach rates for "real" surface area are obtained by dividing crushed sample 1 day leach rates by 1.5 since we estimated "real" geometric surface to be 1.5 times cubic geometric surface.

Full data for MCC-1 leaching results on S29 are given in Table 12 along with solution concentrations calculated from the leach data. The leach rates for all elements decreased steadily with time. This could be due to the

formation of a protective surface layer on the sample during leaching and control of subsequent leaching by diffusion through the surface layer. However, examination of leached SYNROC-D samples does not show any protective layer formation on nepheline (R. Ryerson, personal communication). An alternative explanation for the decrease in leach rates is the formation of insoluble phases which precipitate from the solution. The final concentrations after 28 days of MCC-1 leaching are very similar to those found for crushed sample leaching over 2 to 3 day periods in the Nov. '81 experiments (compare Tables 7 and 12). The surface area/volume of leachant in the Nov. '81 experiments was 0.6 cm^{-1} as opposed to 0.1 cm^{-1} for the MCC-1 tests. We would thus expect saturation affects 6 times earlier for the crushed material.

The Dec. '81A samples which were also affected by precipitation had surface to volume ratios of 0.3 cm^{-1} . For the 1 day leach (Day 1) the solutions were probably only slightly affected by precipitation (compare leach rates for Day 1, Dec. '81A with those for single day Dec. '81B leaches at 90°C , Table 4). Assuming constant leach rates, we would expect precipitation to affect leach results when surface area/volume multiplied by time reached 0.2 to $0.3 \text{ cm}^{-1}\text{d}$. Table 11 showed that results for MCC-1 tests at $0.3 \text{ cm}^{-1}\text{d}$ agreed with leaching of crushed material at $0.2 \text{ cm}^{-1}\text{d}$. Data for Days 2-3 of Dec. '81A set had $(\frac{SA}{V})(t) = 0.6 \text{ cm}^{-1}\text{d}$, and gave Na leach rates of $1.8 \text{ g/m}^2\text{d}$. This is in good agreement with the value of $1.5 \text{ g/m}^2\text{d}$ for MCC-1 after 7 days $(\frac{SA}{V})(t) = 0.7 \text{ cm}^{-1}\text{d}$. The largest value of $(\frac{SA}{V})(t)$ for the crushed material is $2.4 \text{ cm}^{-1}\text{d}$ for Days 7-10 in the Nov. '81 data set in Table 4. This data should compare with the MCC-1 results at 28 days where $(\frac{SA}{V})(t) = 2.8 \text{ cm}^{-1}\text{d}$. Comparison of these results is given in Table 13. The agreement between the data sets is excellent, strongly

supporting the interpretation that both data sets are controlled by precipitation of insoluble phases.

Conclusions

The leaching studies conducted on SYNROC-D (S29) reported in this paper allow us to draw several conclusions concerning leaching mechanisms and testing methods.

- (1) The apparent activation energy for leaching from wasteforms will vary if more than one process is occurring.
- (2) Where precipitation of phases can occur from leaching solutions, the apparent leach rates will depend on solution composition.
- (3) If care is taken to minimize saturation effects, the measured leach rates for different sample geometries will be the same.
- (4) If precipitation reactions occur, leach rates for different sample geometries or leaching times are comparable at equal values of (surface area of sample/volume of leachant) multiplied by leaching time, $(\frac{SA}{V})(t)$. This relationship allows comparison of data from ISO type tests with MCC-1 tests.
- (5) Leach results on different sample geometries show better agreement when geometric surface area is used in calculations rather than BET surface areas.
- (6) In order to obtain data on activation energies for leaching processes and to study leaching mechanisms, the leach testing methods must allow variation of $(\frac{SA}{V})(t)$.

Acknowledgments

The solution data used in this report were determined by ICP analysis performed by A. Langhorst. I am grateful for his careful work and his willingness to adjust schedules to fit the needs of these experiments. Thanks are due to J. Campbell for support and encouragement of this work and to J. Campbell and T. Wolery for review of the manuscript. BET surface area measurements were made by C. Slettevold.

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Table 1. Composition of SYNROC-D sample S29 in weight %.

<u>Compound</u>	<u>Wt%</u>
Fe_2O_3	23.8
Al_2O_3	18.6
MnO	7.4
U_3O_8	2.1
CaO	7.1
NiO	3.0
SiO_2	7.2
Na_2O	3.3
Na_2SO_4	0.6
Cs_2O	0.25
SrO	0.25
Ce_2O_3	0.50
Nd_2O_3	0.50
TiO_2	18.8
ZrO_2	6.6

Table 2. S29 - HP10A Leach rates at 50°C
 Normalized Elemental Leach rate in g/m²d
 wt = 0.166g 177-246μ (Nov. '81)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	3 x 10 ⁻³	0.11	0.17	<0.13	0.035
2-3	9 x 10 ⁻⁴	0.22	0.19	0.07	0.037
4-6	2 x 10 ⁻³	0.15	0.13	0.05	0.024
7-10	4 x 10 ⁻³	0.15	0.12	0.04	0.022

Table 3. S29 - HP10A Leach Data, 70°C
Normalized Elemental Leach rate in g/m²d

wt = 0.0782g, 177 - 246 μ (Dec. '81A)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	0.07	0.73	0.70	0.55	0.13
2-3	0.04	0.58	0.47	0.30	0.09
4-6	0.07	0.50	0.38	0.22	0.07

wt = 0.049g, 177 - 246 μ (Dec. '81B)

<u>Time, day</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	0.03	1.20	1.11	0.74	0.27
2	0.07	1.55	1.30	0.85	0.26
3	0.08	1.47	1.25	0.75	0.25

LS04 Leach Data, 70°C
Normalized Elemental Leach rate in g/m²d

wt = 0.0370, 177 - 246 μ (Jan. '82)

<u>Time, day</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	0.004	0.16	0.23	--	0.065
2	0.04	1.1	1.2	--	0.056
3	0.27	2.5	2.5	--	0.098
4	0.11	2.0	2.1	--	0.072

Table 4. S29-HP10A Leach Data 90°C
Normalized Elemental Leach rate in g/m²d

wt = 0.140g, 177-246 μ (Nov. '81)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	0.48	2.1	1.8	0.67	0.29
2-3	0.40	1.6	1.3	0.48	0.20
4-6	0.22	1.0	0.86	0.30	0.13
7-10	0.17	0.8	0.62	0.23	0.10

wt = 0.0644g, 177-246 μ (Dec. '81A)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	0.53	3.92	3.02	1.47	0.55
2-3	0.40	2.56	1.84	0.91	0.35
4-6	0.46	2.26	1.63	0.78	0.30

wt = 0.0446g, 177-246 μ (Dec. '81B)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	0.68	5.6	4.8	2.3	0.91
2	0.90	5.8	4.4	2.2	0.81
3	1.25	7.3	5.6	2.7	0.97

LS04 Leach Data 90°C

wt = 0.0320g, 177-246 μ (Jan. '82)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	0.94	5.6	6.5	0.94	0.24
2	1.6	7.5	8.7	0.94	0.24
3	1.1	7.2	8.1	0.94	0.23
4	1.0	6.4	7.3	0.86	0.18

Table 5. S29-HP10A Leach Data 120°C
Normalized Elemental Leach rate in g/m²d

wt = 0.134g, 177-246 μ (Nov. '81)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	1.3	5.7	4.9	1.9	0.83
2-3	0.77	3.5	2.9	1.1	0.47
4-6	0.53	2.3	1.9	0.67	0.28
7-10	0.43	2.0	1.6	0.62	0.24

wt = 0.0579g, 177-246 μ (Dec. '81A)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	2.0	9.6	7.3	3.1	1.35
2-3	0.70	4.5	3.1	1.5	0.61
4-6	0.81	4.1	2.8	1.2	0.50

wt = 0.0338g, 177-246 μ (Dec. '81B)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	2.8	16.2	12.5	6.2	2.4
2	3.9	21.9	16.1	7.6	2.9
3	3.0	21.4	15.0	6.6	2.4

LS04 Leach Data 120°C

wt = 0.0223g, 177-246 μ (Jan. '82)

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	4.7	20	23	2.0	0.67
2	3.8	21	24	2.7	0.60
3	3.2	21	24	1.3	0.58
4	3.2	24	28	2.2	0.44

Table 6. S29-HP10A Leach Data
Normalized Elemental Leach rate in $\text{g/m}^2\text{d}$

wt = 0.134g, 177-246 μ (Nov. '81), 150 $^{\circ}\text{C}$

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	1.2	5.4	4.3	1.8	0.75
2-3	0.72	3.3	2.6	1.0	0.45
4-6	0.52	2.6	2.1	0.8	0.35
7-10	0.41	2.2	1.7	0.7	0.28

wt = 0.0406g, 177-246 μ (Dec. '81A), 138 $^{\circ}\text{C}$

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	3.06	16.5	12.2	5.6	2.3
2-3	1.18	7.6	5.2	2.5	0.97
4-6	1.01	6.6	4.3	1.9	0.72

wt = 0.034g, 177-246 μ (Dec. '81B) 150 $^{\circ}\text{C}$

<u>Time, days</u>	<u>Al</u>	<u>Si</u>	<u>Na</u>	<u>Sr</u>	<u>Ca</u>
1	4.3	26	22	0.25	2.56
2	3.6	28	21	0.30	2.78
3	3.4	34	22	0.25	2.33

Table 7. Concentrations in Leach Solutions at 90°C in ppm

	Al	Si	Na	Sr	Ca
Nov. '81	1	3.0	4.5	3.0	0.09
	2-3	5.1	6.7	0.13	1.34
	4-6	4.0	6.2	0.11	1.21
	7-10	4.1	6.1	0.12	1.24
Dec. '81A	1	1.4	3.6	0.08	0.8
	2-3	2.4	5.2	0.12	1.1
	4-6	3.7	6.0	0.14	1.3
Dec. '81B	1	1.2	3.4	0.09	0.87
	2	1.7	3.4	0.09	0.78
	3	2.1	3.8	0.09	0.84
	4	0.6	2.9	0.07	0.79
	5-7	1.9	4.4	0.09	1.01
LS04, Jan. '82	1	1.2	2.5	0.03	0.17
	2	1.9	3.0	(0.02)	0.14
	3	1.2	2.3	(0.02)	0.12
	4	1.1	2.2	(0.02)	0.11
246-417 μ	1	1.4	2.6	0.08	0.66
	2	2.2	3.2	0.08	0.75
	3	3.0	4.4	0.10	0.96
417-840 μ	1	2.0	3.1	0.08	0.76
	2	2.4	3.5	0.09	0.82
	3	2.6	4.2	0.10	0.97
840-1650 μ	1	2.3	4.0	0.11	1.11
	2	2.6	4.2	0.10	0.94
	3	2.1	3.9	0.10	0.92

Table 8. Comparison of Dissolution Rate for
Nepheline and SYNROC-D

Temperature <u>°C</u>	pH	Normalized elemental leach rate g/m ² d	
		<u>Na</u>	<u>Si</u>
50	6	0.19	0.22
60	5.0	0.95	0.60
60	7.0	0.64	0.46
70	6	1.3	1.5
80	5.0	2.91	1.96
80	7.0	2.27	1.54
90	6	5.0	6.5

Data for 60 and 80°C from Tole and Lasaga.

Data for 50, 70 and 90°C, this paper.

Table 9. BET and Geometric Surface Area Data
for crushed SYNROC-D

<u>Sieve fraction</u> <u>(μm)</u>	<u>Kr BET surface</u> <u>area, cm²/g</u>	<u>Geometric surface</u> <u>area, cm²/g</u>	<u>BET</u> <u>Geometric</u>
105 - 177	560	106	5.3
177 - 246	420	71	5.9
246 - 417	310	45	6.9
417 - 840	190	24	7.9
840 - 1650	120	12	10

Table 10. Grain Size Data 90°C S29

Normalized Elemental Leach rate, $\text{g/m}^2\text{d}$

<u>Al</u>	<u>Size Fraction</u>	<u>wt(g)</u>	For specified day using geometric SA			Day 3 using BET SA
			<u>1</u>	<u>2</u>	<u>3</u>	<u>3BET</u>
	177 - 246 μ	0.0446	0.7	0.9	1.2	0.20
	246 - 417 μ	0.0872	0.7	0.9	1.4	0.20
	417 - 840 μ	0.2068	0.8	0.8	1.0	0.12
	840 - 1650 μ	0.5766	0.7	0.6	0.5	0.05

<u>Si</u>	<u>geom SA cm²</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>3BET</u>
177 - 246 μ	3.16	5.6	5.8	7.3	1.2
246 - 417 μ	3.93	3.7	4.0	6.4	0.93
417 - 840 μ	4.94	3.7	3.5	4.5	0.56
840 - 1650 μ	6.95	3.4	2.9	2.5	0.25

<u>Na</u>	<u>BET SA cm²</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>3BET</u>
177 - 246 μ	18.7	4.8	4.4	5.6	0.95
246 - 417 μ	27.0	3.7	3.3	5.0	0.73
417 - 840 μ	39.3	3.4	2.9	3.7	0.46
840 - 1650 μ	69.2	3.2	2.4	2.1	0.21

<u>Ca</u>	<u>Average Vol/SA(G)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>3BET</u>
	<u>cm</u>				
177 - 246 μ	5.0	0.91	0.81	0.97	0.16
246 - 417 μ	4.2	0.62	0.60	0.90	0.13
417 - 840 μ	3.2	0.61	0.54	0.70	0.09
840 - 1650 μ	2.3	0.63	0.44	0.40	0.04

Table 11. S29 Monolith leach rates vs 177-246 μ powders
at 90°C in g/m²d, Geometric S. A.

	<u>Monolith, 3 day</u>		<u>Crushed, 1 day</u>		
	<u>[x] ppm</u>	<u>average l.r.</u>	<u>[x] ppm</u>	<u>l.r.</u>	<u>l.r./1.5</u>
Al	2.4	0.81	1.7	0.90	0.60
Si	2.5	2.50	3.4	5.8	3.9
Na	2.4	2.97	2.2	4.4	2.9
Sr	0.09	1.40	0.09	2.2	1.5
Ca	1.2	0.78	0.78	0.81	0.54

Monolith Data by MCC-1 procedure, Campbell et al., 1982 (Table 24).

Crushed data from Table 4, Dec. '81B set - Day 2.

Table 12. MCC-1 90°C Monolith Leaching

	<u>Normalized Elemental</u> <u>Leach rate, g/m²d</u>				<u>Solution concentration</u> <u>ppm</u>			
	<u>3-day</u>	<u>7-day</u>	<u>14-day</u>	<u>28-day</u>	<u>3-day</u>	<u>7-day</u>	<u>14-day</u>	<u>28-day</u>
Al	0.81	0.50	0.31	0.18	2.4	3.4	4.3	5.0
Si	2.50	1.89	1.06	0.67	2.5	4.4	5.0	6.3
Sr	1.40	0.92	0.60	0.38	0.09	0.14	0.18	0.22
Ca	0.78	0.44	0.26	0.16	1.2	1.6	1.8	2.3
Na	2.97	1.47	0.94	0.62	2.4	2.7	3.5	4.6

Data from Campbell et al., (1982), Table 24.

Table 13. Comparison of Monolith and Crushed sample
leach results at similar values of
(Surface Area/Volume)(time)

	Normalized Elemental Leach Rates, g/m ² d	
	MCC-1, 2.8 cm ⁻¹ d	Crushed, 2.4 cm ⁻¹ d
Al	0.18	0.17
Si	0.67	0.8
Na	0.62	0.62
Ca	0.16	0.10
Sr	0.38	0.23

S 29 Days 2-3

Figure 1 Natural log of leach rate plotted against $\frac{1}{T}$ (°K^{-1}) for S29 Nov. '81 data set. Arrow at 50°C points to Al data point which is off scale. Activation energy (E_A) based on Na data is 9.7 kcal/mole.

S 29

Days 2-3

Figure 2 Natural log of leach rate vs $\frac{1}{T}$ ($^{\circ}\text{K}^{-1}$) for S29 Dec. '81A data set. Activation energy determined using 70, 120, and 138 $^{\circ}\text{C}$ data for Na is 10.5 kcal/mole.

S 29 Day 3

Figure 3 Natural log of leach rate vs $\frac{1}{T}$ ($^{\circ}\text{K}^{-1}$) for S29 Dec. '81B data set plus 50°C data from Nov. '81. Activation energy for Na between 50 and 90°C is 19.3 kcal/mole.

LS 04 Day 4

Figure 4 Natural log of leach rate vs $\frac{1}{T}$ ($^{\circ}\text{K}^{-1}$) for LS04 data set.

Activation energy for Na between 70 and 120 $^{\circ}\text{C}$ is 14.5 kcal/mole.

Figure 5 Natural log of leach rate vs $\frac{1}{T}$ (°K⁻¹) for Na and Si from SNYROD-D and nepheline. Data from Table 8; 60 and 80°C data are the average of the listed pH = 5.0 and 7.0 values.

4.2 AN EXAMINATION OF THE MCC-1 LEACH TEST METHOD, PART 1: ROUND ROBIN RESULTS -- J. L. Daniel, Pacific Northwest Laboratory

The results of the recent interlaboratory round robin on the MCC-1 Static Leach Test method were summarized; a complete report has been issued as PNL-4249 (Johnston and Daniel, March 1982). Twenty-five laboratories participated in the interlaboratory testing over a period of 15 months. The specimens tested, all provided by MCC, included simulated waste glass type MCC 76-68, a clear borosilicate glass fabricated at the National Bureau of Standards, natural basalt rock, and three simulated leachate solutions. Participants reported results of their 28-day, 90°C MCC-1 leach tests and analyses of the leachates, and submitted replicate leachate solutions for analysis at the MCC laboratory. Results of the tests are shown graphically in Figure 1.

The leach test results from individual laboratories varied widely, but the consensus averages for the eight elements analyzed in the test leachates were in satisfactory agreement with results obtained in the MCC laboratory (Figure 1a). The relative precisions obtained varied widely, depending on concentration and element/leachant combination (Figure 1b). The between-laboratory standard deviation was at least twice as great as for the within-laboratory results, illustrating the problem of interlaboratory comparison of data even when data are derived from this standardized test. Figure 1c shows that the imprecision of analytical methods accounts for only a relatively small fraction (about 1/3) of the total imprecision except at very low concentrations of leached materials.

The practical implications of these results are:

1. Within-laboratory comparisons would be able to detect differences between waste forms if the differences are at least 1/3 of the average element loss;
2. For between-laboratory comparisons a difference would be statistically detectable if it is at least equal to the observed average element loss (e.g., factor of two or larger).

a. Participants' Consensus Averages Compared to MCC Lab Analysis For Each Waste Form/Leachant

b. Smoothed Relative Precision Of MCC-1 Test Procedure

c. Composition of Smoothed Total Variability of the MCC-1 Round Robin

FIGURE 1. Summary of MCC-1 Round Robin Results

3. Measured loss of elemental mass per unit area must be at least 5 g/m^2 for the comparisons described above.

The possible sources of imprecision in the test results obtained in the round robin include deviations from the specified procedure, inhomogeneity of the test specimens provided to participants, and a need for additional procedure specifications for some inadequately controlled factors. Independent tests on MCC-1 at National Bureau of Standards (see next presentation) indicate that with tighter control over existing specifications, and improved specimen preparation, greatly improved precision can be achieved when the results justify the increased time and cost required.

