NNWSI WASTE FORM TESTING AT ARGONNE NATIONAL LABORATORY

UCRL--21060-87-1

DE90 011499

Semiannual Report
January-June 1987

Work Performed by

John K. Bates, Thomas J. Gerding, Teofilo A. Abrajano, Jr.,
William L. Ebert, and James J. Mazer

of

ARGONNE NATIONAL LABORATORY
Chemical Technology Division
9700 South Cass Avenue
Argonne, Illinois 60439-4837

November 1988

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. UNSATURATED TEST DEVELOPMENT AND PERFORMANCE	2
A. NNWSI Unsaturated Test Method	2
B. NNWSI Parametric Experiment	33
C. Analog Experiment	55
III. NNWSI GAMMA IRRADIATION TESTING	56
A. 2×10^5 Rad/hr Experiments	56
B. 1×10^4 Rad/hr Experiments	65
C. 1×10^3 and 0 Rad/hr Experiments	65
IV. SURFACE ANALYTICAL SUPPORT	73
A. SIMS Software	73
B. Establishment of a Laser Raman Microprobe Facility	77
C. Development of a Gas Analysis System	77
V. GLASS ANALOG STUDIES	84
REFERENCES	88

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Test Matrix and Component Weights for N2 Test Series	3
2.	Solution Analyses (Cations) for the N2 Test Series	9
3.	Blank Corrected Solution Results from the N2 Test Series . . .	12
4.	Normalized Release of Elements from the Glass in the N2 Tests	15
5.	Normalized Lithium Release through 52 Weeks of Testing	16
6.	Composition of Leachates Collected during the Continuous N2 Tests	18
7.	Test Matrix and Component Weights for N3 Test Series	29
8.	ATM-10 Comparative MCC-1 Leach Tests	34
9.	Description, Purpose, and Status of Parametric Experiments	36
10.	Test Conditions for UO ₂ Tests	38
11.	Solution Analysis from UO ₂ Parametric Tests Series P-VI	40
12.	Analysis of Solution Composition from P-VI Experiments	43
13.	Experimental Matrix and Results from Parametric Experiments (P-VIII Series)	46
14.	Solution Results (Total Nanograms) for P-VIII Experimental Series	48
15.	Blank Corrected Totals for Parametric P-VIII Test Series Solutions	49
16.	Results from the F-1 Unsaturated Test Series	50
17.	1986 Vapor Hydration Experiments for NNWSI	52

Cont'd

LIST OF TABLES - Cont'd

<u>No.</u>	<u>Title</u>	<u>Page</u>
18.	Np and Pu Release from ATM-8 Glasses	62
19.	List of Samples Analyzed using Various Surface Analytical Techniques	75
20.	Composition of Glass Standards (wt %)	86

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Photograph of the Top Surface from Test N2 #7	7
2.	(NL) _i from N2 Batch Tests	13
3.	(NL) _L i Continuous Tests	16
4.	Secondary Electron photomicrograph of the Bottom Glass from Test N2 #8	21
5.	Alteration Products and Corresponding EDS Spectra that Formed on the Glass Surface Shown in Fig. 4	22
6.	Photomicrograph and EDS Spectra of Alteration Products that Formed on the Top Glass Surface from Test N2 #6	23
7.	(a) Buildup of Precipitates at the Interface Around the Circumference of the Punched Holes in the Stainless Steel, Bottom Canister, Test N2 #2, Magnification 250x, Marker = 55 μm	25
	(b) Higher Magnification Micrograph (1200x) of the Central Region of Fig. 4a, marker = 5 μm	25
8.	EDS Spectra of Selected Areas Shown in Fig. 7	26
9.	Micrographs of Polished Cross-Sections of Etched Stainless Steel Waste Form Holders for the N2 Test	27
10.	Photomicrograph and EDXS Spectrum of Precipitate Formed on SRL U Glass	67
11.	Photomicrograph and EDXS Line Profile of Cross Section of ATM-1c Glass	69
12.	SIMS Profile of $^7\text{Li}^+$ and $^{23}\text{Na}^+$ from Sample 423, Experiment Number G-361, SRL U + Tuff, 0 R/h, 80 d	72
13.	Resonant Nuclear Reaction Spectroscopy (RNRS) Result for Sample 400, SRL U, 0 R/h, 180 d	74
14.	Raman Spectrum of CaCO_3 Obtained Using the Laser Raman Microprobe	78

Cont'd

LIST OF FIGURES - Cont'd

<u>No.</u>	<u>Title</u>	<u>Page</u>
15.	Sketch of Temperature Control Unit	79
16.	Temperature Ramp Produced using Two Different Heating Rates (Top) 5°C/minute, (Bottom) 10°C/minute	81
17.	TPD Spectra, $m/e = 19$ HDO, of Hydrated Glass	82

NNWSI WASTE FORM TESTING

Semiannual Report, January-June 1987

John K. Bates, Thomas J. Gerding, Teofilo A. Abrajano, Jr.
William L. Ebert, and James J. Mazer

I. INTRODUCTION

The Nevada Nuclear Waste Storage Investigation (NNWSI) Project is investigating the tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level radioactive waste repository. As part of the waste package development portion of this project, which is directed by Lawrence Livermore National Laboratory, experiments are being performed by the Chemical Technology Division of Argonne National Laboratory to study the behavior of the waste form under anticipated repository conditions. These experiments include (1) the development and performance of a test to measure waste form behavior in unsaturated conditions and (2) the performance of experiments designed to study the behavior of waste package components in an irradiated environment. Previous reports [STEINDLER; BATES-1, -2] document developments in these areas through 1986. This report summarizes progress during the period January-June 1987.

Efforts this period have focused on analyzing components from the N2 Unsaturated Test series, writing a topical report describing the N2 test results, and initiating the N3 Test series using ATM-10 glass. Experiments studying the effect of gamma radiation (1×10^3 and 0 rad/hr) on groundwater composition and SRL 165 type glass reaction have been completed and the results from these experiments are being compiled and the components analyzed. Experiments at 0 Rad/hr using ATM-1c and ATM-8 glasses that are being done to be comparable with previous experiments done in a radiation field, have been completed through 91 days and two reports describing the effect of radiation on the leaching of these glasses have been written. Parametric experiments evaluating physical factors such as relative humidity on glass reaction are in progress.

II. UNSATURATED TEST DEVELOPMENT AND PERFORMANCE

A. NNWSI Unsaturated Test Method (QA Level I, activity #D-20-27)

1. NNWSI Unsaturated Test Method

Additional procedures have been written and approved by NNWSI that guide analysis of test components generated during the test. While these procedures are not explicitly required according to the Unsaturated Test Method, they will allow several additional analyses to be treated as QA level I data, if desired. These procedures include qualitative description of test components, determination of ferrous iron in glasses, and comparative quantitative analysis of glasses using SEM/EDS/WDS.

2. N2 Unsaturated Test

The detailed N2 Test matrix, together with selected results, are presented in Table 1. Tests N2-1 through N2-8 are the batch tests, and tests N2-9 through N2-12 are the continuous tests. At this point the tests have been completed through the 65-week sampling period. All the batch tests have been completed, and three continuous tests and one blank are ongoing. Three types of results including general observations, solution analyses, and component analyses are presented. A combination of each type of result is required to provide a concerted description of the reaction process. Eventually, the results presented here will be combined with a modeling effort to project the long-term performance of the interactions observed in this Test.

a. General Observations

Unlike the F Test series [BATES-3], where there was a marked disparity in the post-reaction appearance of the components from individual tests, the components from the N2 Test series were quite similar in appearance. General observations were made of the test components prior to, during, and after testing. These observations included color photographs of the pre- and post-test waste form holder sections, visual observation of the glass samples before testing, color photographs of the top and bottom sections after testing, and visual observation of the test components during the sampling periods.

Table 1. Test Matrix and Component Weights for N2 Test Series

Description	Test #	Vessel #	Dye Position	Test Period (weeks)	Date Started	Date Stopped	Sample #	Weight Glass IN	Weight Glass OUT	Δ Mass (g)	SA Glass (cm ²)	Top Canister IN (gm)	Top Canister OUT (gm)	Δ Mass
Batch	N2-1	ANL-36	3	13	2/03/00	5/05/00	2 ₃	10.50620	10.50600	(140)	1309	3.13942	3.14033	910
Batch	N2-2	ANL-37	4	13	2/03/00	5/05/00	2 ₄	10.21967	10.21915	(420)	1359	3.17666	3.17758	920
Batch	N2-3	ANL-38	5	26	2/03/00	8/04/00	3 ₁	10.32225	10.32131	(940)	1367	3.14779	3.14869	900
Batch	N2-4	ANL-39	6	26	2/03/00	8/04/00	3 ₂	9.85644	9.85556	(880)	1317	3.10517	3.10609	920
Batch	N2-5	ANL-40	7	39	2/03/00	11/03/00	3 ₃	10.19010	10.19009	(1210)	1363	3.17319	3.17431	1120
Batch	N2-6	ANL-41	8	39	2/03/00	11/03/00	3 ₄	10.20494	10.20453	(410)	1354	3.17702	3.17800	900
Batch	N2-7	ANL-42	9	52	2/03/00	1/31/07	11 ₁	10.50013	10.50971	(420)	1384	3.15554	3.15843	890
Batch	N2-8	ANL-43	10	52	2/03/00	1/31/07	13 ₁	10.39035	10.39791	(440)	1370	3.13933	3.13933	1130
Continuous	N2-9	ANL-34	1	6.5	2/03/00	3/20/00	2 ₁	10.27493			1304	3.15980		
		ANL-45		13	3/20/00	5/05/00								
		ANL-34		19.5	5/05/00	6/19/00								
		ANL-45		26	6/19/00	8/04/00								
		ANL-34		32.5	8/04/00	9/18/00								
		ANL-45		39	9/18/00	11/03/00								
		ANL-34		45.5	11/03/00	12/18/00								
		ANL-45		52	12/18/00	1/31/07								
Continuous	N2-10	ANL-34	2	65	1/31/07	5/04/07	2 ₂	10.40970			1306	3.16255		
		ANL-45		78	5/04/07	6/03/07								
		ANL-35		13	2/03/00	3/20/00								
		ANL-40		19.5	3/20/00	5/05/00								
		ANL-35		26	5/05/00	6/19/00								
		ANL-40		32.5	6/19/00	8/04/00								
		ANL-35		39	8/04/00	9/18/00								
		ANL-40		45.5	9/18/00	11/03/00								
		ANL-35		52	11/03/00	12/18/00								
		ANL-40		65	12/18/00	1/31/07								
		ANL-34		85	1/31/07	5/04/07								
		ANL-34		78	5/04/07	6/03/07								

Cont'd

L3

Table 1 (Cont'd)