4.3 AN EXAMINATION OF THE MCC-1 LEACH TEST METHOD, PART 2: EXPERIMENTAL TECHNIQUE — H. M. Kingston, D. J. Cronin, M. S. Epstein, National Bureau of Standards

The MCC-1 static leach test was evaluated for precision potential. Particular attention was given to the elimination of variables in the test. Most of the test parameters remained as specified in the current MCC-1 procedure, except where they were changed to eliminate potential variation in the test. The effect of strict controls of single parameters is unknown in specific detail since all of the controls resulted in a cumulative contribution enabling a high degree of precision. In the future these controls may be investigated using a system possessing a high degree of reproducibility and the subtle effects of each may be discerned separately. At present the accumulative effects under this precise set of conditions and the precision of the complete test under these conditions will be the subject of this investigation.

The glass samples tested were of 13 different compositions. One of these samples is referred to as the base glass and has a composition similar to that of PNL 76-68; it was, however, produced in a manner to assure a high degree of homogeneity. All of the other 12 glasses were variations of this base glass. There were two samples of each type, except the base glass which had seven replicates. The specific composition matrix and exact composition of each glass is given in the next talk of this series⁽¹⁾.

This presentation will rely almost exclusively on the seven replicate samples of the base glass as its main reference point and on the computer calculated agreement between the other twelve pairs of glass compositions.

The main focus of this presentation is on the precision of the test (as modified for the reasons stated) and the basic reliability of the test conditions and materials which can be observed to influence that precision. The question of precision and reliability is one of importance to the MCC, MRB, and the nuclear waste community at large. Experimental precision and a comparison against standards using a prescribed technique is one way data can be evaluated and accepted for inclusion in the Nuclear Waste Materials Handbook.

The question of accuracy in the realm of analysis is a complex one and is discussed in reference⁽²⁾. Figure 1 gives a working definition of this concept. This definition is for an absolute property such as elemental composition. As it is stated in Figure 2, the leach measurement is totally dependent on the test conditions. Following this concept, this presentation will only discuss precision of the leach measurement and its importance to reliable and useful leach data.

The experimental conditions of the leach test are briefly summarized in Figure 3. They are, however, only outlines and do not mention many subtle but important steps taken to avoid such things as contamination or sample transfer for pH measurement credibility, etc. A complete description of the test conditions will be available in a forthcoming publication⁽³⁾. However, in Figures 3 and 4 obvious increases in parameter control are given, such as

Leach measurements are not absolute measurements;

They are totally dependent upon the leaching conditions.

How can the leach characteristics of a material be determined ?

They may be ranked against a standard using a standard test.

FIGURE 1. Leach Measurements

An accurate measurement system is one that produces precise numerical values of the property or properties under test or analysis that are free of, or corrected for, all known systematic errors. (1)

"Accuracy may be transferred to all laboratories within a measurement infrastructure i.e. through the use of reference materials used in conjunction with Reference methods." (1)

(1) Symposium: "Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis," (1976).

FIGURE 2. Measurement System Accuracy

Sample #	pH	Fluoride (ppm)	Nitrate (ppm)
For Base Glass (Buffer 0.03)			
1 - 1	9.36	0.99	<0.08
2 - 6	9.33		
3 - 11	9.37	1.04	0.11
4 - 16	9.27		
5 - 21	9.39	1.07	0.18
6 - 26	9.35		
7 - 31	9.34		
$\bar{x}$	9.34 $\pm$ 0.04		
For Blank Containers			
32	7.12		
33	6.67	0.85	0.09
34	6.60	0.78	0.13
35	6.69	0.65	
36	6.74	0.74	
37	6.59	0.80	0.26
38	6.54	0.82	0.33
$\bar{x}$	6.71 $\pm$ 0.19		
For New Containers			
41	3.81	3.41	0.40
42	3.81	3.45	0.14
43	3.87	3.50	<0.08
44	3.90		
$\bar{x}$	3.85 $\pm$ 0.05		

FIGURE 3. Experimental Conditions of the Leach Test

Parameter	Conditions
Time	28 days $\pm$ assembly and equilibration time
Temperature	90.00 $\pm$ 0.04°C
Sample	glass
Composition	13 different glasses, varied from base glass
Homogeneity	grade B or better (military)
Surface area to volume (SA/V)	0.010mm ⁻¹
Surface measurement	math. comb. of 8 measurements
Surface roughness and prep.	diamond saw, 600 grit silicon carbide powder
Surface cleaning	ultrasonic, in H ₂ O and alcohol

FIGURE 4. Outline of Leach Test Conditions

temperature, when $90 \pm 0.04^\circ\text{C}$ replaces $90 \pm 1.0^\circ\text{C}$. These increases in parameter control are designed to reduce errors in the final results. For example, the range in the leachate concentration of Ca for a 2°C allowable spread would be approximately 10 percent. Since $\pm 1^\circ\text{C}$ is the MCC-1 specification, a 10 percent error in Ca would automatically be possible. The use of more stringent controls on several such parameters would reduce inherent specified uncertainties in these experimental conditions. A second example is the variability in

the surface roughness. It has been shown that surface roughness is a very significant leach test parameter and elements of the physical processing such as equipment and technique used will determine surface characteristics and change the final mean quantity leached and its distribution about the mean⁽⁴⁾. For this reason the surfaces were prepared using 600 grit silicon carbide powder after the initial saw cutting of the sample.

The results of the pH measurements on the seven base glass replicates, the container and reagent blanks, and on the new containers are given in Figure 5. One standard deviation for the standard buffer measurement was 0.03 pH units while 0.04 was obtained for the seven replicates. This agreement suggests the mean pH values of the seven replicate leach samples were within the measurement uncertainty. However, the accuracy of this measurement should only be stated within 0.1 pH units of the pH determined, due to the difference in ionic strength of the different systems. The pH of the containers used as blanks containing everything except the glass was very close to neutrality. This indicates little effect from the container, the environmental chamber, or the acid used to clean the containers (with these cleaning precautions used to remove it). The new containers do show an alteration of the leach solution. This is largely accounted for by the HF possibly produced through clipping of the molecules upon molding, according to a personal communication with M. F. Bro of E. I. du Pont de Nemours, Inc.

<u>Parameter</u>	<u>Conditions</u>
Container	Teflon , PFA
Cleaning	extensively cleaned as prescribed, in plastic, preheated at 200 °C - 1 week, microwaved to remove HF, HNO ₃
Leach Solution	distilled and Milli-Q treated H ₂ O, reduction of CO ₂ , O ₂ , HNO ₃ and HF (Saturated in Ar)
Environmental chamber	no weight loss of containers (distilled H ₂ O)
Analytical Instrumental Analysis	DC plasma, emission spec. , AAS, ion chromatography, electrochemical

FIGURE 5. Outline of Leach Test Conditions (Continued)

The concentration in g/m^2 (not divided by the glass composition) of the major and minor elemental components in the leach solution is presented in Figures 6, 7, and 8. The number after the dash is the numerical order in which the replicate was prepared; they were dispersed throughout the other sample preparations to detect any bias caused by the small difference in sample preparation time before and after the leaching procedure.

Each of the elemental measurements of the leach solutions made by D. C. Plasma (DCP) (or emission spectrometry in the case of Cs) is given in Figures 6, 7, and 8. These measurements have associated the instrumental uncertainty expressed as a $\pm$ value in g/m^2 . These uncertainties are calculated at the 1 sigma level. The mean uncertainty for the actual seven analyses is also expressed in a similar manner. If there is additional error beyond that of the analysis for each of the seven leach solution replicates, it will be reflected in a greater overall uncertainty for the seven measurements compared to the instrumental uncertainty. Any additional source of error would be from inconsistency in the test itself, or from differences in the seven replicate glasses used. This comparison shows these two types of uncertainties to be the same for Si, Mo, Ba, Sr, and Cs. Very close agreement was found for B and Na while some differences were observed for Ca and Zn.

The statistically identical instrumental uncertainties and actual uncertainties for these replicates demonstrates that errors beyond that of the instrument concentration measurement were not present. There are no additional errors from either the leach test or the replicate samples. These findings demonstrate that the ability to reproduce precise results in this type of leaching experiment is possible. While these tests must be repeated to verify both the mean and standard deviation of these results, the potential for development of a reproducible leach test would appear to be an attainable goal.

What about the Ca and Zn which appeared to have additional sources of error, and were the B and Na results actually outside the statistical limits of instrumental reproducibility?

A second precaution taken during the tests was a splitting of the final leach solution prior to acidification. Samples 6 and 16 were each split and analyzed as separate samples. The new split samples, now 6b and 16b, were also

<u>Sample #</u>	<u>Si</u>	<u>B</u>	<u>Na</u>
1 - 1	5.42 ± 0.10*	1.35 ± 0.016	4.42 ± 0.12
2 - 6	5.47 ± 0.10	1.37 ± 0.017	4.32 ± 0.12
3 - 11	5.31 ± 0.10	1.35 ± 0.016	4.40 ± 0.12
4 - 16	5.62 ± 0.10	1.40 ± 0.017	4.36 ± 0.12
5 - 21	5.49 ± 0.10	1.39 ± 0.017	4.32 ± 0.12
6 - 26	5.53 ± 0.10	1.40 ± 0.017	4.52 ± 0.12
7 - 31	5.38 ± 0.10	1.34 ± 0.016	4.80 ± 0.13
$\bar{x}$	5.46 ± 0.10†	1.37 ± 0.026	4.45 ± 0.17

* These uncertainties represent analytical instrumental uncertainties only, at the 1s level.

† Uncertainties at the 1s level of these 7 samples.

FIGURE 6. Major Components Leached from the Base Glass in g/m²

<u>Sample #</u>	<u>Mo</u>	<u>Ca</u>	<u>Ba</u>
1 - 1	0.527 ± 0.017*	0.135 ± 0.002	0.0077 ± 0.0004
2 - 6	0.531 ± 0.017	0.157 ± 0.003	0.0076 ± 0.0004
3 - 11	0.518 ± 0.017	0.132 ± 0.002	0.0076 ± 0.0004
4 - 16	0.533 ± 0.017	0.137 ± 0.002	0.0078 ± 0.0004
5 - 21	0.529 ± 0.017	0.143 ± 0.003	0.0082 ± 0.0004
6 - 26	0.508 ± 0.017	0.137 ± 0.002	0.0076 ± 0.0004
7 - 31	0.516 ± 0.017	0.128 ± 0.002	0.0074 ± 0.0004
$\bar{x}$	0.523 ± 0.009†	0.138 ± 0.009	0.0077 ± 0.0003

* These uncertainties represent analytical instrumental uncertainties only, at the 1s level.

† Uncertainties at the 1s level of these 7 samples.

FIGURE 7. Minor Components Leached from the Base Glass in g/m²

<u>Sample #</u>	<u>Sr</u>	<u>Cs</u>	<u>Zn</u>
1 - 1	0.0308 ± 0.0009*	0.421 ± 0.007	0.0240 ± 0.0007
2 - 6	0.0296 ± 0.0009	0.433 ± 0.007	
3 - 11	0.0298 ± 0.0009	0.423 ± 0.007	0.0286 ± 0.0007
4 - 16	0.0315 ± 0.0009	0.428 ± 0.007	
5 - 21	0.0323 ± 0.0009	0.435 ± 0.007	0.0212 ± 0.0007
6 - 26	0.0317 ± 0.0009	0.433 ± 0.007	0.0192 ± 0.0007
7 - 31	0.0315 ± 0.0009	0.445 ± 0.007	0.0294 ± 0.0007
$\bar{x}$	0.0310 ± 0.0010†	0.431 ± 0.008	0.0245 ± 0.0045

* These uncertainties represent analytical instrumental uncertainties only, at the 1s level.

† Uncertainties at the 1s level of these 7 samples.

FIGURE 8. Minor Components Leached from the Base Glass in g/m²

acidified, but not in the original container. All of the elemental concentration analyses of these split samples were statistically identical except for the analysis of Zn. These results are given in Figure 9 along with the results of a tracer study done by irradiating the glass and performing the leach test with radio tracers⁽⁵⁾. In both studies the Zn adsorbed onto the container walls and did so non-reproducibly. This behavior would most probably account for the variability of the Zn. Neither the leach test nor the sample cause the variable characteristic of this element. In all of the other elements tested here the concentrations in 6, 16, 6b and 16b were indistinguishable.

What about B and Na? Do they really have some small statistically significant increase in uncertainty over the instrumental ability to measure their concentrations in the leach solution? Figure 10 compares the instrumental uncertainty, the experimental uncertainty of the seven replicates, and the residual standard deviation or the uncertainty for the whole test including the other 12 pairs of glass. It would be expected that the residual standard deviation should be larger since some of the glasses tested are much less resistant to leaching than the base glass. Nevertheless, an examination of the residual standard deviation (which has 18 degrees of freedom) shows that the uncertainty for Na is actually identical to that of the theoretical instrumental measurement, and that B is less than that for the base glasses. Thus, seven of the nine elements tested demonstrate that the leach test and the homogeneous samples tested do not add significant error to that of the instrumental analysis of the final leach solutions. The limiting factor in the precision for these elements is the instrumental concentration analysis, not the material or the leach test. There are many significant implications of this finding.

Split Leachate Prior to Acidification		Percent of Zinc in Solution After Leaching (remainder on container walls)
Sample	$\mu\text{g/ml}$	
6	0.365 ± 0.007	Test 1 $40 \pm 5\%$
6b	0.045 ± 0.007	Test 2 $73 \pm 5\%$
16	0.310 ± 0.007	
16b	0.091 ± 0.007	

FIGURE 9. Zinc Behavior Under Leaching Conditions

Element	Instrumental Uncertainty for the Base Glass	Experimental Standard Deviation for the 7 Base Glasses	Residual Standard Deviation for All 31 Samples (18df)
Ba	0.0004	0.0003	0.00026
Mo	0.017	0.009	0.011
B	0.017	0.026	0.024
Sr	0.0009	0.0010	0.0014
Cs	0.007	0.008	0.009
Si	0.10	0.10	0.13
Na	0.12	0.17	0.12
Ca	0.002	0.009	0.009
Zn	0.0007	0.0045	0.0047

FIGURE 10. Uncertainty of Leachate Measurement at the 1s Level in g/m²

The homogeneity of the potential standard is an important parameter. Figure 11 was constructed to demonstrate the importance of this factor. In this figure the leach solution concentration of the base glass and that of one of the other glasses (comp #6) is given. Using the residual standard deviation for the whole experiment (18 df) the percent of the base glass surface area was calculated, which, when substituted by composition number 6 (a glass 10 percent different), would result in a detectable leachate concentration change (at the 2s level). The results indicate several important trends. First, the ability to measure the element is important; the increased uncertainty for Zn and Ca permit large differences which cannot be distinguished. The ability to distinguish differences in the leach solution also depends on the extent of the

Element	Mean Leachate Conc. For Base Glass in g/m ²	Mean Leachate Conc. for Comp. 6 in g/m ²	Residual S.D. (18 df) in g/m ²	Percent of Comp. to be significant (2s)
Ba	0.0077	0.0020	0.00026	7
Mo	0.523	1.71	0.011	1.5
B	1.37	6.16	0.024	1
Sr	0.0310	0.0076	0.0014	7.7
Cs	0.431	1.17	0.009	1.9
Si	5.46	9.08	0.13	5
Na	4.45	18.6	0.12	2.3
Ca	0.138	0.046	0.009	20
Zn	0.027	0.041	0.0047	78

The percent of the base glass surface area that when substituted by composition number 6 (10 percent different) would be found to be discernibly different at the 2s level.

FIGURE 11. Influence of Homogeneity on the Test

concentration difference of the two leach solutions resulting from the different glasses; in general the greater the difference the more easily they are distinguished. However, the main point observed is it only requires a few percent of the glass surface area to be substituted for different leachate concentrations to be observable. While composition bands or stria are analytically indistinguishable when bulk analyses are used, a dramatic effect in leachate concentration will result from surface area variability.

This source of error has been eliminated in the glasses tested in this study. The future standards must possess this same high degree of homogeneity so that surface composition variability will not lead to undeserved high uncertainty for the test.

During the analysis of the leachate concentrations an empirical equation was used to fit the data. The computer fitted the data and determined the number of factors significant in stabilizing or destabilizing the glasses. The magnitude of the effect of these factors was also given. The maximum number of significant factors possible was 13. The ability to determine the relevance and significance of leach factors is affected by the ability to obtain repeatable results with a known uncertainty. A comparison was made between these factors at the present uncertainty level, and what these factors would be if the uncertainty in the data were to be twice its present level. Figure 12 compares the difference in the number of factors and demonstrates that much of the information would be lost if the uncertainty in the data were increased. This is significant especially when the data is to be used in mechanistic evaluation or modelling when understanding the subtleties of the reactions is the object of the test. Even a moderate increase in these uncertainties would reduce the information obtained from the test. Thus, the uncertainty of the test and the information gained are inversely related. A point can be reached where very little information is obtained in a leach test due to the uncertainty of the results.

The glasses used in this test have proven to be of sufficient homogeneity to allow precise reproducible results. It is critical that any material used as a standard in the leach test give reproducible conditions. These glasses have shown appropriate characteristics for use as standard materials for use in leach test standardization.

Element	At The Current Level of Uncertainty	If The Uncertainty Were Twice as Much
Ba	13	7
Mo	13	9
B	12	9
Sr	12	9
Cs	10	10
Si	9	5
Na	9	8
Ca	7	4
Zn	3	1

FIGURE 12. Number of Significant Factors

This set of experiments has shown that with defined parameters and a high degree of control, precise results are possible in leaching tests of this type. These results should be verified to find the exact mean and assure all parameters are under precise repeatable control. An investigation of the defined controlled parameters should be initiated to understand each of their exact relationships to the test. It may be possible that many of these controlled conditions could be relaxed to a degree in the interest of simplifying the test without significantly increasing the error. The degree of control demonstrated here is necessary to investigate the effect that these subtle changes would produce in the leach test.

The amount of reproducibility and precision possible in leach tests of this type has not been identified in the literature to date. The reproducibility of these leach results is comparable to the uncertainty in the analytical concentration analysis technique. While more work is needed, these results suggest that the test can be made to perform in a highly reproducible manner.