Bottom Canister IN (gm)	Bottom Canister OUT (gm)	Δ Mass	Total Vessel IN (gm)	Total Vessel OUT (gm)	Δ Mass	Water Added During Testing
4.10208	4.10391	110	1340.4	1341.7	1.3	1.95
4.06610	4.06729	119	1335.0	1336.9	1.3	1.95
4.07221	4.07326	105	1330.4	1340.0	2.4	3.90
4.09671	4.09671	000	1335.0	1338.0	3.0	3.90
4.08299	4.08452	153	1330.0	1334.0	4.0	5.85
4.12070	4.12900	1100	1339.1	1343.1	4.0	5.85
4.07907	4.08009	1200	1320.0	1335.2	6.0	7.00
4.10057	4.10182	1250	1320.1	1335.0	6.0	7.00
4.09704			1330.0	1337.2	+0.7	0.975
			1329.4	1330.0	+0.0	0.975
			1330.0	1337.2	+0.7	0.975
			1329.5	1330.2	+0.7	0.975
			1330.7	1337.0	+1.1	0.975
			1329.5	1330.2	+0.7	0.975
			1330.0	1337.1	+0.0	0.975
			1329.4	1329.9	+0.0	0.975
			1330.4	1337.9	+1.5	1.95
			1329.3			
4.12307			1337.9	1338.0	+0.0	0.975
			1341.4	1342.1	+0.7	0.975
			1330.0	1330.0	+0.0	0.975
			1341.0	1342.2	+0.0	0.975
			1330.0	1330.0	+0.0	0.975
			1341.0	1342.3	+0.7	0.975
			1330.0	1338.7	+0.7	0.975
			1341.0	1342.2	+0.7	0.975
			1337.9	1339.4	+1.5	1.95
			1341.0			

Cont'd

Table 1 (Cont'd)

Description	Test #	Vessel #	Oven Position	Test Period (weeks)	Date Started	Date Stopped	Sample #	Weight Glass IN	Weight Glass OUT	Δ Mass (μ g)	SA Glass (cm^2)	Top Canister IN (gm)	Top Canister OUT (gm)	Δ Mass
Blank	N2-11	AHL-44	11	5.5	2/03/86	3/28/86	none							
		AHL-44		13	3/28/86	5/05/86								
		AHL-44		19.5	5/05/86	6/19/86								
		AHL-44		26	6/19/86	8/04/86								
		AHL-44		32.5	8/04/86	9/18/86								
		AHL-44		39	9/18/86	11/03/86								
		AHL-44		45.5	11/03/86	12/18/86								
		AHL-44		52	12/18/86	1/31/87								
		AHL-44		58.5	1/31/87	3/19/87								
		AHL-44		65	3/19/87	5/04/87								
				78	5/04/87	8/03/87								
Continuous	N2-12	AHL-36	3	0.5	6/19/86	7/19/86	13 ₂	10.94878			1384	3.16770		
		AHL-37		13	8/19/86	8/04/86								
		AHL-36		19.5	8/04/86	9/18/86								
		AHL-37		26	9/18/86	11/03/86								
		AHL-36		32.5	11/03/86	12/18/86								
		AHL-37		39	12/18/86	1/31/87								
		AHL-36		45.5	1/31/87	3/19/87								
		AHL-37		52	3/19/87	5/04/87								
		AHL-36		55	5/04/87	8/03/87								

*Inlet line plugged during the test period.

Cont'd

Table 1 (Cont'd)

Bottom Canister IN (gm)	Bottom Canister OUT (gm)	Δ Mass	Total Vessel IN (gm)	Total Vessel OUT (gm)	Δ Mass	Water Added During Testing
			1328.8	1328.8	-0.6	0.975
			1328.8	1328.7	-0.7	0.975
			1328.8	1328.8	-0.6	0.975
			1328.8	1328.8	-0.6	0.975
			1328.1	1328.9	-0.8	0.975
			1328.6	1329.0	-0.5	0.975 ^a
			1328.3	1328.8	-0.3	0.975 ^a
			1328.8	1328.3	-0.3	0.975 ^a
			1328.8	1328.7	-0.7	0.975
			1328.1	1328.5	-0.4	0.975
			1328.8			
4.09651			1348.4	1349.1	-0.7	0.975
			1336.1	1336.7	-0.6	0.975
			1348.6	1341.1	-0.6	0.975
			1336.1	1336.8	-0.7	0.975
			1348.6	1341.2	-0.7	0.975
			1336.1	1336.8	-0.7	0.975
			1348.6	1341.4	-0.9	0.975
			1336.2	1336.8	-0.6	0.975
			1348.6			

The as-prepared glass specimens met the appearance requirements given in procedure NNWSI-05-005. The as-cut sections were uniform in appearance and the sides were reflective and smooth. After testing the top and bottom surfaces were noticeably reacted as shown in Fig. 1. The regions of non-glass metal contact acted to accumulate reaction products. This majority of the reaction products were found surrounding the circumference of the holes in the waste form holder. This is where standing water was observed to exist in some of the tests upon opening the vessels. The regions of glass/metal contact showed little evidence of coverage by alteration products except in some localized cases where channels appeared to exist between the open areas. The extent of coverage by the rust-colored alteration products appeared to increase between the 13- and 26-week samples but was fairly constant thereafter.

The side surfaces of the glass retained their reflective appearance but were covered with random watermarks as shown in Fig. 2 of [BATES-3]. This appearance suggests that some water flowed over the sides but that the strong interactions present on the top and bottom surfaces did not occur. During the sampling and termination periods water was observed standing on the bottom canister section at the interface between the glass

Fig. 1. Photograph of the Top Surface from Test N2 #7

and the metal. Only for a few periods was water observed on the top section of the waste form holder. It is believed that water that collects in this area evaporates during the cool down period before the vessels are opened. Condensed water is always observed on the inner sides and tops of the vessels.

The appearance of the top and bottom waste form holders ranged from a uniform deep blue coverage to a mix of blue and gold coverage. No measure of the extent of sensitization was made on the actual test specimens prior to testing. Such studies were done only after the test periods were complete (Section C).