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4.4 AN EXAMINATION OF THE MCC-1 LEACH TEST METHOD, PART 3: COMPARISON OF GLASS COMPOSITIONS -- D. J. Cronin, H. M. Kingston, National Bureau of Standards

The leach rate, as determined by the MCC-1 test method, was found to be sensitive to relatively minor variations in simulated waste glass composition. The 13 glass compositions tested are shown in Tables 1 and 2. These glasses were prepared as part of a since discontinued program to prepare leachability research materials at NBS (Cronin 1982). A base glass composition was defined (Glass No. 1) and variations in composition were obtained by adding or subtracting constituents from the base composition. In each case, the SiO_2 content was adjusted to balance the addition or subtraction.

The results of 28 MCC-1 leach tests on the 13 glasses were analyzed statistically. Based on total mass loss data it was found that increases in Ti, Sr, Ce, and Nd increased the chemical durability, while increases in Cs, Mo, B and Na decreased the chemical durability of glass. The individual elemental mass loss results showed the same relationship. The results also showed the chemical durability is more sensitive to variations in B content than Na content.

A very good correlation was obtained between measured weight loss and the loss calculated from the total ions found in the leachate. The agreement was within 1% when the leached specimens were dried at 200°C before weighing. The high drying temperature was required because of hydration of the leached glass surfaces.

The elemental mass loss data for the various glasses can be used to estimate the effect of sample inhomogeneity on leach test results. Using the elemental mass loss data and known analytical uncertainty it is possible to calculate the percent of sample surface having a given composition difference that would be required to show a statistically significant difference in leach test results. An example of this is shown in Figure 5 of Section 4.3 comparing the base glass with Glass No. 6 shown in Figure 2 of Section 4.3. This glass composition differs from the base glass by having 5 wt% more of each B_2O_3 and Na_2O and 10 wt% less SiO_2 . This glass showed much poorer durability than

TABLE 1. Base Glass Composition.

Constituents	wt %	Constituents	wt %	Constituents	wt %
SiO ₂	46.10	ZrO ₂	2.10	P ₂ O ₅	0.57
B ₂ O ₃	10.96	MoO ₃	1.96	La ₂ O ₃	0.63
Na ₂ O	15.32	TeO ₂	0.31	CdO	0.00
ZnO	5.75	Cs ₂ O	1.36	Nd ₂ O ₃	5.78
TiO ₂	3.43	BaO ₂	0.66	Pr ₆ O ₁₁	0.63
CaO	2.31	CeO ₂	1.41	Y ₂ O ₃	0.25
Fe ₂ O ₃	0.00	Cr ₂ O ₃	0.00		
SrO	0.45	NiO	0.00		

TABLE 2. Glass Compositions (Presented as Variations from Base glass, Table 1) for the Evaluation of the Influence of Composition on Leaching(a)

Glass/Component No.	Si	B	Na	Ti	Sr	Mo	Cs	Ce	Nd
1	0	0	0	0	0	0	0	0	0
2	10	-5	-5	0	0	0	0	0	0
3	0	-5	5	0	0	0	0	0	0
4	-5	5	0	0	0	0	0	0	0
5	0	5	-5	0	0	0	0	0	0
6	-10	5	5	0	0	0	0	0	0
7	-5	0	5	0	0	0	0	0	0
8	-5	0	0	1	1	1	0	1	1
9	-5	0	0	1	1	1	1	0	1
10	-5	0	0	1	1	1	1	1	0
11	-4	0	0	1	0	0	1	1	1
12	-4	0	0	0	1	0	1	1	1
13	-4	0	0	0	0	1	1	1	1

(a) 1 = increase from base glass of 1 wt%
0 = no change
-1 = decrease from base glass of 1 wt%

any of the other glasses tested. Figure 5 shows that the percent of this composition required to show a detectable difference in leach results varies for the different elements involved. This is related to analytical precision. This shows that for B a sample with one percent of the surface having the composition of the Glass No. 6 could be determined as significantly different from the base glass alone. Since this particular composition shows the greatest difference in leach results, compared to the base glass, other of the compositions tested required greater than one percent of the sample surface to show a significant effect on leach results (Table 3).

These results show the importance of working with homogeneous samples. If inhomogeneous samples are used, then sample variability could contribute to the overall uncertainty of the test and information relating to the leaching behavior would be lost.

TABLE 3. Influence of Homogeneity on the Test

Element	Mean Leachate Conc., For Base Glass, g/m ²	Mean Leachate Conc., For Glass No. 6, g/m ²	Residual S.D., (18 df), g/m ²	Percent of Comp. To Be Significant (2s) ^(a)
Ba	0.0077	0.0020	0.00026	7
Mo	0.523	1.71	0.011	1.5
B	1.37	6.16	0.024	1
Sr	0.0310	0.0076	0.0014	7.7
Cs	0.431	1.17	0.009	1.9
Si	5.46	9.08	0.13	5
Na	4.45	18.6	0.12	2.3
Ca	0.138	0.046	0.009	20
Zn	0.027	0.041	0.0047	78

(a) The percent of the base glass surface area that when substituted by Glass No. 6 (10 percent difference) would be found to be discernably different at the 2s level.

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4.5 A MODEL FOR LEACHING OF SRP WASTE GLASS -- R. M. Wallace and G. G. Wicks,
Savannah River Laboratory^(a)

The leachability of glass has been studied by many different techniques. Most of the theoretical work has focused on only very simple glass systems.¹ This work has lead to the identification of two main stages of glass corrosion - interdiffusion and matrix dissolution. These corrosion modes alone are inadequate to fully describe leaching of the more complicated waste glass systems.

Recent work at Savannah River Laboratory (SRL) has identified a further stage of corrosion for waste glass compositions - surface layer formation.² The formation and stability of protective surface layers are believed to be the most important factors affecting long-term performance of waste glass products during permanent storage.

An SRL leachability model has been developed which assumes that glass corrodes congruently. The rate of corrosion is controlled by the rate of reaction of amorphous silica with water as well as the rate of diffusion of soluble silicates through the insoluble layer between the glass and the bulk solution. The thickness of the insoluble layer is proportional to the amount of glass that has dissolved from the start of the experiment. The silicate concentration gradient in the layer is equal to the difference between the silicate concentration at the glass layer interface and that in the bulk leachate divided by the layer thickness.

The following general equation for leaching of waste glass was derived from this model (symbols are identified at end of this article)

$$\frac{dL}{dt} = \frac{K_r(1-y)}{1 + \beta L}$$

(a) The information contained in this article was developed during the course of work under Contract No. De-AC09-76SR0000 with the U.S. Department of Energy

In the special case of a closed system where the products of leaching are allowed to accumulate in the leachant, the equation becomes

$$\frac{dL}{dt} = \frac{K_r(1-\alpha L)}{1 + \beta L}$$

Upon integration the equation becomes

$$(1 + \beta/\alpha) \ln (1 - \alpha L) + \beta L = \alpha K_r t$$

In the limiting case of an open system where $y = 0$ or $\alpha = 0$, this equation becomes

$$L + 1/2 \beta L^2 = K_r t$$

It was also shown that the slope of a plot of $\log L$ vs $\log t$ for the closed system would be given by the equation:

$$S = - \frac{1}{\alpha L} \frac{(1 - \alpha L)}{(1 + \beta L)} [(1 + \beta/\alpha) \ln (1 - \alpha L) + \beta L]$$

and for the open system by

$$S = \frac{1 + 1/2 \beta L}{1 + \beta L}$$

The model predicts that the slope of the log concentration vs. log time plot should be initially 1, then shift to 0.5 at a later time and finally approaches 0 as the leachate becomes saturated with silicates.

SYMBOLS

K_r = Reaction rate constant

L = Amount of glass leached

S = Slope of a log L vs log t plot

t = Time

y = Fractional saturation of leachate with respect to silica

α = A parameter proportional to the ratio of surface area to volume

β = A parameter proportional to the ratio of the reaction rate constant to the diffusion coefficient

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4.6 EFFECT OF SOLUBILITY ON LEACHING -- B. Grambow, Pacific Northwest Laboratory^(a)

THE ROLE OF METAL ION SOLUBILITY LIMITS IN THE MECHANISM OF LEACHING OF NUCLEAR WASTE GLASSES

(This was essentially the same presentation that B. Grambow made at the Fifth International Symposium on the Scientific Basis for Radioactive Waste Management in Berlin on June 7, 1982. The full text will appear in the proceedings of that meeting to be published this fall. The following is an extended abstract.)

SUMMARY

A number of studies have qualitatively considered solubility limits to be important in the leaching of nuclear waste forms with respect to reaction layer formation and the prediction of long-term behavior under accidental conditions in a repository. These considerations are quantified in this paper by the application of data from soil chemistry^(1,2) to the conditions of leach tests with PNL 76-68 and other glasses.

In some cases probable solid reaction products, which may govern the concentrations of metal ions in solution, could be identified by use of thermodynamic calculations including hydrolysis, complexation, mass balance and temperature dependence.

RESULTS AND CONCLUSIONS

By assuming the existence of certain solid reaction phases and their solubility characteristics, good agreement between the theoretical and the observed concentrations of Ca, Sr, Nd, Fe, and Zn in the leachates from PNL 76-68 glass was obtained. This indicates that the solids CaCO_3 (calcite),

(a) Work performed while at Battelle, Pacific Northwest Laboratory. Current address is Hahn-Meitner-Institut für Kernforschung Berlin GmbH 1000 Berlin 39, Glienicke Str. 100

SrCO_3 , Nd(OH)_3 , Fe(OH)_3 (amorphous) and several zinc phases such as Zn_2SiO_4 (willemite) or Zn(OH)_2 may be controlling the solution concentrations. These solids or their microcrystalline precursors, some of which have been experimentally observed are probably responsible for the "enrichment" of these elements in the "gel" layer. The good agreement between predicted and experimentally observed solution concentrations was found for a broad range of leachants, temperatures, and SA/V ratios in both static and dynamic tests.

By converting solution concentrations from leach tests to normalized elemental mass loss, $\text{NL}_i^{(3)}$, the leaching behavior of a specific element i can be compared with that of other elements. To study the influence of solubility limits on the general mechanisms of leaching, the theoretical equilibrium concentrations can also be normalized to concentrations in the glass. This yields a normalized solubility (NS_i) which can then be easily compared to the normalized elemental mass loss of any element. For studies of silicate glasses, the comparison of solubilities to the normalized elemental mass loss of silicon is important. The ratio of the normalized solubility to the normalized silicon loss ($\text{NS}_i/\text{NL}_{\text{Si}}$) is a convenient parameter to consider in this regard.

For the particular application to PNL 76-68 glass leached in a MCC-1 test at 90°C for 28d, NL_{Si} is 20 gm^{-2} and calculations for various solids yield Figure 1 when $\text{NS}_i/\text{NL}_{\text{Si}}$ is plotted against pH. Using this figure and the available experimental data, it can be shown that the leaching behavior of various elements is similar to that of silicon, as long as the solubility limit for that element is not exceeded. If the solubility limit is exceeded, the solution concentration of that element is not controlled by network dissolution but by certain solid species. The experimental results will generally be shown to fit the pH dependence indicated in Figure 1. Moreover, the composition of some elements in the leached surface layer on PNL 76-68 glass can be predicted, if the leachate pH is known.

References

- 152

4.7 THERMODYNAMICS OF GEOCHEMICAL SYSTEMS -- S. L. Phillips, Lawrence Berkeley Laboratory

(The content of this presentation was from the draft of a document that has since been published.⁽¹⁾ The document contains recommended hydrolysis and formation constants for Al, Am, Cs, Cu, Cm, Eu, Fe, Pb, Np, Ni, Pu, Sm, Sr, Tc, Th, Sn, U, and Zr. Complexing liquids for the various ionic species of these metals include OH, F, Cl, SO₄, PO₄, and CO₃. Phillips concluded his presentation, and his document, with some recommendations for future research, which are reproduced below.)

Future research on stability constants for nuclear waste disposal might include the following recommended research:

1. Development of methods for extrapolation of data from low temperatures such as 25°C up to 200°C to 300°C. Stability constants at elevated temperatures are useful for estimating leaching of waste nuclides from storage canisters; in corrosion research for power plants; and, in solution mining of ores. Current approaches include use of the Criss-Cobble approach, and the integrated van't Hoff equation^(2,3).
2. Derivation of a theoretically based equation for calculating stability constants as a function of supporting electrolyte concentrations which is applicable to 3 molal or greater concentrations. This would permit calculation of stability constants in a variety of natural media such as sea water and brines. At present, empirical approaches such as the Davies equation and addition of polynomial terms to the Debye-Huckel equation are widely used.
3. Gibbs energy values for the formation of multiligand complex ions such as CuCl₄²⁻ and PbCl₄²⁻. These can be used to calculate stability constants for comparison with experimental values, and also may show trends which could be used to estimate other Gibbs energy values, e.g., for higher complexes. Current CODATA and NBS tabulations generally include the first or second complexation values.

4. Experimental measurements of stability constants at high temperatures; especially above 100°C. Much of the data above 100°C are calculated; leading to the dual question of how accurate is the calculation, and whether particular species even exist at 100–200°C. The publication by Tremaine and LeBlanc provides needed data on Fe^{2+} at high temperatures⁽⁴⁾.
5. Instrumental methods for both identifying specific species, and measuring at ambient concentrations. The existence of some species, e.g., $\text{U}(\text{OH})_4$, are inferred, some are a result of computer fits such as $\text{Zr}_3(\text{OH})_4^{8+}$; while the existence of others is a scientific guess e.g., $\text{Al}(\text{OH})_3^\circ$.

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5.0 SESSION III: NEAR-FIELD HYDROLOGICAL, DIFFUSION AND
CONVECTION PHENOMENA

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5.1 TUTORIAL ON GROUND WATER HYDROLOGY -- C. R. Faust, Geotrans, Inc.

A tutorial was presented to familiarize the investigators doing leach testing with some of the terminology and basic concepts of ground wastes hydrology. The presenter recommended Freeze and Cherry [R. A. Freeze and J. A. Cherry (1979), Groundwater, Prentice-Hall, Englewood Cliffs, N.J.] as an excellent source book.

5.2 INFLUENCE OF DIFFUSION THROUGH A CONCENTRATION BOUNDARY LAYER ON THE DISSOLUTION RATE OF WASTE FORMS -- W. L. Kuhn, Pacific Northwest Laboratory

Review of "Solubility-Limited Dissolution Rate in Groundwater," by P. L. Chambre, T. H. Pigford, and S. Zavoshy (Revised March 1982), UCB-NE-4016, University of California, Berkeley, CA 94720. Since none of the authors could attend the workshop, W. L. Kuhn presented the review.

The authors have calculated fractional release rates, based on solubilities, for several important radionuclides from an interred canister of nuclear waste glass, that are several orders of magnitude below the 10^{-5} /year criterion proposed by the NRC, as follows:

<u>Element</u>	<u>Rate (yr⁻¹)</u>	<u>Assumed Solubility (g/cm³)</u>
U	8.0×10^{-6}	2.0×10^{-6}
Pu	4.0×10^{-7}	1.0×10^{-9}
Tc	7.0×10^{-8}	3.0×10^{-9}
Np	5.7×10^{-10}	2.4×10^{-11}
Am	2.3×10^{-10}	1.8×10^{-12}

The calculation is made assuming that ground water flows horizontally past a vertical cylinder surrounded by a homogeneous, isotropic porous medium. As an upper bound, the radionuclide concentrations at the surface of the cylinder are assumed to be the maximum values possible, which are the respective solubilities. The release rate is found by calculating a mass transfer coefficient for diffusion into the ground water flowing in a pattern characteristic of the geometry and boundary conditions considered. By assigning to the cylinder the dimensions of a typical waste package and the radionuclide inventories from 460 kg of fuel, by assuming a ground water velocity of 1 m/yr and a porosity of 0.01 in the media, the above results are obtained. Solubilities are taken from the literature, and are presumed to be typical.

The significance of the paper is that it illustrates that radionuclide solubilities can be combined with a mass transfer resistance, of which diffusion into flowing ground water is only one that could be considered, to establish important constraints on the rates of release of radionuclides, independent of the durability of the waste form. Also, the point is made correctly that surface-to-volume ratios are not to be used to scale laboratory experiments to a repository.

There are perhaps two difficulties with the analysis presented by the authors. First, the flow media in a repository would be inhomogeneous as a result of mining and backfill, and the flow pattern and velocity through it would probably be determined by thermal-bouyancy forces, rather than by ground water flow characteristic of the undisturbed site. Second, solubilities need to be calculated on a site specific basis, since they can be strongly influenced by pH, redox, and complexing ligands. However, the significance of the paper should stand up under future refinements regarding repository hydrodynamics and geochemistry.

5.3 STATUS REPORT ON REFERENCE FLOW REGIONS FOR GEOLOGIC REPOSITORIES

5.3.1 BASALT -- M. J. Apted, Rockwell Hanford Company

The information presented was preliminary and not for publication.

5.3.2 TUFF -- F. R. Stevens, U.S. Geological Survey, Reston, Virginia

The information presented was preliminary and not for publication.

5.3.3 SALT -- J. F. Kircher, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, Ohio

The information presented was preliminary, and not for publication

6.0 SESSION IV. STATUS OF MULTICOMPONENT INTERACTION TESTING

6.1 INTERACTIONS TESTING AT PNL -- D. G. Coles, Pacific Northwest Laboratory

(This presentation by PNL introduced the session on the status of multi-component testing. Dave Coles discussed the background of waste package testing. A summary of this discussion prepared by the workshop chairman follows.)

The goal of waste-package testing is to demonstrate that a given waste package will meet NRC licensing requirements. The licensing requirements are still evolving but it seems clear that the NRC will need the following waste-package performance information:

- Behavior and interactions of candidate waste-package materials under repository conditions
- Conditions leading to waste-package failure
- Limitations of analytical and test techniques used for waste-package performance verification.

In other words, the behavior of the complete waste package, for its design lifetime, should be established under repository conditions.

The waste-package design is flexible and will likely vary depending upon the geologic setting of the repository, but the basic elements are those shown in Figure 1. All the components in Figure 1, except the rock, are generally considered parts of the waste package. The question then becomes how should testing of the potential interactions within this complex system be conducted. PNL's, and other's, answer is to 1) study the degradation behavior of individual components, which provides fundamental understanding of materials properties necessary for interpreting interaction tests; and 2) study the interactive behavior of adjacent package components, which provides synergistic information to help assess component compatibility.

In the study of the behavior of waste-package systems, does the summation of individual component behavior describe the behavior observed from whole systems tests?

- Yes → Problem Solved
- No → Find reason for discrepancy.

FIGURE 1. Waste Package Components

The experimental matrix is potentially very large. Some of the possible variables that must be considered in waste-package interactions testing are shown in Table 1. Obviously the variables must be prioritized. The steps in prioritization are:

1. Review existing literature -- Establish "state-of-the-art" (both understanding and experimental)
2. Pick "most likely" conditions and components
3. Conduct statistical design for experiments which maximize information from minimum experimental effort.

Most of the current waste-package work is directed toward one of the first two steps.

TABLE 1. Some of the Possible Variables in a Waste-Package Experimental Matrix

<u>Materials</u>	<u>Repository Conditions</u>	<u>Package/General</u>	<u>Others?</u>
Waste Forms	Rock Type	Time	
Canisters	Solution Chemistry	Temperature	
Overpacks	pH/Eh	Radiation	
Backfills	Flow Rate		
	Anion/Cation Conc.		
	fO_2		
	fCO_2		
	$aSiO_2$		
	Pressure		

6.2 OVERVIEW OF HYDROTHERMAL TESTING OF WASTE PACKAGE BARRIER MATERIALS AT THE BASALT WASTE ISOLATION PROJECT -- M. J. Apted, Basalt Waste Isolation Project, Rockwell Hanford Operations

ABSTRACT

The current Waste Package Department (WPD) hydrothermal testing program for the Basalt Waste Isolation Project (BWIP) has followed a systematic approach for the testing of waste-barrier-basalt interactions based on sequential penetration of barriers by intruding groundwaters. Present test activities in the WPD program have focused on determining radionuclide solubility limits (or steady-state conditions) of simulated waste forms and the long-term stability of waste package barriers under site-specific hydrothermal conditions. The resulting data on solution compositions and solid alteration products have been used to evaluate waste form degradation under conditions specific to a nuclear waste repository located in basalt (NWRB). Isothermal, time-invariant compositional data on sampled solutions have been coupled with realistic hydrologic flow data for near-field and far-field modeling for the calculation of meaningful radionuclide release rates. Radionuclides that are not strongly sorbed or precipitated from solution and that, therefore, may require special attention to ensure their isolation within the waste package have been identified. Taken together, these hydrothermal test data have been used to establish design requirements for waste packages located in basalt. Hydrothermal testing with flowthrough autoclave systems and use of tracer-loaded/fully-loaded radioactive waste forms (hot-cell testing) are in progress. Results from these tests will be used to confirm performance assessment models based on test results of simulated waste forms under static hydrothermal conditions.

INTRODUCTION

The principal goal of the BWIP is to evaluate the feasibility of permanent storage of nuclear waste in a geologic repository mined in basalt. This evaluation must be based on proposed regulatory criteria (NRC, 1981; EPA, 1982) that determine the required long-term performance of a nuclear waste repository in basalt. These performance criteria can be used to evaluate the performance

required of the engineered repository system. The geologic barriers of the repository site plus the manmade, engineered barriers of the waste package comprise the total barrier to release of materials to the biosphere. Where the natural barriers of the repository itself cannot meet or exceed the regulatory criteria, the performance of engineered barriers must supplement the performance of the geologic barriers to insure regulatory compliance and to insure isolation of waste materials.

The BWIP adopted an approach to performance assessment of barrier materials that relies on site-specific, hydrothermal testing of waste package components, both individually and as an integrated assembly. It is neither economically nor experimentally feasible to conduct such hydrothermal tests for durations approaching containment times (1,000 to 10,000 years) demanded in currently proposed regulatory criteria. It is, therefore, imperative that expert scientific judgment guide the design and interpretation of such a testing program. Laboratory tests, coupled with expert professional opinion, are key to the meaningful extrapolation of short-term laboratory data to the much longer time periods expected during the functional life of a nuclear waste repository in basalt.

GENERAL APPROACH TO HYDROTHERMAL TESTING

The Waste Package Department of the BWIP has endorsed the concept of a sequential hydrothermal testing program for waste package barrier materials based on the progressive penetration of barriers by intruding groundwaters (Figure 1). This approach emphasizes early hydrothermal stability tests of individual waste package components, including compositional changes of coexisting solutions under site-specific repository conditions. Results from these early tests, in turn, are compared with results on successively more complex hydrothermal interaction tests of multiple waste package components. Data from these earlier tests serve also as input into later tests to model more realistically the chemical evolution of hydrothermal reactions within the waste package. This step-wise approach enables the test program not only to isolate chemical degradation reactions specific to individual waste package components, but also to identify synergistic effects that may develop between multicomponent systems, as required in Nuclear Regulatory Commission (NRC)

FIGURE 1. Groundwater Intrusion Through a Waste Package in Basalt.

guidelines (NRC, 1981b). Both the primary reaction of hydrothermally altered groundwaters with nuclear waste forms and subsequent reaction of radionuclide-bearing groundwaters with waste package and repository components are key interactions that can be affected by such synergism. This approach emphasizes the explicit focus of the WPD on the fate of radionuclides as opposed to the sole study of the chemical durability of the waste form.

Current WPD data on hydrothermal reaction of waste forms (simulated spent fuel, borosilicate glass and tailored ceramic) under basalt-specific conditions have been compiled (Apted, 1981; Holloway, et al., 1981; Jenkins, et al., 1982). These studies indicate that near-field radionuclide release rates can be defined usefully as the product of the radionuclide concentration in the groundwater reacted with the waste form and the hydrologic flow rate of the groundwater. Previous hydrothermal testing on waste forms has emphasized the collection of short-term, time-dependent, leach rate data (e.g., Friedman, et

al., 1980; McVay, et al., 1981). It has been argued recently (NWTs, 1981; MCC, 1981) that time-independent solubility limits or steady-state reactions^(a) are more realistic and useful data for evaluating long-term radionuclide release rates, particularly for slow flow-rate conditions expected in a repository.

Solubility and Steady-State Limits

The extrapolation of results from barrier material testing is closely allied to the common dilemma encountered by geoscientists who attempt to extrapolate similar laboratory data (tests of less than two years duration) to natural geochemical and mineralogic processes that occur over hundreds to millions of years. Geochemists and experimental petrologists have accordingly developed several theories, based on chemical thermodynamic and kinetic reaction principles, to address this extrapolation problem. These theories have been validated by observation of repeated agreements between theoretical predictions and observed natural examples in a variety of geochemical systems. These interpretive theories, already in common use by the geochemical community, should serve as the basis for expert judgment regarding extrapolation of waste/barrier/basalt test results to time scales appropriate to regulatory isolation criteria.

The long-term stability and performance of candidate barrier materials is chiefly, though not exclusively, determined by their chemical interaction with the groundwaters that will eventually fill the repository. The dominant process for hydrothermal interactions in the waste/barrier/basalt system is gradual dissolution of coexisting primary solid phases. Dissolution will be accompanied by precipitation and growth of an assemblage of secondary, alteration phases that are more stable under the given repository conditions. These dissolution and precipitation processes represent an overall irreversible

(a) Under steady-state reaction conditions, solution compositions are controlled by simultaneous dissolution and growth of primary and secondary alteration products, respectively (Mottl and Holland, 1978; Lasaga, 1981).

reaction (Helgeson, 1968; Giggenbach, 1981; Wolery, 1981) that may be summarized by the expression:

The Ostwald step rule is a useful, albeit empirical, observation from natural and experimental studies of hydrothermally altered rocks (Fyfe and Verhoogen, 1958; Dibble and Tiller, 1981a). It states that the transition from an unstable to a stable phase(s) generally occurs through the formation of a series of intermediate metastable phases, and that the thermodynamic instability of these intermediate phases will decrease as the reaction progresses. The thermodynamic parameter measuring the relative stability of a phase in a hydrothermal system is its free energy, that is, the total driving force for reaction between solids and solution. This free energy is also a direct measure of solubility of a solid phase (Garrels and Christ, 1965; Giggenbach, 1981). The relative hydrothermal stability of phases, therefore, can be determined directly from relative solubilities (i.e., the most soluble phase will be the least stable). At any point during a stepwise alteration-reaction process, the composition of the solution will be governed by the relative solubilities of coexisting phases.

In the limiting case, in which only the most stable solid phases are present, solubility data can be measured directly (Wood and Rai, 1981; Rai, et al., 1981) from solution composition or evaluated from thermodynamic data, when available (Pourbaix, 1966; Garrels and Christ, 1965; Langmuir, 1978). It is important to stress that such solubility data is defined to be independent of time and reaction pathway because of the assumed equilibrium nature of the system. Because all chemical systems evolve toward equilibrium (i.e., an assemblage of stable phases), and because of the very low flow rates of groundwater expected in nuclear waste repositories (NWTs, 1981; MCC, 1981; Arnet, et al., 1981) the use of solubility limits models to predict long-term release rates of radionuclides from a waste/package/repository system is justifiable.

The application of thermodynamic solubility constraints can be extended to a more general model for hydrothermal reactions between solution and

metastable solids. A schematic representation of the measured solution concentration as a function of time (experiment duration) in a hydrothermal system is presented in Figure 2. In this case, there is assumed to be a solid phase in solution that is metastable relative to one (or more) compositionally-related solid phase. Note, this more stable phase is not necessarily the most stable of all compositionally-related phases. At time t_0 , a solution in contact with the initial metastable phase will be undersaturated with respect to the dissolving chemical component that is measured. At this point the entire free energy of the hydrothermal reaction of the solid with solution will be available to drive the dissolution process. The initial rate of dissolution ("leaching"), i.e., the change in solution composition with time, will be extremely high as represented by the tangential slope drawn at Point A in Figure 2. As the concentration of the dissolved component increases, at time t_B , the available free energy to drive the dissolution decreases, with a concomitant decrease in "leach rate" (i.e., a more gentle slope of the line tangential to Point B in Figure 2). Eventually at time t_C , assuming no precipitation of new, more stable solid phases, the solution reaches a metastable equilibrium concentration (solubility limit^(a), Point C in Figure 2) of the dissolved component, and the "leach rate" is zero. It is important to stress that while the "leach rate" is zero, combined dissolution and precipitation of the metastable phase continues at equilibrium.

Parabolic dissolution rates, as portrayed in Figure 2, have been characteristically interpreted in "dissolution" studies as indicating that diffusion through a leached surface layer is the rate-controlling step. It has recently been demonstrated, however, that observed parabolic time dependences for dissolution of minerals can be artifacts of precipitation of secondary phases (Holdren and Adars, 1982), time-dependent, surface detachment processes (Dibble and Tiller, 1981b) or sample preparation methods (Grandstaff, 1980; Schott, et al., 1981). Although there is clear evidence of a leach layer on hydrothermally reacted glass waste forms (e.g., McVay, et al., 1981) the possibility

(a) Solution concentrations above this solubility limit can occur but are exceptional, transitory events. They will be dismissed from this elementary discussion.

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FIGURE 2. Schematic Illustration of Solution Concentration as a Function of Time for a Hypothetical Waste/Barrier/Rock/Water System.

remains that observed parabolic dissolution rates for glass waste forms may be the results of several parabolic rate processes. Clearly, the use of experimental "leach rates," which strongly vary as a function of time, can lead to overly pessimistic and thermodynamically unjustified interpretations of the dissolution behavior and stability limits of solids in the presence of slow-flowing or static solutions. The measured solubility of a phase in hydrothermal solution will better represent the true stability of that phase as well as the maximum concentration of dissolved components.

Because the equilibrium represented at Point C is stated to be metastable, there is a probability of precipitation of new, successively more stable phases. As a new, more stable phase nucleates and begins to grow, the dissolution rate of the less stable phase and the concurrent growth rate of the more stable coexisting phase are opposing processes seeking to establish their own

solubility control of solution composition (Holloway, et al., 1981; Apted, 1981; Berner, 1978; Mottl and Holland, 1978; Lasaga, 1981).

For example, if the irreversible dissolution of an unstable phase such as glass is rapid relative to the growth of a more stable alteration phase, the solution composition will reflect mainly the solubility of the glass (for equal areas of glass and alteration phase). If the relative reaction rates were reversed so the alteration phase grows much faster than the primary phase dissolves, then the bulk solution composition will be determined primarily by the solubility of the alteration phase (Berner, 1980; Dibble and Tiller, 1981a). Intermediate, steady-state reactions (note, these are not equilibrium reactions) exist between these extremes (Figure 2, Point D). These reactions represent a balancing of the rates at which chemical components are being dissolved from unstable primary phases and the rates at which the same components are removed from solution into more stable, secondary phases. Steady-state conditions will eventually change with time, as more stable phases nucleate and grow or unstable phases become totally consumed. This, in turn, will cause the solution to attain new steady-state compositions (see Figure 2, Point E). The concentration of dissolved components represented by these evolving steady-state reactions must decrease with reaction progress (i.e., longer periods of time) because each new phase must be more stable, hence less soluble, than the previous phases. Eventually a true equilibrium assemblage of solid phases will form, representing the limiting case previously discussed. It can be expected, therefore, that if hydrothermal tests are conducted for durations sufficient to attain a steady-state reaction, this data will provide conservative radionuclide release rates relative to equilibrium solubility expected to control the actual long-term release rates.

Kinetic Effects

The length of time needed to attain steady-state (or solubility) conditions is a key factor in evaluating the appropriateness of using steady-state or leach rate data in performance assessment of waste forms. Under the nearly static hydrologic flow regime anticipated for a NWRB, it is almost certainly true that steady-state solution data will provide a better estimate of the long-term release rate of radionuclides. However, for static, hydrothermal

tests performed at expected repository conditions, the time necessary to reach steady-state conditions could be greater than that feasible for laboratory testing.

This problem of slow reaction kinetics can be addressed through the recognition that dissolution and growth rates are functions of several variables (Dibble and Tiller, 1981b), including temperature, reaction activation energy, reactive surface area (or reactive surficial mass), solution concentrations, and the available free energy of the system, which is the difference in free energy between the unstable reacting phase(s) and the stable product phase(s). This kinetic model, based on the energetics and mechanisms controlling dissolution and growth processes, serves as the justification for a variety of experimental techniques that can be adopted to accelerate the test. By speeding up the rates of dissolution and growth, the results of short-duration laboratory tests can be made to approach a state of reaction similar to that achieved in nature over much longer time periods.

The Interface Working Group on Accelerated Testing (USDOE, 1981), for example, has suggested that increasing the temperature of laboratory tests can dramatically increase the reaction rates of hydrothermal interaction tests on waste package components. This same technique is in common use in chemical engineering technology (e.g., Boudart, 1968) and in geochemical/petrological research (e.g., Mottl and Holland, 1978). The assumption that the same dissolution/growth mechanisms are operative at both high and low hydrothermal temperature is, however, often not justified. This is particularly true for hydrothermal studies of glass reactions, which apparently are dominated initially at low temperature (25°C) by ion-exchange (surface leaching) (White and Classen, 1980) and controlled at high temperature (200°C) by matrix dissolution (Karkhanis, et al., 1980).

Standard experimental studies of alteration products and resultant water chemistry of basalt/water reactions utilize powdered samples of basalt (e.g., Seyfried and Bischoff, 1979 and 1981; Mottl and Holland, 1978). The accepted rationale for this procedure is that by effectively increasing the reactive surface area (or surficial mass) of the basalt relative to the fixed volume of the water, the time required for reaction and formation of new solid phases is

greatly expedited. For powdered samples, the high surface area to mass ratio of the sample ensures that the entire mass added will be the effective reactive surficial mass. Uncertainty in estimating reactive surficial mass of monoliths, and uncontrollable changes in this parameter because of cracking, create problems of interpreting or extracting meaningful kinetic data from dissolution or solubility tests.

Finally, it has been shown recently that non-thermodynamic parameters such as porosity and permeability (i.e., flow rate) may affect the alteration mineral assemblage produced in hydrothermal systems (Dibble and Tiller, 1981; Potter and Dibble, 1981). High flow rates of solution through a rock system result in thorough mixing of interface and bulk solutions, permitting a relatively greater portion of the available free energy of the system to be used in surface detachment and attachment processes. This increases the rates of dissolution and growth, resulting in more rapid formations of most of the stable phases (Dibble and Tiller, 1981a). The great advantage of this technique is that use of variable flow rate to accelerate kinetic reaction rates will not involve any change in the operative reaction mechanism.

Hydrothermal Test Equipment Requirements

Hydrothermal experiments have been conducted from the viewpoint of a host of different scientific disciplines (e.g., chemical engineering, metallurgy, chemistry, and petrology). There is a commonality in approach and apparatus for hydrothermal experimentation. Major considerations are listed below.

- The material under study (e.g., borosilicate glass plus groundwater) must be isolated from any other reactive components. This generally means material must be encapsulated in noble- or inert-metal containers.
- There must be a method for controlling and monitoring environmental parameters, such as temperature and pressure, at desired experimental conditions.
- The ability to sample periodically solutions directly from an experiment at the prescribed experimental conditions is desirable. This

capability enables the experimenter to document and interpret reaction kinetics of the hydrothermal system under study.

Direct sampling is difficult because the hydrothermal apparatus usually must be cooled and depressurized before samples can be taken. "Cold-seal" pressure vessels are an example of this type of apparatus (Boettcher and Kerrick, 1971). Cooling and depressurization of an experiment, or quenching, invariably leads to a certain degree of retrograde reaction and chemical readjustment between solution and coexisting solids. This reaction is highly undesirable, particularly for solution analysis, because the sampled solution at room conditions will not represent the solution composition at the desired experimental conditions. Therefore, experiments using cold-seal apparatuses (e.g., Barnes and Scheetz, 1979) have limited utility in the characterization of solutions from waste/barrier/rock interaction tests.

The Waste Package Department of the BWIP has adopted the use of sampling autoclaves for barrier materials testing (Holloway, et al., 1981; Patera, 1981; Apted, 1981). These types of hydrothermal apparatuses use gold (Dickson-type), titanium, or Teflon (E. I. du Pont de Nemours Co.) inner reaction vessels. The entire cylindrical assembly of reaction vessel and outer pressurizing vessel (Figure 3) can be agitated continuously either by a rolling motion parallel to the cylinder axis or by a rocking motion perpendicular to this axis. This agitation promotes more rapid reaction between the solids and solution as they mix. Dickson-type autoclaves have a special sampling valve (Dickson, et al., 1963; Seyfried, et al., 1979; also see Figure 3) that enables the experimenter to take direct solution samples at the pressure and temperature of the experiment, while also permitting the examination of the solid alteration products at the conclusion of the experiments. These sampling autoclaves are ideal for obtaining data on barrier material stability and associated solution composition under expected repository conditions. Procedures for conducting hydrothermal tests in such apparatuses are available in existing literature (Dickson, et al., 1963; Mottl and Holland, 1978; Seyfried and Bischoff, 1981) and have been documented by the Waste Package Department (Holloway, et al., 1981).

FIGURE 3. Cross-Sectional View of Dickson-Type Sampling Autoclave

Flow rates of groundwater have been identified as a possibly important environmental parameter in the testing of barrier materials (NWTs, 1981; Coles, 1981). In particular, it has been demonstrated experimentally that by increasing flow rate, it may be possible to accelerate the kinetic rate of reactions in hydrothermal systems (Potter and Dibble, 1981; Potter, 1981). The Dickson-type autoclave, despite the acknowledged effect of agitation on reaction rates, still more closely represents the static flow conditions anticipated for a nuclear waste repository in basalt (NWRB). A flow-through pressure vessel, using a Teflon-lined or gold reaction tube surrounded by a hydrostatic pressurizing vessel, has been designed from an existing Dickson-type apparatus (Potter, 1981). An operational prototype will be constructed and operational by the end

of FY 1982. It is important to stress that this apparatus causes solution to flow through a packed column of solids in comparison to other designs (Coles, 1981) that cause solution to flow by 'marbles' of solids. With this flow-through apparatus Waste Package Department personnel will confirm the range in flow rates over which steady-state solution data from static tests in Dickson-type autoclaves are applicable to the long-term solution behavior anticipated for waste package/basalt interactions.