After testing, the top and bottom holders were discolored in the glass contact region attaining a dark brown to rust-colored appearance. The interface where the glass contact ended was clearly marked by a buildup of precipitates. However, the extent of precipitate coverage did not visually increase with the length of testing period. This observation agrees with the measured weight gains of the top and bottom canister sections which are constant throughout the 52-week test period.

b. Solution Analysis

The test solutions were analyzed either at the end of a test period or, for the continuous tests, during the sampling period. At the termination of a test, the waste package assemblage (WPA) was rinsed with 10 mL of high purity water, while for the continued tests, only the water collected in the bottom of the vessel was analyzed. Thus, the terminated tests contained a rinsed component that was not present in the continuous tests. A blank test was also run in the continuous mode. The purpose of this test was to evaluate whether any cross-contamination of radionuclides had occurred during sample handling and to serve as a check of the EJ-13 water composition collected during a test period. The solutions were analyzed for components of the glass frit, the EJ-13 water, and for radionuclides.

The as-analyzed solution compositions are presented in Table 2. This table presents the total amount of each element detected in solution and the total volume of solution measured in the vessel upon sampling. The sampled volume differs from the total amount of liquid

Table 2. Solution Analyses (Cations) for the W2 Test Series

Test Type	Test #	Test Period (weeks)	Solution ^b Volume (ml.)	Sample ID	Total Element in Solution (nanograms) ^a										
					Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U
Batch	W2-1	13	1.58	TF-384		8569	25389	226	17969	1906	11289	163169	969	44169	239
	W2-2	13	1.35	TF-385		13969	48169	476	21569	4269	1869	213469	2699	12169	549
	W2-3	26	2.34	TF-386		38369	75569	626	54169	7969	62769	42969	8899	368469	1469
	W2-4	26	3.78	TF-341		35869	64669	486	57469	6669	62769	42969	8899	316669	1469
	W2-5	39	4.17	TF-379	C1469	35869	81169	849	83369	9369	82969	427869	NA	378669	1659
	W2-6	39	4.17	TF-388	C1369	21669	71269	236	83969	8669	82969	427869	NA	194169	639
	W2-7	52	5.88	TF-488	C1369	23769	71869	246	81269	8669	82969	427869	NA	267269	1169
	W2-8	52	6.73	TF-489	C1369	25869	83669	586	83369	8769	83969	623169	NA	279769	1169
Continuous ^c	W2-9	5.5	6.6	TF-284	C1869	4869	2169	C169	8369	169	5869	61869	C329	28769	34
		13	6.22	TF-382	C1169	3469	9969	676	9369	649	17469	166269	1669	34169	45
		19.5	6.71	TF-326	C1669	4469	2369	C169	7669	1969	16469	181669	5469	25669	95
		26	1.16	TF-355	C1169	1969	5369	236	2669	699	4569	55769	1269	33669	118
		32.5	6.68	TF-351	C1169	1669	7669	616	C359	616	11169	31669	6669	76669	143
		39	1.26	TF-376	C1169	1269	17269	C126	7669	1769	6369	133369	NA	51169	249
		45.5	1.99	TF-395	C1169	2969	3769	296	C229	489	1369	24669	NA	15569	669
		52	1.33	TF-484	C1669	6569	21769	C169	8669	2769	11369	163269	NA	59669	469
Continuous ^c	W2-10	6.5	1.66 ^d	TF-439	C1269	6969	12569	296	5469	1669	5469	116269	2269	49369	159
		13	6.8	TF-285	C1669	4769	2669	C169	C329	269	16369	23669	C329	19269	68
		19.5	1.89	TF-383	C1169	2369	3669	746	C229	449	14569	24769	746	21569	146
		26	6.93	TF-327	C1169	1969	14669	516	8669	936	8969	182169	4369	34769	31
		32.5	1.85	TF-337	C1169	1269	11969	706	6969	836	3569	93669	1169	37369	129
		39	6.98	TF-352	C1169	1669	17369	216	4269	1269	12269	75769	3669	48969	139
		45.5	1.16	TF-376	C1169	1269	11969	299	4969	1859	6469	94169	NA	34769	109
		52	1.16	TF-398	C1169	1869	3169	329	C239	369	666	23369	NA	16669	669
Continuous ^c	W2-12	6.5	1.67	TF-485	C1769	3169	19369	129	5669	1369	5369	187969	NA	36669	165
		13	6.96	TF-446	C1269	3169	19369	129	7169	1869	7669	171269	3369	68969	278
		19.5	6.96	TF-329	C1169	6369	3669	186	4469	176	1369	63669	346	27669	659
		26	1.85	TF-339	C1669	2169	2969	C149	5169	269	1169	66369	516	31769	779
		32.5	1.63	TF-354	C1669	1669	6269	C169	3669	336	969	61369	676	26669	689
		39	1.16	TF-378	C1269	1569	9369	C126	4669	476	1469	68169	NA	36569	97
		45.5	1.16	TF-398	C1169	C349	11369	C369	4569	776	1669	82169	NA	33569	115
		52	1.22	TF-487	C1669	1369	13669	C169	7869	936	2369	119269	NA	48469	149
Continuous ^c		45.5	1.26	TF-428	C1169	1169	6469	129	3469	656	1669	7669	7669	37669	59
		52	1.87	TF-442	C1269	1169	18569	229	4269	849	2469	95169	1369	4669	136

Cont'd

Table 2 (Cont'd)