Techniques for in-situ monitoring of pH and Eh under high-temperature and high-pressure hydrothermal test conditions have been proposed and tested (MacDonald, 1978; Niedrach, 1980; Danielson, 1980). Currently, the BWIP is developing these solid-state probes and modifying their design to be compatible with Dickson-type autoclaves. Direct monitoring of these environmental parameters during testing improves the experimental design. The monitoring eliminates the difficulty of preserving the actual pH and Eh values of groundwater solutions once they are removed from reactive barrier materials and brought into the ambient conditions of the laboratory.

A supplemental technique for monitoring groundwater redox potential (Eh) is to measure coexisting redox couples dissolved in the solution, such as bisulfide/sulfate or Fe(II)/Fe(III). Recent studies (Cherry, et al., 1979) indicate that monitoring groundwater Eh by speciation analysis of naturally occurring arsenic is possible. Work currently underway in the Basalt Materials Research Laboratory suggests that this technique can be extended to provide information about the prevailing Eh during hydrothermal tests. Trace amounts of arsenic (<50 µg/L) can be predoped into the solution phase. Arsenic (III) and Arsenic (V) undergo rapid redox reactions under hydrothermal conditions, so that a measurement of their relative abundance in solution indicates the prevailing redox potential, assuming that all other redox couples react to the same Eh value of the system. Other redox couples involving selenium, antimony, or tin are also being considered as possible redox indicators.

Analytical Equipment Requirements

Hydrothermal barrier materials are chemically analyzed to assess in detail the interactions of groundwater with the components of a NWRB including the host rock, the engineered barriers, and the waste form. The purpose of the

repository system is to prevent unacceptable release of radionuclides to the biosphere (EPA, 1982). Analyses of hydrothermally reacted groundwater and associated solid alteration phases, therefore, are key to confirming the ability of the repository system, particularly the engineered barriers of the waste package, to meet or exceed performance criteria under expected repository conditions.

There are three types of required analyses of hydrothermal test products:

- Characterization of solids
- Solution analysis of stable elements
- Radioassays of solutions for radioactive elements

Each part requires distinct analytical instruments and techniques. Taken together, data from all three analytical parts are needed to evaluate the relevant hydrothermal interactions and the implications of these reactions for long-term behavior and performance of a NWRB.

The primary goal in analyzing solids is to identify the phases that are significantly altered by hydrothermal reaction and the secondary phases that are formed. Of particular interest are those radionuclide-bearing phases that may impose solubility limits on the concentration of radionuclides in solution. The identification of these phases is required in the geologic modeling of the long-term release of radionuclides from a NWRB.

Hydrothermal alteration of all primary barrier materials is qualitatively characterized by a progressive sequence of optical petrography, X-ray diffraction (XRD), and use of a scanning electron microscope (SEM) with an energy-dispersive spectrometer (EDS). The information gathered from these analyses are complementary, and cover a wide range of macroscopic and microscopic properties, as well as chemical and mineralogic characterization. However, the fine-grain size ($<1\ \mu\text{m}$) of many alteration phases, the poor resolution and large excitation area of conventional microprobes ($10\ \mu\text{m}$) and the interferences in the response of EDS detectors from gamma radiation preclude the use of conventional microprobes or SEM/EDS systems for characterization of solids from a hydrothermal testing program.

Only the SEM with a wavelength spectrometer and an analytical scanning transmission electron microscope (ANSTEM) with energy loss spectrometer, shielded EDS (for hot-cell work), and conventional electron diffraction modes can analyze fine-grained alteration phases adequately. These instruments uniquely combine the necessary chemical [using wavelength dispersive spectrometer (WDS) or shielded EDS^(a)] and mineralogic (using electron diffraction) techniques with the required spatial resolution (0.1 μm for SEM/WDS and 20 μm for ANSTEM). There are other analytical techniques for surface analysis, such as Auger spectroscopy and extended X-ray absorption fine-structure (EXAFS) spectroscopy, but these techniques cannot provide the necessary 3-dimensional spatial resolution nor the necessary mineralogical data that can be obtained from SEM/WDS and ANSTEM analyses. Without SEM/WDS and ANSTEM systems, hydrothermal alteration phases cannot be analyzed adequately.

A combination of sensitive, rapid, and species-specific analytical techniques are required to analyze hydrothermally reacted groundwaters. The limited volume of solution available for the large number of required elemental analyses dictates analytical methods appropriate to small sample size.

An inductively coupled plasma (ICP) spectrometer, capable of analyzing the maximum number of elements, is required. The ICP spectrometer is used to obtain the maximum number of elemental analyses, with minimum sample (consistent with the small sample size) and manpower requirements. The ICP is also the only available instrument for the rapid, sensitive determination of the rare earths in the radioactive waste forms.

An atomic absorption spectrophotometer (AAS) with a heated graphite atomizer is also required to complement the ICP spectrometer. The AAS analyzes those elements expected to occur at very low concentrations that cannot be analyzed by the ICP spectrometer. Atomic absorption spectroscopy is a very sensitive technique for a number of the elements that may be important (e.g., aluminum, cesium, molybdenum, selenium).

(a) EDS shielding from gamma radiation can be successful in the STEM only because of the extremely small sample size. It is not an effective measure in a SEM. WDS systems can be used in a SEM because they do not suffer from the interfering effects of gamma radiation.

The anion composition (Cl^- , F^- , HS^- , SO_4^{2-}) of the solution samples from hydrothermal testing is analyzed by an ion chromatograph and/or selective ion electrode. Dissolved carbon is determined by a total carbon analyzer. Titrations of small volumes of samples are then required to determine the proportions of acid-base related species (i.e., HCO_3^- and CO_3^{2-}). The pH is measured by a conventional pH meter equipped with a glass electrode. Solid-state pH probes will also monitor the pH during testing (see previous discussion).

The most important information about solutions sampled from hot-cell hydrothermal tests is the concentration of radionuclides that appear in solution. Steady-state concentration values for these radioactive elements are necessary for the calculation of meaningful, long-term release rates. The rate of change in radionuclide concentrations, whether approached from oversaturated or undersaturated conditions, can also be used to define the types and rates of dissolution and growth processes that will govern radionuclide solubility. Alpha, beta, and gamma spectrometry data are determined in detail on solution samples to obtain the requisite concentration data. In many cases, careful chemical separation, by standard procedures, is required before meaningful radioassays can be made. Because such separations necessitate significant sample volumes (perhaps as much as 15 ml for an entire stable and radioactive element analysis), certain radioassays can be made on an alternating basis. Solution radioassays focus on those particular isotopes that have been identified as key, hazardous radionuclides (Wood, 1980; Barney and Wood, 1980).

Conclusion

The Waste Package Department (WPD) of the Basalt Waste Isolation Project (BWIP) has endorsed a sequential hydrothermal testing program for waste package materials, including waste forms, based on progressive penetration of barriers by intruding groundwaters. The explicit focus of the Waste Package Department program is based on the fate of radionuclides as opposed to the sole study of the chemical durability of the waste form. Isothermal, steady-state (time-invariant) compositional data on sampled solutions from waste form hydrothermal tests have been found to provide a more realistic and scientifically

justified measure of waste stability and radionuclide release rates than do leach rate data. This is especially true for the slow flow rates anticipated for a NWRB.

The current use of nonflow-through (static) tests in the rocker-type autoclaves for the bulk of the experimental program is justified by lower cost, simplicity of operation, greater experimental control, and the fact that the relatively slow rates of solution flow in a NWRB are probably well approximated by the confined flow in a rocker-type autoclave. Interpretation of hydrothermal test results require both microcharacterization of primary and secondary (alteration) phases and chemical analysis of all solution species. Flow-through hydrothermal autoclaves and high temperature-high pressure probes for in situ measurement of redox potential and pH are being developed and constructed by the BWIP. The freedom to vary flow rate and temperature (up to 300°C) with minimal loss of scientific relevance between experiments will permit a thorough examination of alteration under hydrothermal conditions, minimizing the need for long-term experiments. By promoting rapid attainment of more stable phases using high flow rates, it will be possible to confirm the range in flow rates over which the steady-state results from static tests are applicable to the long-term performance of a waste package located in a NWRB.

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6.3 A SEMI-UNIFIED APPROACH TO LEACH TESTING -- K. B. Harvey, Whiteshell Nuclear Research Establishment

INTRODUCTION

No decisions have yet been made in the Canadian nuclear power program regarding either the principle or the methods of reprocessing irradiated fuel or of the disposal of any reprocessing wastes. Within the current phase of concept evaluation, it is assumed that the long-term disposal of high-level reprocessing wastes would be by burying them deep in the hard rock of the Canadian Shield.

Under these disposal conditions, the dose consequence to man is being evaluated by means of SYVAC (Systems Variability Analysis Code), a computer code that takes account of the magnitude and mechanisms of radionuclide release into the disposal vault, transportation to the biosphere, and assimilation by man through the various pathways and food chains within the biosphere⁽¹⁾. The input data for each SYVAC run is obtained by a Monte Carlo sampling of the required parameters from within defined limits. It is desirable, therefore, that the input parameters are as free as possible from preconditions or interlinking.

In the case of leach testing, it is desirable to develop a format within which leach test results can be presented independently of the particular testing method or testing geometry. Other than providing "pure" data for SYVAC, developing such a format would have the subsidiary advantages of first allowing the adoption of a convenient and economical method of leach testing and, second, allowing the development of a leaching model applicable to that method, rather than having to solve the general case.

BACKGROUND

In the first model developed for SYVAC, groundwater is assumed to have suffused the intact buffer, a low-permeability clay jacket surrounding the waste form, and the waste form is dissolving. The release of a radionuclide to the disposal vault is assumed to be driven by the concentration gradient (of that radionuclide) across the buffer as shown in Figure 1.

FIGURE 1. Release (F) of a Radionuclide is Driven by Concentration Gradient Across Buffer

As leaching proceeds, the concentration of radionuclides inside the buffer will rise until the outflux of loss through the buffer is balanced by the leach rate of the waste form at steady state. Thus, the relationship between the leach rate and the solution concentration is of interest:

$$\text{outflux} = \text{leach rate} = f(c)$$

For conceptual purposes only, consider a simple solid that is dissolving in a limited quantity of water towards its saturation solubility, c_s . The integrated first-order dissolution equation is:

$$c = c_s (1 - e^{-kt})$$

where

c = solution concentration at time t

c_s = saturation solubility

k = rate constant

$$\frac{dc}{dt} = k \cdot c_s \cdot e^{-kt}$$

or

$$\frac{dc}{dt} = k (c_s - c)$$

Since dc/dt in a closed system is proportional to the leach rate, a rate constant k' can be defined such that:

$$\text{leach rate} = k'(c_s - c)$$

where

$$k' = B \cdot \frac{Vk}{SA}$$

B = a numerical factor whose value depends on the units used

V = volume of leachant

SA = surface area of specimen

This situation is shown diagrammatically in Figures 2(a) and 2(b).

Consider further Figure 2(c), where a dissolving solid is moving down the line AC_s until, at B , a more stable phase begins to precipitate out from solution. The concentration of the solution would thereafter remain constant, but the solid would continue to lose weight at a constant leach rate, BF . If the solid considered were a silicate, which commonly supersaturates in solution, the actual path followed might be $ABDEF^{(a)}$.

EXPERIMENTAL

Because only a small volume of water is anticipated within the buffer and in contact with the waste form, the pH of that water will rapidly be established at a value determined by the waste form. Subsidiary experiments showed the equilibrium pH in contact with the sodium borosilicate glasses used here, Glass 200 and Glass 204, to be 10.45 and 10.32, respectively, at 100°C.

-
- (a) It is not intended to imply that a glassy waste form dissolves according to first-order dissolution kinetics. Indeed, a more rigorous derivation⁽²⁾, based on classical diffusion theory, suggests the relation:

$$\frac{\text{Leach Rate}}{1 + A (\text{Leach Rate})} = B(c_0 - c)$$

where

A, B = constants

c_0 = the concentration of ion in the waste form

FIGURE 2(a)

FIGURE 2(b)

Initial Leaching Models

FIGURE 2(c). Leaching with Supersaturation

To avoid complications from a changing pH, leaching solutions used in both the static and replenished experiments to be described were deionized water/NaOH solutions set at pH 10.5

The leaching temperature throughout was 100°C and all tests were quadruplicate.

Weight losses of the specimens were monitored and converted to leachant solution concentrations for each SA/V ratio, assuming that no hydration or precipitation occurred.

Figures 3(a), 3(b), and 3(c) show the leach rate/specimen weight loss/solution concentration curves for VYCOR (96% silica) leached in static tests at SA/V of 1:5, 1:10, and 1:20, respectively. In Figure 3(a) the dotted line, the result of curve fitting, shows a minimum in the curve located at a solution concentration of ~0.116 g/L. When Figures 3(a), 3(b), and 3(c) are superimposed as in Figure 3(d), it can be seen that all of the results lie within a well-defined band, as do the leach rate and solution concentration values obtained under steady-state conditions in replenished tests at three replenishment schedules. At each replenishment schedule, the stated amount of leachant was removed each day and replaced by fresh deionized water/NaOH solution.

Figure 4(a) shows the leach rate/weight loss curve for Glass 204, a high-silica sodium borosilicate (10 wt% Na₂O, 11.5 wt% B₂O₃, 78.5 wt% SiO₂) at the SA/V ratio of 1:5. Note the well-defined minimum in the curve. In Figure 4(b), curves for SA/V ratios of 1:5, 1:10 and 1:20 from static tests are superimposed, together with rectangles that indicate the range at leach rate/solution concentration values obtained under steady-state conditions in replenished tests at four replenishment schedules.

Figure 5 shows the results of a similar experiment using Glass 200 (16.5 wt.%, Na₂O, 19 wt.% B₂O₃, 64.5 wt.% SiO₂), a sodium borosilicate glass with a silica content typical of those currently being considered for waste disposal purposes.

DISCUSSION AND CONCLUSIONS

The experimental work described here suggests that the leach rates of major matrix ions of sodium borosilicates glasses under a variety of static and replenished leaching conditions are the same when expressed as a function of concentration dissolved into the leachant, and are independent of the geometry of the test. This finding is intuitively reasonable, and it may then be capable of extension to other matrices and also to minority ions diffusing from the matrix. However, since this treatment does not take into account either of changing pH or of changing temperature, it can only be termed a semi-unified approach.

FIGURE 3(a). VYCOR at 1:5 SA/V ratio

FIGURE 3(b). VYCOR at 1:10 SA/V ratio (g/L)

FIGURE 3(c). VYCOR Leaching of 1:20 at SA/V ratio

FIGURE 3(d). Static Leaching of VYCOR at 1:5, 1:10 and 1:20 SA/V Ratios, and at Leachant Replenishment Rates of 3%, 1% and 0.33%/day

FIGURE 4(a). Leach Rate/Solution Concentration Curve for Glass 204 Leached at SA/V ratio 1:10

FIGURE 4(b). Leach Rate/Solution Concentration Curves for Glass 204, Leached at SA/V Ratios 1:5, 1:10 and 1:20, and with Leachant Replenishment Rates of 0.2, 0.33, 1.0 and 3.0%/day

FIGURE 5. Leached Rate/Solution Concentration Curves for Glass 200, Leached at SA/V Ratios 1:5, 1:10 and 1:20, and with Leachant Replenishment Rates of 1%, 2%, 3%, and 5%/Day.

The results suggest that leaching numbers obtained from static tests can be applied to flowing conditions, particularly to the very low-flow conditions ($\sim 10^{-5}\%$ volume turnover yearly) that might be anticipated under hard-rock burial conditions, which are difficult to simulate experimentally.

It follows that a static test is more economical since it gives a series of leach rate/solution concentration readings, rather than the single result obtainable from a flow test. With the use of active isotopes and counting techniques, this opens the way to completely sealed and maintenance-free leaching systems that could be monitored over a period of years. Leaching models that are appropriate to static leaching conditions are being developed.

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6.4 REPOSITORY SYSTEMS INTERACTIONS -- G. G. Wicks, B. M. Robnett, and W. D. Rankin, Savannah River Laboratory^(a)

The leachability of borosilicate glass, a potential nuclear waste form, is being studied at the Savannah River Laboratory.¹ An important part of the program is the assessment of waste glass durability as a function of separate and synergistic effects of elements of the multibarrier isolation system. To accomplish this task, static and dynamic repository system tests are being conducted. The results of a three-phase static-repository program were presented and a new dynamic-testing station introduced. In the static-repository tests, the effects of five potential repository rock types, including salt, basalt, shale, granite, and tuff, on the leachability of simulated waste glasses were evaluated as a function of the ratio of sample surface area to volume of leachant (SA/V). Next, the effects of simulated, rock-equilibrated water, and one actual groundwater composition on glass leaching were studied, and the results were compared to leaching by deionized water. Finally, the effects on glass leaching of the complete engineered system consisting of rock, canister materials, and backfill were assessed. Following are some of the conclusions resulting from this study:

- Leachability decreases as the SA/V ratio increases. This is a beneficial result for long-term storage because of the small quantities of water that are anticipated in the repository. The amount of species in solution also generally decreases, but only slightly, for leaching of waste glass in the presence of rock (salt, basalt, shale, granite, and tuff).
- Simulated groundwaters are generally less aggressive leachants than deionized water. Hence, glass performance involving groundwaters in a repository should be better than indicated by data from laboratory tests using deionized water as leachant.
- In system tests involving waste glass, canister material, overpack metal, backfill, and five different rock types, the backfill

(a) The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

constituent generally most strongly influenced the release rate of species of interest. The backfill can be beneficial, marginal, or even detrimental depending on the choice of material.

- Key elements such as Fe, Mn, and Mg found in the surface layers formed during leaching of waste glasses show very low leach rates for all systems and SA/V ratios studied. Since these elements are also retained in the leached surface layers in these simulated, static-repository tests, product leachability in repositories would also be expected to improve with time in accordance with the SRL Leachability Model.

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6.5 THE DIFFUSION OF LEACHED CONSTITUENTS IN BACKFILL BARRIERS -- E. J. Nowak, Sandia Laboratories^(a)

It is essential to measure mass transport rates in backfill barrier materials for actinide species that have been leached from a waste form under simulated repository conditions. The simulation should include chemical interactions among leachates and waste package materials. These mass transport measurements serve as scoping tests to detect unusually mobile actinide species that may be produced by the leaching process and other chemical interactions.

An experimental plan for these mass transport measurements has been outlined. Conditions are for a defense high level waste repository in salt. Actinides that have been leached from simulated glass waste forms are to be introduced one at a time as instantaneous sources of diffusing radionuclides in diffusion experiments. Leaching from glass samples is to be done both in the presence and absence of stainless steel and titanium coupons in the leachant. The leaching procedure is similar in principle to the MCC-1 procedure. One-dimensional diffusion of the leached actinides is to be measured in cylindrical columns of highly compacted bentonite.