Test Type	Test #	Test Period (weeks)	Solution ^b Volume (mL)	Sample ID	Total Element in Solution (nanograms) ^a											
					Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	Sr	U
Reference EJ-13			1.475		1600	260	6170		185	580		70000		53900	57	
Continuous ^c	M2-11	6.6	0.8	TF-285	<1500	<320	6500	190	<150	560	15300	66200	3400	48300	<100	<0
Blank		13	0.89	TF-300	<1100	230	6100	300	<220	570	18900	67100	17200	45400	<100	<10
		19.5	0.88	TF-320	1900	280	9500		<210	770	16600	71100	9400	55200	50	<11
		28	0.88	TF-330	<1000	1400	8000	190	<260	850	17300	78200	6800	38600	<70	<13
		32.6	1.89	TF-353	<1700	1800	8900	<170	<330	890	2100	72200	1800	47800	<90	<16
		39	0.98	TF-377	2800	2300	9100	5600	<220	730	24100	69200	NA	43300	50	<11
		45.5	0.72	TF-397	<1100	<240	6700	3900	<230	420	1200	63200	NA	35200	57	<11
		52 ^d	0.56	TF-400	<1500	<500	5100	<150	<320	360	600	59800	NA	25300	<50	<10
		58.5	0.66		<1200	<350	5900	<150	<150	410	350	68700	970	49800	<50	<12
		85	0.88		<1200	<350	6400	190	<120	390	370	85000	1100	34600	<50	<12
EJ-13 Water	11/22/85		1.0		720	180	4400	<10	71	400	<5	45500	<20	36900	41	4
	5/14/86		1.0		750	180	4200	<10	70	400	<5	47000	<20	36500	41	4
	8/05/86		1.0		710	170	4100	<10	71	390	<5	48000	<20	36900	37	4
	11/03/86		1.0	TF-374	700		4100	<10	70	400	<5	48700	NA	36200	37	3
	1/31/87															

^aThe solution consists of 0.6 mL added at the beginning of the test plus the volume of EJ-13 added during the test. The elemental values have not been "blank" corrected, but they have been corrected for the volume of solution removed for alpha detection.

^bThe reported volume is that remaining in the test vessel upon sampling or termination. It is not the total solution added during testing.

^cValues are for each individual sampling period.

^dEstimated based on M2-10.

^eInlet line partially plugged thereby reducing the injected solution volume slightly.

NA = not analyzed, elements for which no values are entered have been analyzed but not yet reported.

injected during testing. This difference could be due to evaporative losses during handling or losses that occurred during injection. Analysis of the blank solutions suggest that most of the water loss occurred due to evaporation. This is because the amount of Na, Ca, and Mg detected in solution was near that predicted from the amount of EJ-13 water injected during a test period. For Si, the measured amount is usually less than predicted. The reason for this is not known, but the same observation was made during the F Test series [BATES-3].

The Ca and B levels in the blank solutions were larger than predicted from the input EJ-13 values for some sampling periods. This probably resulted from leaching of the gasket material, which during pre-test experimentation was shown to release small amounts of these elements when soaked in water. At no time was any significant amount of ^{237}Np , ^{239}Pu , or ^{241}Am detected in the blank solutions, indicating that a minimal risk of cross-contamination existed due to handling procedures.

The raw solution results can be used in two ways: (1) after correction for components present in the EJ-13 water the extent of glass reaction can be monitored, and (2) for the continuous tests an estimate of the composition of the water in contact with the waste package assemblage can be made. This water compositional information, in combination with the identification of alteration products formed on the test components, can be used to model the interactions that occurred during the test.

1. Glass Reaction

The extent of glass reaction is best measured by monitoring elements whose presence in solution can be associated mainly with the glass, as opposed to the EJ-13 water or the metal components of the system. Such elements include Li, U, ^{237}Np , ^{239}Pu , ^{241}Am , and to some extent B. Boron is present in the starting EJ-13 water at an insignificant level, but as noted previously, some B may be introduced into solution due to interaction with the gasket material. However, the data are presented assuming that most of the B comes from the glass.

Blank corrected solution results are given in Table 3 (glass frit and EJ-13 components plus actinides). These results demonstrate several things:

Table 3. Blank Corrected Solution Results from the N2 Test Series

Test #	Duration (weeks)	gm x 10 ⁻⁹								gm x 10 ⁻⁸	gm x 10 ⁻¹⁰	gm x 10 ⁻¹¹
		B	Ca	Li	Mg	Na	Si	Sr	U	237Np	238Pu	241Am
N2-1	13	6100	14900	17700	900	48000	(47000)	130	120	6.2	22.7	6.8
N2-2	13	13400	29700	24300	3200	95100	(79000)	440	700	13.9	40.4	14.9
N2-3	26	37600	53800	54300	6100	267000	144000	1200	2300	43.6	63.7	18.4
N2-4	30	34800	61300	52100	6200	211000	153000	1200	2000	62.0	73.0	22.9
N2-5	39	38800	54100	62000	6800	224400	142000	1400	4600	42.3	64.2	16.6
N2-6	39	23500	44200	36400	3100	126400	(41000)	600	400	14.3	22.0	6.4
N2-7	52	21700	36300	50000	3200	264800	(41300)	800	2000	19.4	37.7	10.4
N2-8	52	24300	28500	54700	3400	222400	(28800)	800	1300	26.7	70.0	12.7
N2-9	13	7700	(600)	15400	(400)	24800	(54000)	140	70	3.9	11.3	3.1
	26	13400	18200	25500	1100	39700	(105300)	400	300	11.8	17.8	5.1
	39	15700	80400	83100	2300	62400	(88800)	600	700	15.5	21.7	
	52	23700	43300	41700	4200	107800	(122400)	900	2200	30.6	26.4	
	65	29200	45400	40000	4700	105700	(163600)	1040	2300	33.3	20.7	
N2-10	13	6500	(6000)	800	(500)	(83800)	(60000)	140	10	0	0	0
	26	9000	8000	15800	100	(30500)	(100600)	290	140	3.0	5.6	2.0
	39	11300	24600	24700	1200	(3100)	(140700)	400	640	6.3	9.5	3.7
	52	13500	27500	20700	1600	(22400)	(197100)	570	1000	8.2	11.6	4.6
	65	16100	30500	30000	2400	30000	(231300)	740	1400	8.2		
N2-12	13	7200	(6700)	9400	(800)	(30200)	(50400)	100	50	2.0	22.4	4.6
	26	8500	(4800)	17700	(1200)	(31200)	(101500)	240	80	4.6	29.1	6.9
	39	9000	8000	29000	(700)	27700	(129300)	300	250	6.5	35.9	8.3
	52	11300	14300	30300	(400)	59100	(154500)	400	430			

- (1) All elements except Si show a net release from the glass. Silicon shows a net release in Tests N2 #3, 4, and 5, but has a fairly constant net abstraction from solution in the remaining tests;
- (2) An intercomparison of the batch test results indicates an apparent trend of increasing reaction through 26 weeks, followed by little additional reaction thereafter (Fig. 2). This trend is borne out by a consistency in the release of all elements. The trend may be real, but more likely, when interpreted in conjunction with all the test data, is skewed by increased reaction in tests N2 #3, 4, and 5.