Contact for information exchange will be maintained with Swedish investigators (Eriksen et al., 1981; Torstenfelt et al., 1981; Eriksen and Jacobsson, 1982) who are doing related diffusion measurements in similar apparatus. Contact will also be maintained with Italian investigators (Avogadro et al., 1981) who are studying the mobilities of actinide species in leachates.

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6.6 LABORATORY ANALOG EXPERIMENT -- D. Bowers, S. Fried, T. Gerding, D. Lam, G. Vandergift, M. G. Seitz (presenter), Argonne National Laboratory

(The following synopsis of this presentation was prepared by the workshop chairman from visual aids provided by M. G. Seitz.)

The status of the Laboratory Analog Program being conducted for the Nuclear Regulatory Commission at ANL was reviewed. This is an integrated experiment designed to determine how well the behavior of a breached repository, in this case a basalt repository, is understood. A diagram of the apparatus is shown in Figure 1. The five tests, each nine months long, that are planned are shown in Table 1.

FIGURE 1. Configuration for the Laboratory Analog Experiments

TABLE 1. Laboratory-Analog Test Matrix

Test	Waste Form Backfill and Rock	Apparatus
1	Unaltered	Hastelloy
2	Thermo-, Hydro- (1000 Yr)	Hastelloy
3	Unaltered	Hastelloy, Gamma-Field
4	Unaltered	Monel
5	Thermo-, Hydro- (2000 Yr)	Hastelloy

The simulated ground water is sparged and stored under N_2 that is deoxygenated with a chromous chloride solution. Initial tests showed that the bentonite would swell and plug the system, therefore the method of introducing bentonite shown in Figure 1 (inset) was adopted. The bentonite is originally placed in a smaller tube open at the top. As the bentonite swells it overflows the tube and settles out as a layer through which water can pass. The waste form used is 76-68 borosilicate glass of the type used in the MCC-1 round robin to which was added 3.4 wt% U and tracer levels of radioactive isotopes of eight other elements (Cs, Sr, Ba, Ce, Eu, Am, Pu and Np). The fissure in the basalt core is held open with pieces of 10-mil gold foil. If this is not done it was found that basalt alteration products rapidly plugged the fissure.

Three of the five tests are underway and some very preliminary results were presented at the workshop. However, since the main purpose of this session of the workshop was to review the experimental approaches being taken to interactions testing, these preliminary results are not given here.

6.7 SENTINEL GAP BASALT REACTED IN A TEMPERATURE GRADIENT --

R. W. Charles and G. K. Bayhurst, Los Alamos National
Laboratory

ABSTRACT

Six Basalt prisms were reacted in a controlled temperature gradient hydrothermal circulation system for two months. The prisms are centered at 72, 119, 161, 209, 270, and 310°C. Total pressure is 1/3 kbar. All prisms show large weight loss: 5.5% to 14.9%. The matrix micropegmatite and natural nontronitic alteration readily reacts to clays at all temperatures. The first four prisms are coated with a Ca-smectite while the last two prisms are covered with discrete patches of K rich phengite and alkali feldspar. The clays may act as adsorbers of various ions.

I. INTRODUCTION

Basalt is being considered as a host rock for a radioactive waste repository (Smith, 1980; Taylor et al., 1980a, Taylor et al., 1980b, and Coons et al., 1980). One of the basalts under consideration is the Grande Ronde Basalt of the Yakima Subgroup of the Columbia River Basin group. Chemical reactions involving such basalt with groundwater are of interest to those working with any repository involving basalt. The present experiments reacted a basalt sample from one of the flows of the Sentinel Bluff flows in a controlled temperature gradient circulation system under constant pressure with initially distilled water for a period of two months in order to define some of the reaction relations between the fluid and basalt as well as the mass transport.

II. EXPERIMENTAL

Figure 1 exhibits the controlled temperature gradient system. Flow is clockwise. Details of the system's operation are given in Charles and Bayhurst (1980) and Charles et al. (1979). Six polished prisms of basalt (2.5 cm x 0.6 cm x 0.6 cm) were placed in the temperature gradient vessel centered at temperatures of 72, 119, 169, 209, 270, and 310°C with fluid flow from cool to hot. Total pressure was 1/3 kbar. All prisms were removed after 60 d reaction time.

Solution was sampled at the two points labeled with constant pressure and temperature samplers at 1, 2, 6, 14, and 30 d. The samplers are explained in the forementioned articles. A final sample was taken at 60 d from the cooled fluid. This showed fractionation and is not included herein. The fluid reached a steady state after 6 to 14 days. Solutions were analysed by plasma emission spectrometry. Rock prisms were examined by a scanning electron microscope (SEM) with a nondispersive detector, electron microprobe, and optical microscope. Thin sections were prepared for each rock prism. Interiors as well as surfaces could be examined.

Fig. 1. Controlled temperature gradient circulation system.

The aphanitic basalt shows a subophitic texture with intersertial nontronite and micrographic alkali feldspar plus quartz. The principle phases are augite, pigeonite, sodic labradorite, titaniferous magnetite, nontronite and matrix. The matrix is a micropegmatite with a rhyolite norm. Normalized to Or-Ab-Q, the groundmass, while showing wide scatter, plots near granite minimum melting (see Figure 2). The basalt is quartz-hypersthene normative. See Table I for details of phase composition, whole rock analyses, and norm.

III. RESULTS

A. Weight Loss

The basalt prisms showed rather high weight losses (Figure 3 and Table II). Even the prism at 72°C showed a loss of 5.5% in two months of reaction time increasing to 14.9% at 310°C. Included for comparison is an experiment under identical run conditions except the rock was a granodiorite, 9519 from the Fenton Hill HDR reservoir. At no time does the basalt show actual weight gains as does the granodiorite (at 72 and 119°C).

Fig. 2. Quartz-nephelene - kalsilite projection with "keyhole" shaped plot of basalt matrix compositions near granite minimum melting.

Fig. 3. Weight change.

TABLE II
WEIGHT LOSS

<u>Prism</u>	<u>Original Weight (g)</u>	<u>Final Weight (g)</u>	<u>Change (g)</u>	<u>Change(%)</u>
1	3.0377	2.8708	-0.1669	- 5.5
2	3.0145	2.8373	-0.1722	- 5.9
3	3.0595	2.8445	-0.2150	- 7.0
4	3.0525	2.7980	-0.2545	- 8.3
5	3.0640	2.6438	-0.4202	-13.7
6	3.0172	2.5675	-0.4497	-14.9

B. Solution Analyses

Solutions in contact with basalt seemed to reach a steady state at about 6 d (hot sample) and continue at this level for the remainder of the experiment (Table III, Figure 4). Hot sample was extracted at 310°C and the cold sample at room temperature. Initial maximums were observed (cold solution) for SiO_2 , K, Na, and possibly Fe and Ca.

C. Morphological Changes

Plate 1 is a scanning electron photomosaic of a part of an unreacted rock prism. Darkest material is plagioclase and micropegmatite. Gray material is pyroxene. Opaques are lightest. The only surface relief is some plucking due to polishing.

Overgrowth morphology occurs in two types.

- 1) All pervasive clay at 72, 119, 161, and 209°C.
- 2) Discrete clay overgrowths plus feldspar at 270 and 310°C.

Plate 2 is a portion of the rock prism reacted at 72°C. Much reaction has occurred. "Fracture" openings and voids represent dissolution of micropegmatite. Secondary precipitation consisting of botriodal platey aggregates are shown in Plate 3. The platey aggregates cover the rock surface more completely at 119°C (Plate 4). A higher magnification is shown in Plate 5. Cavities are in the matrix. Plate 6 shows the same overgrowth, in this case at 161°C. The same overgrowth persists to 209°C (Plate 7).

Overgrowth morphology changes strikingly at 270°C (Plate 8). Two phases now cover the basalt surfaces. Clay of a different composition surrounds laths of recrystallized feldspar. Plate 9 presents a portion of the 310°C prism showing similar morphology with possibly slightly better crystallization of the feldspars. See in particular the euhedral crystals at 6 o'clock and 9 o'clock.

D. Chemical Changes

Reactivity of the basalt varied from nonexistent to major. Table IV displays the reactivity of some of the primary phases. The analyses are from thin sections prepared from each of the six prisms. Plagioclase, augite, and pigeonite show little reaction.

Micropegmatite shows the most reactivity. Most important is the lack of free silica from norms calculated for the reacted micropegmatite (Figure 5a).

TABLE III
SOLUTION ANALYSES (ANALYSES IN PPM)

Duration (d)	SiO ₂		K		Na		Fe		Al		Ca		Total	
	h*	c**	h	c	h	c	h	c	h	c	h	c	h	c
1	-	294	-	9.6	-	8.1	-	0.20	-	7.6	--	0.20	-	320
2	335	222	13.0	8.9	9.7	6.4	0.20	0.20	11.6	7.6	0.20	0.10	370	245
6	373	250	12.4	9.5	9.2	6.8	0.30	0.10	10.8	7.5	0.10	0.10	406	314
14	372	325	13.4	10.4	11.9	10.6	0.07	0.07	10.9	8.4	0.09	0.09	408	355
30	359	314	12.3	9.9	12.7	11.4	0.08	0.09	10.3	7.8	0.20	0.20	395	343

* h = hot sample.

** c = cold sample.

Fig. 4. Solution analyses.

TABLE IV
SUMMARY OF PHASE COMPOSITIONS:
ANALYSES OF THIN SECTIONED PRISMS (ATOMIC FORMULAS)
Plagioclase (8 ox)

T (°C)	Na	Ca	K	Al	Si	Fe
72	0.49±.03	0.53±.04	0.03±.01	1.46±.03	2.49±.04	0.03±.01
119	0.44±.04	0.51±.06	0.03±.01	1.44±.07	2.51±0.7	0.03±.01
161	0.45±.03	0.54±.03	0.02±.01	1.48±.03	2.49±.03	0.03±.01
209	0.43±.01	0.56±.01	0.03±.01	1.50±.01	2.45±.01	0.03±.01
270	0.43±.01	0.56±.01	0.02±.01	1.47±.01	2.47±.02	0.04±.01
310	0.43±.03	0.57±.01	0.01±.01	1.50±.01	2.46±.01	0.04±.01

Augite (6 ox)

T (°C)	Na	Mg	Al	Si	Mn	Fe	Ca	Ti
72	0.02±.01	0.81±.02	0.07±.01	1.92±.01	0.01±.01	0.51±.02	0.67±.02	0.02±.01
119	--	0.84	0.08	1.90	0.01	0.48	0.70	0.02
161	0.02±.01	0.89±.03	0.07±.01	1.90±.01	0.01±.01	0.42±.03	0.70±.01	0.02±.01
209	--	0.79	0.07	1.92	0.01	0.60	0.60	0.02
270	0.02±.01	0.82±.03	0.08±.01	1.91±.01	0.01±.01	0.53±.02	0.65±.04	0.02±.01
310	0.02±.01	0.86±.02	0.07±.01	1.91±.01	--	0.48±.02	0.69±.01	0.03±.01

Pigeonite (6 ox)

T (°C)	Mg	Al	Si	Mn	Fe	Ca	Ti
72	0.94	0.03	1.93	--	0.87	0.21	--
119	0.80	0.03	1.94	0.02	1.00	0.23	0.02
161	0.80	0.07	1.89	0.02	0.97	0.27	0.01
209	0.93	0.03	1.95	0.02	0.84	0.23	--
270	0.90	0.03	1.93	0.02	0.87	0.25	0.02
310	1.07	0.03	1.93	0.02	0.76	0.20	--

TABLE IV (cont)
SUMMARY OF PHASE COMPOSITIONS:
ANALYSES OF THIN SECTIONED PRISMS (ATOMIC FORMULAS)

Matrix:Micropegmatite

Ab = albite, Or = Kspar, An = anorthite, Q = quartz

T(°C)	Ab	Or	An	Cl
Fresh	29	29	2	39
72	46	7	46	1
119	56	20	33	1
161	47	22	30	1
209	18	28	49	1
270	14	35	50	1
310	14	3	83	0

Nontronite (24, 0,OH)

T (°C)	Na	Ca	K	Mg	Fe ⁺²	Ti	Al	Si
72	0.03±.01	0.14±.05	0.02±.01	1.65±.14	4.87±.33	0.02±.01	3.19±.12	5.21±.15
119	0.13±.03	0.20±.03	0.12±.07	1.75±.15	4.93±.33	0.05±.03	3.09±.21	5.34±.21
161	0.23±.01	0.20±.01	0.26±.05	2.00±.18	4.22±.08	0.01±.01	2.62±.03	5.67±.11
209	0.11±.03	0.20±.05	0.05±.04	1.92±.06	4.53±.25	0.03±.01	3.24±.25	5.30±.30
270	0.22±.03	0.19±.06	0.62±.18	1.43±.06	4.71±.23	0.05±.03	2.63±.14	5.80±.02
310	0.22±.03	0.07±.04	0.12±.04	2.33±.17	4.97±.26	0.06±.02	2.92±.11	4.95±.20

Normative anorthite shows a more or less steady increase (Figure 5b) while normative albite steadily decreases (Figure 5c). Normative Kspar may actually peak at about 270°C, becoming more reactive at 310°C (Figure 5d). Cumulative norms are shown in Figure 5e.

Nontronite also displays a gross change in composition from the original. Generally, Si is leached. The resultant product has a more variable iron content than before and possibly higher Mg. The Si/Al ratio for original nontronite is compared with reacted material in Figure 6.

Surface analyses by electron microprobe and scanning electron microscope yielded particularly poor analyses (Table V) from the standpoint of variability

Fig. 5a. Matrix norms.

Fig. 5b. Matrix norms.

Fig. 5c. Matrix norms.

Fig. 5d. Matrix norms.

Fig. 5e. Matrix norms.

Fig. 6. Si/Al for original nontronite and reacted nontronite.

TABLE V
SURFACE ANALYSES

T	Phase
72°C, 119°C 161°C, 209°C	Clay approx. $\text{Ca}_{0.5}\text{Mg}_2\text{Fe}_{3.5}\text{AlSi}_5\text{Al}_3\text{O}_{20}(\text{OH})_4$ "Smectite"
270°C, 310°C	Clay approx. $\text{KMg}_3\text{Fe}_{3.5}\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$ "Phengite" Feldspar approx. $\text{Na}_{0.5}\text{K}_{0.5}\text{AlSi}_3\text{O}_8$

and poor totals. The rough surface and possibly variable composition contributed to this problem. A clay was identified on the 72, 119, 161, and 209°C prisms with the composition shown. Total Mg + Fe was near constant at about 5.5 and Al + Si at about 8, although Mg, Fe, Al, and Si varied about 0.5 atoms over the range of several dozen analyses. Composition and morphology indicate the material to be a smectite with magnetite inclusions. The Si/Al ratio is similar to the interior reacted nontronite mentioned above (Figure 7).

A different clay, potassium bearing with a different Si/Al ratio than the previous clay, appears on the 270 and 310°C prisms. Also appearing is a phase with prismatic habit with alkali feldspar composition. Na and K contents for this second phase are variable and Al/Si almost 1/3.

IV. DISCUSSION

A. General

All of the primary (original) rock minerals reacted to some extent. Augite, pigeonite, and plagioclase showed clear surface recrystallization to clay. Analyses on the interior of each prism showed these phases to be resistant to alteration. Original nontronite and matrix rapidly recrystallized both at the surface and in the interior of the rock. Nontronite reacts at all temperatures with solution to form smectite similar in composition to that shown in Table V.

Fig. 7. Si/Al for surface alterations.

Matrix, although rare at higher temperatures (270 and 310°C) becomes increasingly anorthitic and is almost completely devoid of free silica even at 72°C.

At temperatures of 72 to 209°C the entire surface is covered by a Ca, Mg - Al silicate with very variable Fe content. SEM examinations suggest the material is a smectite with some enclosed magnetite. At 270°C and 310°C, phengite (Krich) clay plus magnetite and sanidine covers principally original plagioclase and pyroxene.

The clays are reasonable phases for the physical conditions of the experiment. Adularia, analcime, and silica presumably would be the stable phases instead of sanidine. Exsolution under these conditions would be quite sluggish. The anorthite matrix will eventually recrystallize to a Ca-zeolite.

Amorphous silica scale and a small amount of sanidine indicates depletion of silica and to some extent K and Na from the original rock matrix.

A. Chemical Geothermometry

The Na-K-Ca, Na-K, and silica geothermometers were empirically developed from hydrothermal systems equilibrated with granitoid rock. Employing these techniques to basaltic systems is hazardous. In the present experiment because of the micropegmatite, we felt the Na-K-Ca geothermometer may have some application. As Table VI shows, this chemical geothermometer yields high temperatures.

The silica chemical geothermometer will yield temperatures too low. More experimentation must be done to develop a suitable chemical geothermometer for basaltic rock.

B. Phase Relations

This section will attempt to define some of the phase relations occurring on the prisms in more detail. The original minerals and secondary minerals are approximated in Table VII. Because of the small amount of pigeonite, pyroxene is simplified as augite.

TABLE VI
CHEMICAL GEOTHERMOMETER TEMPERATURES BASED UPON THE Na-K-Ca GEOTHERMOMETER

Duration (d)	Cold Solution (°C)	Hot Solution (°C)
1	345	--
2	369	364
6	368	375
14	349	367
30	326	340

TABLE VII
COMPOSITIONAL APPROXIMATION USED IN THE SCHREINEMAKER
DEVELOPMENT BASED ON MICROPROBE AND SEM ANALYSES

Phase	Composition
augite (A)	$\text{Ca}_{0.5}\text{Fe}_{0.5}\text{MgSi}_2\text{O}_6$
plagioclase (P)	$\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8$
nontronite (N)	$\text{Ca}_{0.33}\text{Mg}_{1.5}\text{Fe}_{3.5}\text{Al}_{1.33}\text{Si}_{7.33}\text{O}_{20}(\text{OH})_4$
magnetite (M)	Fe_3O_4
phengite (F) (illite)	$\text{KMg}_3\text{Fe}_{3.5}\text{Al}_2\text{Si}_6\text{O}_{20}(\text{OH})_4$
smectite (S)	$\text{Ca}_{0.5}\text{Mg}_2\text{Fe}_{3.5}\text{Al}_4\text{Si}_5\text{O}_{20}(\text{OH})_4$

In this experiment, a rock displaying at least two mineral assemblages out of thermodynamic equilibrium reacts with a fluid initially out of equilibrium with both assemblages. Both rock and fluid change in bulk composition as the experiment proceeds. After about two weeks a steady state is reached which continues for the duration of the experiment. At this point there is a transient equilibrium reflected by relatively constant fluid composition causing precipitation of secondary phases uniform in composition, with the exception of Fe which is thought to be due to included magnetite crystals in secondary clay, within a given prism and from prism to prism with respect to major element content. These reactions are not reversible, but the secondary phases are reasonable for the intensive parameters of the experiment. These reactions may be treated as infiltration metasomatism after the method of Korzhinskii (1970).