Fig. 2. $(NL)_i$ from N2 Batch Tests, $\circ$ = B, Δ = Li, $\square$ = Na, $\times$ = wt loss

- (3) Release values (Table 4) were calculated normalized to the total surface area of the glass and the mass fraction of each element in the glass. These standard (NL)_i values indicate that the alkali elements Li and Na are released from the glass at nearly equivalent rates which are larger than that calculated for B or the actinide elements. Note the normalized release of B is nearly equivalent to that of Np which is greater than U which is greater than Pu and Am. The plotted releases (Fig. 2) are calculated based on the measured amount of each element released from the waste package assemblage after rinsing. However, if the amount of Pu, Am, and U remaining with the metal components of the WPA is measured via complete stripping (Table 4) of the metal, and it is assumed that the release of these elements is associated mainly with the glass that is in contact with metal, then modified (NL)_{Pu,Am,U} values can be calculated, which are much nearer to the values of B and Np.

In the continuous tests, where the components have not been rinsed before the solution is analyzed, several elements, including Ca, Mg, Na, and Si, are depleted in the analyzed solution compared to the starting EJ-13 water. Normalized release values for Li in the continuous tests are plotted in Fig. 3. While these values will be slightly lower than the batch tests due to the rinse component, it is seen that there is continuous release from the glass through the 65-week time period. For Li, the element that apparently is least affected by interaction with test components, the normalized release values after 52 weeks of testing are highlighted in Table 5. The values for the continuous tests have been calculated assuming that 7000 ngm of Li will be rinsed from the waste package assemblage to make the continuous values comparable with the batch tests. The 7000 ngm value was taken from measured differences between batch and continuous tests in the F-1 Test series [BATES-3]. The consistency of these values at 52 weeks, combined with the continued increasing reaction trend observed in the continuous tests, suggests that the plateau in reaction progress seen by comparing batch test results is due to a physical effect that accelerated the reaction in tests N2, 3, 4, and 5 compared with the other tests. This possibility will be discussed later.

Table 4. Normalized Release of Elements from the Glass in the N2 Tests

Test #	Duration (weeks)	Solution Only							Solution Plus Acid Strip		
		(NL) _{Li}	(NL) _B	(NL) _{Na}	(NL) _{Np}	(NL) _{Pu}	(NL) _{Am}	(NL) _U	(NL) _{Pu}	(NL) _{Am}	(NL) _U
N2-1	13	0.7	0.2	0.4	0.2	0.008	0.008	0.01			
N2-2	13	0.9	0.6	0.9	0.4	0.016	0.018	0.06	0.3	0.4	0.8
N2-3	28	2.0	1.3	1.9	1.3	0.024	0.022	0.21			
N2-4	28	2.0	1.3	2.0	2.0	0.028	0.028	0.19	0.7	1.1	0.9
N2-5	39	2.4	1.4	2.1	1.3	0.024	0.020	0.42			
N2-6	39	1.4	0.8	1.1	0.4	0.008	0.008	0.04	0.6	0.7	0.7
N2-7	52	1.9	0.8	1.9	0.6	0.014	0.012	0.18			
N2-8	52	2.0	0.8	2.1	0.8	0.020	0.016	0.12	0.6	0.7	0.7
N2-9	13	0.6	0.3		0.1	0.004	0.004	0.01			
	28	1.0	0.6		0.4	0.007	0.006	0.03			
	39	1.2	0.6		0.5	0.008		0.06			
	52	1.6	0.8		0.9	0.009		0.20			
	65	1.8	1.0		1.0	0.010		0.21			
N2-10	13	0	0.2		0	0	0	0			
	28	0.6	0.3		0.1	0.002	0.002	0.01			
	39	0.9	0.4		0.2	0.003	0.004	0.06			
	52	1.1	0.6		0.2	0.004	0.005	0.10			
	65	1.4	0.8		0.2			0.12			
N2-12	13	0.3	0.2		0.1	0.003	0.000	0			
	28	0.7	0.3		0.1	0.003	0.000	0.01			
	39	1.1	0.3		0.2		0.010	0.02			
	52	1.3	0.4					0.04