The minerals are part of the system K_2O - Na_2O - CaO - MgO - FeO - Fe_2O_3 - Al_2O_3 - SiO_2 - H_2O . K_2O , Na_2O , O_2 , SiO_2 , Al_2O_3 , and H_2O are considered as mobile components while CaO , MgO , and FeO are the inert components. Mobile and inert components maybe chosen in any reasonable manner. Because of the relatively low solution concentration of Ca, Mg, and Fe, these elements are chosen as inert. Additional elements will result in a more complex chemographic net but will still contain this subnet. Mobile phases are quartz, water, sanidine (actually adularia plus albite) oxygen, and complexes containing K^+ , Na^+ , and Al^+ . The entire chemographic system consists of three components and six phases (Table 7) and, thus, has one negative degree of freedom. No compositional degeneracies exist for this system. All 6 invariant assemblages, 15 univariant assemblages, and 20 divariant assemblages exist.

A connected net for this system is shown in Figure 8. All divariant fields are labeled. Important divariant assemblages are: smectite bearing, phengite bearing, and non hydrous phase bearing (high temperature). Some observations limit the pertinent assemblages with respect to this experiment.

- 1) Magnetite appears to be present with smectite and phengite.
- 2) Smectite and phengite do not appear together.
- 3) Nontronite never appears in the reacted rock.
- 4) Augite is metastable at low temperature.

These observations lead to a low temperature assemblage of magnetite, plagioclase and smectite, a moderate temperature assemblage of magnetite, plagioclase, and phengite and a high temperature assemblage of magnetite, plagioclase, and augite.

Fig. 8. Connected net and compositional polyhedron.

The two possible nets oriented in $\mu_{\text{H}_2\text{O}} - \mu_{\text{SiO}_2}$ space are shown in Figures 9 and 10. Only the important phase assemblages are labeled in these figures. One possible reaction path is labeled. This is the only region on the two diagrams which presents the proper sequence of reaction from more to less hydrous phases with relatively constant silica content.

Fig. 9. $\mu_{\text{H}_2\text{O}} - \mu_{\text{SiO}_2}$ oriented net with [S] to [F] homotypical metastable.

Fig. 10. $\mu_{\text{H}_2\text{O}} - \mu_{\text{SiO}_2}$ oriented net with [S] to [F] homotypical stable.

V. CONCLUSIONS

Sentinel Gap basalt reacts readily at low temperature with water to produce an assemblage including clay minerals throughout the range of experimentation. These minerals may be useful as adsorbers for material emplaced in the basalt. Sorption capabilities should be investigated with specific ions in mind.

Plate 1. SEM photomosaic of a portion of a polished unreacted basalt prism.

Plate 2. SEM photomosaic of a portion of a prism reacted at 72°C.

72 ° C

72 ° C

Plate 3. Secondary platey material grown at 72°C.

Plate 4. SEM photomosaic of a portion of a prism reacted at 119°C.

119°C

161°C

Plate 5. Reaction at 119°C and 161°C.

Plate 6. SEM photomosaic of a portion of a prism at 161° C.

Plate 7. SEM photomosaic of a portion of a prism reacted at 209°C.

Plate 8. SEM photomosaic of a portion of a prism reacted at 270°C.

Plate 9. SEM photomosaic of a portion of a prism reacted at 310°C.

6.8 WASTE GLASS - SEABED INTERACTIONS: OBSERVATIONS OF THE SORET EFFECT --

L. H. Brush, Sandia Laboratories

CONSTANT TEMPERATURE AND THERMAL GRADIENT INVESTIGATIONS OF THE NEAR-FIELD SUBSEABED ENVIRONMENT: CHEMICAL AND THERMODIFFUSIONAL EFFECTS --

C. C. Thornton and W. C. Seyfried, Jr., University of Minnesota, and
L. H. Brush, Sandia National Laboratories

Subseabed disposal of high level radioactive waste might provide a viable alternative to mined geologic disposal. Before this option can be realized, however, it is necessary to evaluate the physicochemical effects that would occur in a seawater-saturated sedimentary medium surrounding a heat source to estimate corrosion rates for the waste package and radionuclide mobility in case of early failure of the engineered barriers. With this in mind, we have conducted both constant temperature (200°, 300°C) and temperature gradient experiments. These experiments examined interactions of sea-water with sediment from our study area 1000 km north of Hawaii (PAC II) and permitted sampling of solutions at experimental temperatures and pressure (500 or 600 bars).

Results from constant temperature experiments clearly showed that fluid chemistry is controlled primarily by sediment composition, although temperature induced changes in seawater chemistry influence solution pH¹. Figure 1 illustrates the changes in fluid chemistry that occurred during an experiment with an illite and smectite-rich clay from the PAC II area upon reaction with seawater at 300°C, 500 bars, and at a seawater/sediment mass ratio of 5. The fluid was moderately acidic throughout the experiment owing to smectite and magnesium-hydroxy-sulfate precipitation, with a corresponding continuous decrease in the concentration of Mg in solution (Figure 1). At a sufficiently low Mg concentration, a pH reversal occurred because alumino-silicate minerals (e.g., illite) hydrolyzed, and high concentrations of K in solution were achieved. Ca concentration in solution was controlled by anhydrite solubility. Conditions during this experiment became highly oxidizing; the f_{O_2} at 300°C was estimated in excess of 10^{-15} atmospheres. The presence of ferromanganese oxide phases in the sediment undoubtedly contributed

FIGURE 1. Results of a Typical Constant Temperature (Closed System) Experiment Conducted with Seawater and Illite- and Smectite-Rich Clay from PAC II (Seawater Sediment Mass Ratio = 5) in a Modified Dickson Hydrothermal Apparatus. Dissolved concentrations of all species except hydrogen ion are given in parts per million (ppm). For comparison, the concentrations of these species in seawater (time = 0) are: SiO₂ = ~1 ppm; K = 380 ppm; Mg = 1,270 ppm; Ca = 400 ppm; and pH = ~8.

to the high f_{O_2} . In contrast, experiments with sediment containing significant amounts of organically derived carbon compounds appear to generate slightly more reducing conditions, characterized by f_{O_2} values of $\sim 10^{-20}$ atmospheres.²

Thus results of constant temperature (closed system) experiments in pelagic sediment indicate that hydrothermal interaction of sediment and seawater will generate an oxidizing to moderately oxidizing environment, depending upon the relative abundance of organic carbon and ferromanganese phases, and result in production of H^+ due to removal of Mg^{2+} from seawater. This latter event is characterized by formation of Mg-rich, hydroxyl-bearing alteration phases, most notably smectite. However, the accuracy with which these results model chemical processes in open systems (i.e., natural systems) depends on the extent to which Fickian and thermal diffusive effects contribute to the chemical system. In an attempt to understand better how diffusive reactions affect the chemical model generated from closed system, isothermal experiments, we can use two sources of data: (1) results from a heat transfer experiment (ISIMU) conducted with 1 m^3 of pelagic clay by the U. S. Subseabed Disposal Program³; and (2) results from thermal gradient experiments².

Figure 2 illustrates the experimental equipment utilized in ISIMU (In situ Heat Transfer Simulation experiment), a scaled-down prototype of a system ultimately intended for an in situ heat transfer experiment at a seabed location (ISHTE). The equipment included an electrical heat source embedded in the sediment and surrounded by a system of thermocouples and a pore water sampler, which permitted monitoring of the thermal gradient in the sediment surrounding the heater and the collection of pore fluids at the end of the experiment.

Figure 3 shows the variation of pore fluid chemistry from ISIMU with respect to the thermal gradient. A notable concentration gradient developed for Na, Cl, and Mg, whose concentrations decreased towards the heater. We interpret this trend as a result of thermodiffusional transport (the "Soret" effect) which produced a large scale flux of these components down the thermal gradient. This phenomenon markedly decreased the ionic strength of the "hot" zone; the Na and Cl concentrations of the 150°C zone were roughly half that of the overlying free water at 5°C . K and Ca show only a slight tendency to decrease in concentration towards the heater, apparently because of their

ISHTE SIMULATION VERTICAL CROSS SECTION TROUGH HEATER

FIGURE 2. Schematic representation of the In situ Heat Transfer Experiment Simulation (ISHTE) experiment that was carried out recently in the large pressure vessel at the Naval Ship Research and Design Center in Annapolis, Md. The figure shows locations of pore-water and sediment samples with respect to selected isotherms. Also shown are the boundaries of the baked zone, within which sediments were somewhat lithified, and the reduced zone. Sediments within the latter zone were reduced (color changed from red to green) because the heater was coupled electrically to the galvanized water tank above the sediments.

FIGURE 3. Variations in the concentrations of dissolved species with respect to temperature in ISIMU. For comparison, the concentrations of these species in seawater (initial fluid composition) are: NA = 10,560 ppm; Cl = 18,980 ppm; K = 380 ppm; Ca = 400 ppm and Mg = 1,270 ppm.

involvement in seawater-sediment interaction processes. The pH and alkalinity show a slight tendency to increase towards the heater (Figure 4) due to the removal of Mg and the "hot" zone, which precludes H^+ generation by the precipitation of smectite. Thus, thermal diffusion in an open system may effectively reduce near field acidity relative to a closed system at constant temperature.

FIGURE 4. Variations in pH and Alkalinity with Respect to Temperature in ISIMU. For comparison, the pH of seawater (initial fluid composition) is ~8, and its alkalinity is ~2 milliequivalents/l

In addition to ISIMU, several thermal gradient experiments have been conducted with a titanium-lined vessel (Figure 5). By heating the lower end of the vessel while cooling the upper end, we have succeeded in establishing a nearly linear temperature gradient along the interior of the cell of approximately 200°C at 600 bars pressure. As shown in Figure 5, the hottest portion of the cell was maintained at about 300°C and the cool zone at about 100°C over a distance of 30 cm. Our principal experiment to date with this equipment has involved a sediment from PAC II similar to that described for the constant

FIGURE 5. Titanium-lined Pressure Vessel Used for Temperature Gradient (open system) experiments at the University of Minnesota.

temperature experiment and has included, in addition, a small portion of waste glass simulant, PNL 76-68. The waste glass was positioned in the "hot" zone (Figure 5) and covered with ~60g of seawater-sediment mixture with a mass ratio of 5. Subsequent settling of the sediment produced a zone of clear fluid at the top of the cell which was periodically sampled for analysis. The reacted sediment and waste simulant were recovered at the end of the experiment and examined by x-ray diffraction, SEM, and wet chemical and neutron activation analysis.

Diffusion of Na and Cl from the hot zone towards the cool zone is apparent from the rapid increase in the concentration of these components in cool zone fluids during the first 750 hours of the experiment (Figure 6). K and SiO_2 increased steadily in the cool zone during the experiment because of illite and amorphous silica dissolution, respectively. Ca and Mg tend to migrate towards the cool zone early in the experiment, but subsequently diffuse back towards the hot zone owing to the temperature-dependent stability of anhydrite and smectite phases, respectively. The behavior of Mg suggests that the pH of the near field region will initially be close to neutrality due to the removal of Mg by thermal diffusion, but more acidic conditions may develop later as Mg is drawn back into the near-field region by seawater-sediment interaction processes.

Chemical analysis of reacted sediment and waste glass revealed significant mobilization of major and minor elements during the experiment (Figure 7). Na was effectively leached from the waste glass and transported down the thermal gradient as indicated by a decrease in Na_2O in the waste glass from 12.79 to 2.12% and an enrichment of Na_2O in the sediment from 3.18 to 5.10% in the hot zone. The Na_2O content of the sediments increased rapidly in the cool zone below 220°C, reaching a maximum enrichment of 7% over the unreacted sediment. Mg remained essentially immobile in sediment reacted at low temperature in the cool zone. At a temperature of ~230°C, however, Mg uptake by reacted sediment is indicated by the increase of MgO: MgO increased to 6.10% in the 275°C zone from an original concentration of 3.41% in the unreacted sediment. Coincident with Mg enrichment is K depletion probably caused by replacement of illite by smectite, an inference supported by recent x-ray diffraction studies completed on the reaction products. K_2O and MgO also increased in the reacted waste

FIGURE 6. Variations with time in the Composition of Fluids Sampled From the Cold (100°C) Zone of the Temperature Gradient Apparatus. (For comparison, the composition of seawater is: Cl = 18,980 ppm; Na = 10,560 ppm; K = 380 ppm; SiO₂ = ~1 ppm; Ca = 400 ppm; and Mg = 1,270 ppm.)

glass. Ca concentration in reacted sediment was highest in the 230–255°C zone, probably as a result of anhydrite precipitation.

The results of the experimental studies presented illustrate that the chemistry of the near field environment is determined by a combination of water-rock interaction and thermal diffusion effects. Most important with respect to a thermal gradient is the thermal diffusion effect which results in large scale fluxes of Na and Cl from the hot zone towards the cool zone. This phenomenon serves to markedly decrease the ionic strength of the hot zone.

FIGURE 7. Variations with Temperature of the Concentrations of Some Major Elements in the Sediments, Measured after the Temperature Gradient Experiment. Initial concentrations of these species are given in the text.

Other elements, however, appear to be influenced by water-rock interaction processes as well as thermal diffusion. The behavior of Mg is particularly important in this regard because of its potential of generating an acidic environment in the near field region. Resolution of the relative importance of these processes is necessary to determine the suitability of the subseabed environment as a repository for high level radioactive waste.

Moreover, thermal diffusion could well be important in a mined repository if groundwaters of moderate or high ionic strength saturate the backfill during the thermal period. If so, solutions considerably more dilute than these host-

rock groundwaters would be appropriate for high temperature waste package component interactions tests. In any case, thermal diffusion should be evaluated and included in near-field chemical models if necessary.

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7.0 SESSION V. WHAT IS MCC-14?

7.1 SOME THOUGHTS ON MCC-14: RECOMMENDED PRACTICE FOR EXPERIMENTALLY
EVALUATING WASTE FORM LEACHING IN A GEOLOGIC REPOSITORY --
J. E. Mendel, Materials Characterization Center

INTRODUCTION

The Materials Characterization Center was set up by the U.S. Department of Energy (DOE) to promote the use of uniform, approved test methods for the characterization of nuclear waste materials. The test methods are subjected to a DOE-mandated, peer-review process by the Materials Review Board (MRB). Five standard leach tests have been defined by the Materials Characterization Center:

- MCC-1 Static Leach Test Method
- MCC-2 Static, High-Temperature Leach Test Method
- MCC-3 Agitated Powder Leach Test Method
- MCC-4 Low-Flow-Rate Leach Test Method
- MCC-5 Soxhlet Leach Test Method

MCC-1 and 2 have received provisional approval by the Materials Review Board⁽¹⁾; the other three tests have been submitted to the Materials Review Board but have not yet been approved.⁽²⁾ Texts of those test methods may be obtained by request to:

Materials Characterization Center
Pacific Northwest Laboratory
Box 999
Richland, WA. 99352

The MCC-1 through 5 Leach Test Methods are relatively simple tests, involving only waste form specimens in contact with leachant solutions. Although the leachants can be site-specific solutions, in addition to reference solutions, the main utility of MCC-1 through 5 is to compare the chemical durability of waste forms under standard conditions, and to obtain information about the mechanism of the waste form-water reaction. The latter is facilitated by an important feature of the tests, which is characterization of the leached surface morphology and analysis of its chemical composition as a function of time.

Although knowledge of comparative chemical durabilities and the mechanism of water attack on waste form surfaces is important, this knowledge does not

enable prediction of the long-term behavior of a specific waste form in a repository setting. This is a much more complex undertaking, which requires an understanding of the effects of the other waste package components and of the repository setting. Tests that can include all of these effects have come to be called interactions tests. The presentations in Section 6.0 give an indication of the present status of interactions testing in the U.S. The MCC's efforts toward documentation and standardization of waste form leaching/interactions testing have been given the working title, MCC-14 Recommended Practice for Experimentally Evaluating Waste Form Leaching in a Geologic Repository. A submission by the MCC to the Materials Review Board on this subject is scheduled for June of 1983.

APPROACH

The MCC will utilize input from the potential waste form producers (presently Savannah River Laboratory and West Valley Nuclear Services, Co., Inc.), and from the three projects developing candidate repository locations, for its submission to the MRB in June, 1983. Because of inherent differences in the geologic sites, each will probably utilize a different waste package design, and each will have some unique testing requirements. The reference waste form in all cases is borosilicate glass; the composition of the glass is a variable, however.

As shown in Figure 1, the goal of interactions testing is to produce data that, when used in conjunction with mathematical models, will yield predictions of long-term waste package behavior in a repository. In essence, MCC-14 is a test method that will "qualify" a waste form for disposal in a given repository. In contrast to MCC-1 through 5, which are test methods with strictly defined limits, it is anticipated that MCC-14 will be rather more a carefully peer-reviewed test methodology. This methodology will include many separate tests in order to adequately define site-specific materials interactions. Tests that will probably become part of the MCC-14 methodology are already in use by the geologic repository R&D programs. The MCC plans to work with the repository projects to integrate these existing tests into a comprehensive

FIGURE 1. Interactions Testing: Input and Output

MCC-14 methodology for peer review by the MRB. Three separate methodologies, one for each major candidate geologic medium -- basalt, tuff and salt -- may be submitted to the MRB.

The MCC proposed the following criteria for MCC-14 methodology at the workshop and is seeking comments.

1. Output data is to be used in extrapolatable mathematical models.
 - The test must be able to distinguish effects of individual interactions.
2. Emphasize times beyond 1000 years, but be amenable to shorter time repository conditions.

- The test should use pre-aged component specimens, emphasize long-lived radionuclides, and temperatures $<100^{\circ}\text{C}$, but be capable of temperatures $>100^{\circ}\text{C}$.
3. Output data must be treated statistically, i.e., confidence limits established.
- The test should be relatively simple to facilitate replicate testing.

Based on the above criteria, it was proposed that the MCC-14 methodology can be tied to the existing MCC-1 through 4 leach test methods. The MCC is seeking comments on this approach, which is shown schematically in Figure 2.

The proposed approach would build on the waste form leaching data base that is being obtained by the MCC-1 through MCC-4 leach test methods, essentially by adding more variables to the tests, as shown in Figure 1. Important features of the existing MCC test methods would be retained, such as the extensive replication to provide data for statistical treatment and the post-examination of test specimens.

The approach of going from simple to more complex systems is illustrated in Figures 3 and 4. Figure 3 shows results for the leaching of borosilicate glass in deionized water using the standard MCC-1 test. The concentration of both plutonium and cesium was found to reach a steady-state after about three months of 90°C . These probably indicate solubility limits, controlled by PuO_2 in the case of plutonium and a clay-like glass surface alteration product in the case of cesium. Glass leaching does not stop at three months, however, since the thickness of the surface alteration layer continues to grow, but at an apparently continually diminishing rate. Now, what would be the effect of other system components? Would different species become solubility controls? Would the rate of formation, or the composition, of the alteration layer on the surface of the glass be altered? The MCC-14 test matrix is designed to answer questions of this type.