Fig. 3. $(NL)_{Li}$ Continuous Tests, O = N2 #9, Δ = N2 #10, $\square$ = N2 #12

Table 5. Normalized Lithium Release through 52 Weeks of Testing

Test #	$(NL)_{Li}$, (g/m ²)
N2 #7	1.9
N2 #8	2.0
N2 #9	1.8
N2 #10	1.4
N2 #12	1.6

11. Solution Composition

The composition of the solution that was in contact with the waste package assemblage can be estimated from the results of the continuous tests. This solution composition is important because it is the interaction between the leachate and the waste package components that results in the formation of alteration products that are more stable than the glass and may over the course of the repository time period influence which reactions will occur. In the continuous tests the volume of water collected in the test vessel after WPA contact was measured and its composition was determined. While the process by which the water was removed from the WPA was a combination of evaporation and dripping, the collected water should be somewhat representative of the water as it reacted with the WPA. Indeed, it is unlikely that the composition of the water that collected on the top and bottom sections of the waste package assemblage had exactly the same composition due to the flow characteristics of the test. Regardless, the elemental concentrations of the leachates in the continuous tests are given in Table 6. These values have been calculated by assuming that all the water injected during a test period has contacted the WPA, reacted, and was released and collected in the test vessel. The solution collected in the test vessels consisted of injected EJ-13 water that had reacted with the waste package assemblage, plus 0.5 mL of EJ-13 water that was placed in the bottom of the test vessel before the test began and at each sampling period. The elemental concentrations were determined by subtracting the volume and compositional effect of the EJ-13 water that was added initially to the bottom of the test vessels before the test and at each sampling period, from the analyzed results, and then dividing the remaining elemental values by the volume of injected liquid. Values have been combined for two 6.5-week periods because of inconsistent releases from the waste package assemblage for one 6.5-week period. For example, in the N2-10 test no liquid dripped from the waste package assemblage during the first two test periods (ref. Li and actinide solution values), although the waste package assemblage was visually reacted to the same degree as the other tests. These solution compositions will be used with information obtained during the analyses of the test components to provide input to the modeling effort.

Table 6. Composition of Leachates Collected during the Continuous N2 Tests

Test #	Sampling Period (weeks)	Solution Composition (ppm)							
		B	Ca	Li	Mg	Na	Si	Sr	U
Initial	EJ-13	0.2	4.5	0.1	0.4	48	37	0.04	0.004
N2-9	13	4.1	4.0	8.0	0.2	61	9.0	0.1	0.04
	26	3.1	13.9	5.2	1.2	56	11	0.2	0.12
	39	1.3	10.6	4.0	1.0	60	46	0.1	0.21
	52	4.2	10.8	4.5	1.4	71	20	0.2	0.77
	65	3.0	5.3	2.8	0.7	47	16	0.1	0.08
N2-10	13	3.5	1.2	0.2	0.2	5.3	1.8	0.1	0
	26	1.5	11.4	8.0	0.7	76	18	0.1	0.07
	39	1.3	12.8	4.6	0.9	62	20	0.1	0.26
	52	1.3	5.8	2.6	0.6	38	8.2	0.1	0.22
	65	1.5	8.8	3.6	0.8	75	20	0.1	0.17
N2-11	13	3.9	0.8	4.8	0	33	11	0	0.03
	26	0.9	5.3	4.3	0.2	48	11	0.1	0.02
	39	0.8	10.7	5.8	0.7	79	23	0.1	0.08
	52	1.0	7.5	3.9	0.6	64	24	0.1	0.11

c. Analysis of Test Components

To characterize the interactions that have occurred during testing, the components of the test have been examined using SEM/EDS and XRD. The purpose of such characterization is (1) in combination with the solution results, to provide a description of the reaction progress; and (2) to catalog and, if possible, identify alteration products that form during the course of the reaction. Both of these issues need to be addressed to provide input to be used in projecting the performance of the waste form to repository time frame.

At the end of a test period, the test components were separately rinsed with high-purity water and placed in a dust-free environment to dry. The weight change for each component was determined and then

components from selected tests (N2 #s 2, 4, 6, and 8) were analyzed. The components from the remaining tests (N2 #s 1, 3, 5, and 7) were maintained in storage to be analyzed using additional techniques as they become available. The methods and rationale used to perform and interpret the SEM/EDS analyses have been described previously [BATES-3]. The specimens were photographed using a low resolution optical microscope in order to map the surface and to identify regions of interest. The glass samples were then examined using SEM/EDS to obtain a qualitative description of the phase present. Micrographs and EDS spectra were taken extensively. After removal from the SEM, phases amenable for XRD study, e.g., unique composition, crystalline structure, large enough, were picked from the surface and analyzed.

SEM/EDS can be used to provide a description of the phases and alteration products, but cannot be used for absolute identification. Additionally, after exposure to the coating process and vacuum conditions of the SEM, the sample may be altered to make examination by other spectroscopic methods such as infrared or Raman spectroscopy difficult, if not misleading. For this reason not all of the samples were immediately analyzed.

The canister components were also photographed and examined via SEM/EDS and XRD. They were then acid-stripped to remove all residual radioactivity, mounted in epoxy, polished, and subjected to an oxalic acid etch process to measure the extent of sensitization that occurred during the heat treatment step.

These component analyses have resulted in an extensive collection of micrographs and spectra. In the following discussions, only a representative selection of these analyses will be presented to provide a description of the reaction process. A complete compilation of the data set is available for review at ANL.

i. Glass

The weight change measurements for the glass samples are given in Table 1. All samples lost weight, although, as shown in Fig. 1 the glass samples were covered extensively with reaction products. The weight loss normalized to the surface area of the specimens, $(NL)_{wt}$, closely followed the reactive trend observed for the glass as determined by

the solution results (see Fig. 2), e.g., those tests in which the largest weight loss was observed also had a concomitant release of glass components to solution. The $(NL)_{wt}$ in all tests was about 50% the value for $(NL)_B$.

All of the glass surfaces (top and bottom) had the general appearance shown in Fig. 1. The top surfaces gave the appearance of being slightly more reacted than the bottom mainly due to an apparently greater coverage of the rust-colored precipitates and the lighter appearance of the glass where there was contact between glass and metal. This appearance of reduced reaction likely resulted because the interface between the glass and the metal was better maintained on the bottom section due to the weight of the glass, while a looser interface existed at the top. However, the nature of the reaction products was the same for both the top and bottom sections.

The greatest extent of precipitate buildup occurred around the circumference of the holes where the metal contacted the glass. Precipitate buildup typical of that located in the non-metal contact regions of the glass is shown in Fig. 4. Such regions are where standing water collected during the test and the bulk of the precipitates were composed of Fe or Fe/Ni/Cr/Mn combined with Si and a smaller amount of Al. The compositions of these alteration products as determined by EDS (Figs. 5 and 6) were not unique, varying continuously over a range between pure Fe and Fe-enriched Si/Al. XRD of the main regions of precipitate buildup indicated both $\alpha\text{-Fe}_2\text{O}_3$ and FeO(OH) to be present; however, no pattern was obtained that could be attributed to the Si/Al phase.