An example of MCC-14-type testing, taken from a paper presented at the MRS meeting in Berlin, is shown in Figure 4. In this case a potential repository host rock, granodiorite, was added to the borosilicate glass-leachant system.

FIGURE 2. Proposed MCC-14 Interactions Leach Test Matrix, Relationship to Existing MCC Leach Tests

FIGURE 3. Examples of MCC-1 Static Leach Test Results (3)

FIGURE 4a. Log Concentration (ppm) of Total SiO₂ Monomeric SiO₂, Total CO₂, Na, B, Mo, Li, SO₄ and Cl Versus Run Duration (4)

FIGURE 4b. Log Concentration (ppm) of Cr, Cs, Sn, Rb, Al, Zn, Zr, Fe, Sr and Ba Versus Run Duration (4)

The static test had a duration of 200 days, and was performed at 100°C rather than 90°C. Again, as shown in Figure 4a, the concentration of several leached constituents reached an apparent equilibrium concentration within 2-3 months. But others, including Cs, Rb and even Zr, did not, as shown in Figure 4b. It is not yet clear whether the granodiorite influenced the behavior of these elements.

ESTABLISHING TESTING PRIORITIES

Since many of the tests require months or even years to complete, it is immediately obvious that a test matrix of the type indicated in Figure 2 is a utopian concept, even if data were being obtained in a cooperative manner by all of the laboratories that could potentially be involved. A statistical approach toward establishing testing priorities is called for, based on conventional statistical designs, such as fractional factorials, if possible. Available evidence should be used to identify which main effects and interactions among the input parameters can be expected to be negligibly small and thus

omitted. Pressure, for example, is a parameter that has already been omitted from those shown in Figure 2, because of evidence that its effect is negligible.

THE ROLE OF DEMONSTRATION TESTS

Demonstration tests are tests in which it is attempted to mock up at least some of the physical attributes of the repository system. Tests such as those described in Sections 6.6 and 6.8 fall at least partially in this category. Demonstration tests are specialized, often one-of-a-kind tests, that are necessary to show that there are no unexpected interactions, due to geometric configuration, for instance, that are not predicted by MCC-14-type tests. It is anticipated that a large proportion of interactions testing can be of the MCC-14-type, but a certain amount of demonstration testing will certainly be required, especially when waste package design and repository siting decisions become more firm.

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7.2 THE ROLE OF OXIDATION POTENTIAL, Eh, IN THE DISSOLUTION OF NUCLEAR WASTE

WASTE MATERIALS -- W. B. White and W. P. Freeborn, Pennsylvania State University

INTRODUCTION

Many elements occur in high level radioactive waste in more than one valence state. The valence state in the final waste form is an important factor in determining both equilibrium solubility and rate of dissolution of the waste form. Table 1 lists some of these redox couples. Table 1 contains two kinds of redox reactions: those in which an ionic species is reduced to a metal and those in which there are oxidation or reduction of one ionic species to another. Some elements exhibit both.

Reactions connecting different valence states require an exchange of electrons such as an acid-base reaction requires an exchange of protons. Since most waste forms are oxides, these reactions can be described by oxidation potentials. In a complex system such as a nuclear waste, there are many reactions underway simultaneously. If the system is to be at equilibrium, all of these must be adjusted to a single oxidation potential which may be regarded as a system variable.

The question is: how does one measure the oxidation potential in a complex system and how does one control it?

TABLE 1. Some Redox Couples Relevant to Nuclear Waste

<u>Ion - Metal Pairs</u>	<u>Ion - Ion Pairs</u>	<u>Mixed Ion - Ion - Metal Couples</u>
$\text{Ru}^0 - \text{Ru}^{4+}$	$\text{U}^{4+} - \text{U}^{6+}$	$\text{Cu}^0 - \text{Cu}^+ - \text{Cu}^{2+}$
$\text{Pd}^0 - \text{Pd}^{2+}$	$\text{Np}^{3+} - \text{Np}^{4+} - \text{Np}^{5+}$	$\text{Tc}^0 - \text{Tc}^{4+} - \text{Tc}^{6+} - \text{Tc}^{7+}$
$\text{Ag}^0 - \text{Ag}^+$	$\text{Pu}^{3+} - \text{Pu}^{4+} - \text{Pu}^{6+}$	$\text{Mn}^0 - \text{Mn}^{2+} - \text{Mn}^{4+}$
$\text{Pb}^0 - \text{Pb}^{2+}$	$\text{Ce}^{3+} - \text{Ce}^{4+}$	$\text{Fe}^0 - \text{Fe}^{2+} - \text{Fe}^{3+}$
$\text{Ni}^0 - \text{Ni}^{2+}$	$\text{Cr}^{3+} - \text{Cr}^{6+}$	$\text{Co}^0 - \text{Co}^{2+} - \text{Co}^{3+}$
	$\text{Mo}^{4+} - \text{Mo}^{6+}$	

DEFINITION OF Eh

Redox potential is usually described by Eh, a macroscopic parameter related to the electron activity. Consider the analogy to pH.

$$\text{pH} = -\log [\text{H}^+] \quad (1)$$

An equivalent parameter can be defined for electrons.

$$\text{pe} = -\log [\text{e}^-] \quad (2)$$

If the redox reaction is written as an oxidation reaction, then

$$\text{Eh} = \frac{2.303}{F} \frac{RT}{nF} \text{pe} = - \frac{\Delta G_R}{nF} \quad (3)$$

which connects the electrochemical quantities of pe and Eh to the thermochemical quantity of Gibbs free energy of reaction. Since

$$\Delta G_R = \Delta G_R^\circ + RT \ln K \quad (4)$$

The equation for Eh can be related to the equilibrium constant

$$\text{Eh} = - \frac{\Delta G_R^\circ}{nF} - \frac{RT}{nF} \ln K \quad (5)$$

The standard free energy of reaction can be related to a standard electrochemical potential

$$E^\circ = - \frac{\Delta G_R^\circ}{nF} \quad (6)$$

This leads to the usual expression for the Nernst Equation

$$E_h = E^\circ - \frac{RT}{nF} \ln \frac{[\text{oxidation products}]}{[\text{reduced reactants}]} \quad (7)$$

which serves as the usual working definition for E_h .

In the above equations, n = number of electrons exchanged, F = Faraday constant ($96.487 \text{ kJ V}^{-1} \text{ mole}^{-1}$ or $23.062 \text{ kcal V}^{-1} \text{ mole}^{-1}$) and R = gas constant.

Redox reactions pertinent to nuclear waste materials and nuclear waste repositories are likely to take place in aqueous solution or in an aqueous environment. In this case there is a direct connection between E_h and pH. The redox potentials and hydrogen ion activities must also be in equilibrium with the reduction and ionization of water.

$$f_{\text{H}_2} \cdot f_{\text{O}_2}^{1/2} = 10^{-41.55} \quad (25^\circ\text{C})$$

$$[\text{H}^+] [\text{OH}^-] = 10^{-14.00} \quad (25^\circ) \quad (9)$$

Both equations are written at unit activity of H_2O . When these equations are combined through the Nernst Equation, we obtain

$$\frac{1}{2} \log f_{\text{O}_2} = \frac{E_h F}{2.303 RT} + 2\text{pH} + \log[\text{H}_2\text{O}] - 41.55 \quad (10)$$

which connects the oxygen fugacity (often called the "oxygen partial pressure") with E_h and pH. Thus the system parameters for aqueous environments are linked by equation (10) and specification of any two of them permits calculation of the third.

The reactions described by equations (8 - 10) also put limits on the stability of liquid water. If Eh - pH conditions are such that either $f_{O_2} > 1$ or $f_{H_2} > 1$ at atmospheric conditions, oxygen or hydrogen gas will be released. Many metals cannot be in equilibrium with liquid water. Iron, for example, will reduce water, become oxidized, and release hydrogen gas. Increasing the system pressure to the several hundred bar values expected for a sealed repository will shift these equilibria but not by much.

DISPLAY OF Eh - pH RELATIONS

Quick and easy interpretation of the chemistry of complex redox systems is difficult because of the large number of variables. These include P, T, pH, Eh, and the activity of any species deemed to be mobile. The most widely used display devices are Eh-pH diagrams (as they are called by geochemists) or Pourbaix diagrams (as they are called by metallurgists).

Figure 1 is a well-known example. Eh (in volts) and pH form the y and x axes. T = constant, usually 25°C. P = 1 (atmosphere or bar; the literature is often ambiguous). The two parallel lines at the top and bottom of the diagram mark the upper and lower stability limits for water. The polygonal "fields" denote regions where the labeled species are dominant.

Various techniques can be used to add concentration data to the diagram. One way is to contour the dominant species (Figure 2). Here we see that the concentration of Fe^{2+} is very sensitive to pH and Eh, rising rapidly as pH and Eh are lowered. In contrast, the concentration of the neutral species $Fe(OH)_3^0$ is extremely low and essentially independent of pH and Eh. Thus, over a wide range of pH and Eh, iron would be immobile, precipitating out as $Fe(OH)_3$.

Other information can be displayed by constructing various kinds of speciation diagrams. Figure 3 shows the speciation of Fe^{2+} . Since all concentrations are normalized to (Fe^{2+}) , the diagram is Eh-independent and displays the changing concentrations of divalent iron species as a function of pH. Figure 4 shows the same kind of diagram for Fe^{3+} species.

Many other displays have been used. Activities (or fugacities) of other mobile species (e.g., CO_2) can be used as variables. Oxygen fugacity can be

FIGURE 1. pH - Eh Diagram for the System Fe-O-H Showing Dominant Dissolved Species.

FIGURE 2. pH - Eh Diagram for the System Fe-O-H Showing Concentration Contours for Dominant Species.

FIGURE 3. Speciation Diagram for Ferrous Iron Species

FIGURE 4. Speciation Diagram for Ferric Iron Species

used instead of Eh. The latter is particularly useful in describing solid-solid redox equilibria as a function of temperature.

MEASUREMENT OF Eh

It seems to be generally conceded that Eh measurements in aqueous solutions are simple in principle and difficult in practice. The reference electrode for Eh is the hydrogen electrode which can be replaced with a platinum electrode. With a reference electrode of calomel or Ag/AgCl, Eh can be read directly from the cell voltage. The difficulty is that many solutions have little oxygen buffer capacity and the kinetics of the redox reactions may be sluggish. The electrode potential is then not well defined. Voltages drift and it is difficult to relate observed Eh to calculated Eh. Eh measurements in aqueous solutions require at least one reaction with mobile electrons. The situation with nuclear waste leach solutions seems to be poorly known perhaps because not too many people have tried.

A better approach is to calculate Eh from thermochemical data if such are available using equations (5-7). This is the approach used to calculate the Eh-pH diagrams for uranium, plutonium, and technetium-bearing species that have appeared. The problem with enlarging these individual metal-oxygen-water systems to a complete suite of elements representative of nuclear waste materials is that thermochemical data may be required that are not available. The comprehensive computer codes for speciation calculations will be helpful here.

At high temperatures, oxygen fugacity, rather than Eh, can be measured directly using sensors that make use of the anion conductivity of zirconia ceramics. These give good results at high temperatures but do not work well below 500°C and are thus out of the range of most dissolution experiments.

Perhaps the most promising technique for the 90 to 300°C temperature range of interest is the use of silver or palladium membranes which are permeable to hydrogen. One then measures hydrogen fugacity and pH and from this calculates back to Eh. Experimental chambers with thin hydrogen permeable membranes seem like a promising approach. These measurements will work best at the higher temperatures and will become difficult at temperatures where the hydrogen

reactions become sluggish. One should first determine whether hydrogen fugacity measurements can be made to overlap the region where direct electrochemical measurements are possible.

HOW TO BUFFER Eh

If measurement of Eh is difficult, control of Eh is even more difficult. Two approaches have been tried, mostly at higher temperatures.

Any metal/metal oxide pair will have an equilibrium oxygen pressure at any temperature and so long as neither solid is completely consumed, the pair will serve to buffer oxygen fugacity. Metal/metal oxide (and oxide/oxide) buffers work well above 500°C, where kinetics are rapid, but become sluggish at repository temperatures.

Control of hydrogen pressure over a system remains a possible approach to Eh buffering just as it is an approach to Eh measurement. The questions which must be answered experimentally deal with the effectiveness of hydrogen-permeable membranes at experimental temperatures and with the rate of reaction of gaseous hydrogen with the various redox pairs in the nuclear waste system.

ACKNOWLEDGMENTS

The participants in the leaching mechanisms program wish to thank all of the attendees at the workshop for their many perceptive questions and comments. We much appreciate contributions of the speakers from outside the program, particularly these from the NWTs projects. They gave the workshop a fully-rounded perspective that was valuable to all.

Special thanks go to Charlie Faust and Sid Phillips, who stepped in as substitute speakers at virtually the last minute and did excellent jobs. Billie Neth, as always, was very helpful to all. Judy Hooper's editing of the report is much appreciated as well as the preparation of the camera-ready copy by Scott Dudley.

APPENDIX A

WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS,

MAY 19-21, 1982

AGENDA

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SECOND SEMIANNUAL WORKSHOP ON THE LEACHING
MECHANISMS OF NUCLEAR WASTE FORMS

MAY 19-21, 1982

GAITHERSBURG HOLIDAY INN, GAITHERSBURG, MD

MAY 19, 1982

8:00 - 8:15 am Introductions and Welcome

 W. K. (Warren) Eister, DOE-Hdqs.

 P. H. (Phil) Permar, SRL HLW Lead Office

SESSION I. PROGRESS REPORT ON LEACHING MECHANISMS PROGRAM

8:15 - 9:00 am University of Florida - LL (Larry) Hench, Principal Investigator
9:00 - 9:45 Catholic University of America - PB (Pete) Macedo, Principal Investigator
Coffee Break
10:00 - 10:45 Pennsylvania State University - WB (Will) White, Principal Investigator
10:45 - 11:30 Rockwell Science Center - AB (Alan) Harker, Principal Investigator
11:30 - 12:15 Pacific Northwest Laboratory - GL (Gary) McVay, Principal Investigator

LUNCH

1:30 - 2:15 pm Lawrence Livermore National Laboratory - DD (Don) Jackson, Principal Investigator

SESSION II. SPECIAL TOPICS IN STATIC AND LOW-FLOW RATE LEACH TESTING

2:30 - 3:00 Leach Testing of Waste Forms: Interrelationship of IAEA and MCC-Type Tests - VM (Virginia) Oversby, Lawrence Livermore National Laboratory
3:00 - 3:15 An Examination of the MCC-1 Leach Test Method, Part I: Round Robin Results - JL (Lee) Daniel, Materials Characterization Center
Coffee Break
3:30 - 3:50 An Examination of the MCC-1 Leach Test Method, Part II: Experimental Technique - HM (Skip) Kingston, National Bureau of Standards
3:50 - 4:10 An Examination of the MCC-1 Leach Test Method, Part III: Comparison of Glass Compositions - DJ (Dave) Cronin, National Bureau of Standards
4:10 - 4:40 Glass Dissolution Mechanisms: MCC-1 Static Leach Test Data - RM (Dick) Wallace, Savannah River Laboratory
5:30 - 7:00 SOCIAL HOUR (Cash Bar)

MAY 20, 1982

SESSION II. (Continued)

8:00 - 8:30 am	Effect of Solubility on Leaching - B (Bernd) Grambow, Hahn-Meitner Institute
8:30 - 9:30	Thermodynamics of Geochemical Systems - SL (Sid) Phillips, Lawrence Berkely Laboratory
Coffee Break	

SESSION III. NEAR-FIELD HYDROLOGICAL, DIFFUSION AND CONVECTION PHENOMENA

9:45 - 11:15	Tutorial on Groundwater Hydrology - CR (Charlie) Faust, GeoTrans, Inc., Reston VA
11:15 - 11:45	Influence of Diffusion through a Concentration Boundary Layer on the Dissolution Rate of Waste Forms - Review of paper by PL Chambre, TH Pigford, and S Zavoshy, University of California - WL (Bill) Kuhn, Pacific Northwest Laboratory.

LUNCH

Status Report on Reference Flow Regimes for Geologic Repositories	
1:15 - 1:30 pm	Basalt - MJ (Mick) Apted, Rockwell Hanford
1:30 - 1:45	Tuff - PR (Pete) Stevens, U.S. Geological Survey
1:45 - 2:00	Salt - JF (John) Kircher, ONWI

SESSION IV. STATUS OF MULTICOMPONENT INTERACTIONS TESTING

2:00 - 2:30	Interactions Testing at PNL - DG (Dave) Coles and JW (John) Shade, Pacific Northwest Laboratory
2:30 - 3:00	Interactions Testing at BWIP - MJ (Mick) Apted, Rockwell Hanford
Coffee Break	
3:15 - 3:45	Interactions Testing for a Nuclear Waste Repository in Granite - KB (Keith) Harvey, Whiteshell Nuclear Research Establishment
3:45 - 4:15	Interactions Testing at SRL - GG (George) Wicks, Savannah River Laboratory
4:15 - 4:45	The Behavior of Leached Constituents in Backfill - EJ (Jim) Nowak, Sandia National Laboratories

DINNER

8:00 - 10:00	Tour of Catholic University facilities
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MAY 21, 1982

SESSION IV. (Continued)

8:00 - 8:30 am	Laboratory Analog Experiment - MG (Marty) Seitz, Argonne National Laboratory
8:30 - 9:00	Rock-Water Interactions in a Controlled Temperature Gradient Circulation System - R (Bob) Charles, Los Alamos National Laboratory

MAY 21, 1982

SESSION IV. (Continued)

9:00 - 9:30 am Waste Glass-Seabed Sediment Interactions: Observations of the Soret Effect - LH (Larry) Brush, Sandia National Laboratories

Coffee Break

SESSION V. WHAT IS MCC-14?

9:45 - 10:00 Some Thoughts on MCC-14: Recommended Practice for Experimentally Evaluating Waste Form Leaching in a Geologic Repository - JE (John) Mendel, Materials Characterization Center

10:00 - 10:30 The Role of Eh in Simulated Geologic Repository Leach Testing - WB (Will) White, Pennsylvania State University

10:30 - 10:45 More Thoughts on MCC-14 - PB (Pete) Macedo, Catholic University of America

10:45 - 10:55 More Thoughts on MCC-14 - NE (Ned) Bibler, Savannah River Laboratory

10:55 - 12:00 Open Discussion on Evaluating Waste Form Leaching in a Geologic Repository

12:00 - 12:30 Wrap up

12:30 Adjourn

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APPENDIX B
WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS,
MAY 19-21, 1982
PARTICIPANTS

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APPENDIX B
WORKSHOP ON THE LEACHING MECHANISMS OF NUCLEAR WASTE FORMS,
May 19-21, 1982

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