In addition to these prominent regions of phase buildup, other alteration products were located in a random fashion over the glass surface. In several instances, only a limited number of each phase was found on the surface. In many cases, the phases were of micron size and were too small for XRD analysis, and only SEM/EDS information has been collected to date. Several representative micrographs of alteration phases are shown in Figs. 5 and 6.

Fig. 4. Secondary Electron Photomicrograph of the Bottom Glass Surface from Test N2 #8. Magnification 19x.

(a)

(b)

(c)

(d)

Fig. 5. Photomicrographs and EDS Spectra of Alteration Products Shown in (a) the Center of Fig. 4, Magnification 700x; (b) the Lower Center of Fig. 4, Magnification 350x; (c) the Upper Center of Fig. 4, Magnification 1500x; and (d) the Upper Center of Fig. 4, Magnification 1500x.

Fig. 6. Photomicrograph and EDS Spectra of Alteration Products that Formed on the Top Glass Surface from Test N2 #6, Magnification 3000x.

ii. Canister Sections

As with the glass, the greatest buildup of reaction products was found in regions where standing water could accumulate. Such regions existed around the rims of the punched holes and at the edge of the glass/metal interface. Selected regions of reaction product buildup are shown in Fig. 7. Iron oxides and hydroxides together with an Al/Si mat (not shown) were the prominent reaction products. EDS spectra of localized reaction products are shown in Fig. 8.

After the canister sections were examined using SEM/EDS, they were acid stripped, mounted in epoxy, and subjected to an oxalic acid etch to determine the extent of sensitization for samples N2 #s 2, 4, 6, and 8, a reference sample, and the canister sections from the analogue experiment. Typical micrographs of the metal sections are shown in Fig. 9. Different degrees of sensitization were observed for different groups of samples. The entire surface of the analogue canisters showed only random pitting that was not associated with grain boundaries and represented non-sensitized metal (Fig. 9c). Samples from test N2 #6, and N2 #8 showed extensive sensitization of the bulk metal, but significantly less sensitization near the flat surfaces of the canister that were in contact with the glass (Fig. 9b). The gap where there was incomplete sensitization ranges between 30 and 40 μm for these samples. Samples from tests N2 #2 and N2 #4 also showed complete sensitization of the bulk, but showed a non-sensitized gap of only 10-15 μm (Fig. 9a). Note that the gap only existed on the surfaces of the steel that had been subjected to some processing (cold working) during manufacturing which was not altered during component preparation procedures. Only where the edges of the canister sections had been machined did the sensitization extend to the surface of the metal.

d. Discussion

A complete discussion of the results is presented in the topical report "Application of the NNWSI Unsaturated Test Procedure to Actinide Doped SRL 165 Type Glass." A synopsis of the findings are:

(a)

(b)

Fig. 7. (a) Buildup of Precipitates at the Interface Around the Circumference of the Punched Holes in the Stainless Steel, Bottom Canister, Test N2 #2, Magnification 250x, Marker = 55 μm .

(b) Higher Magnification Micrograph (1200x) of the Central Region of Fig. 4a, Marker = 5 μm .

Both micrographs are SEM images using secondary electrons.

Fig. 8. EDS Spectra of Selected Areas Shown in Fig. 7. The areas of the sample which correspond to the spectra are shown in Fig. 7.

(a)

(b)

(c)

Fig. 9. Micrographs of Polished Cross-Sections of Etched Stainless Steel Waste Form Holders for the N2 Test. (a) N2 #4 bottom canister; (b) N2 #8 top canister; (c) analog III #1, top canister. All micrographs were collected using backscattered electron imaging and the magnification is 375x.

- (1) The extent of glass reaction is dependent mainly on the interaction that occurs between the glass, the metal, and standing water. In all tests heat treatment of the metal resulted in the extensive formation of iron oxide/hydroxide and alumina silicate reaction products. For those tests which had the greatest degree of sensitization, the extent of glass reaction was greatest;
- (2) The (NL) of the alkali metals was the largest of the elements measured and was not much different from that observed in the F-1 series of tests (only localized heat treatment near the welded pins existed in these tests) [BATES-3]. However, the release of elements released by matrix breakdown of the glass, e.g., B, actinides, was comparatively greater in the N-2 tests because the matrix breakdown promoted by the presensitized metal was more widespread in the N2 test series than in the F-1 series where only the weld-affected regions showed enhanced reaction; and
- (3) The release of Pu and Am from the glass was controlled mainly by breakdown of the glass matrix in the areas where glass metal contact occurred. A large fraction of the actinides remained with the metal surfaces and could only be removed by acid stripping. The amount of Pu and Am actually released, including a water rinse, resulted in $(NL)_{Am, Pu}$ of $<0.01 \text{ g/m}^2$, and that for the testing periods to date, no saturation of the capacity of the metal to effectively remove actinides from solution was observed.

3. Unsaturated Test N-3

The N3 Unsaturated Test will be done using ATM-10 glass (simulated West Valley glass containing actinides plus ^{99}Tc) that was received from the MCC. Preparations and inspections of the glass and test components have been completed, and the test was started 7/6/87 according to the matrix shown in Table 7.

Table 7. Test Matrix and Component Weights for N3 Test Series

Description	Test #	Vessel #	Oven Position	Test Period (weeks)	Date Started	Date Stopped	Sample #	Weight Glass IN	Weight Glass OUT	Δ Mass (μ g)	SA Glass	Top Canister IN (gm)	Top Canister OUT (gm)	Δ Mass
Batch	N3-1	ANL-49	3	13	7/06/87	10/05/87	202	10.42933				3.16609		
Batch	N3-2	ANL-50	4	13	7/06/87	10/05/87	203	10.50925				3.15144		
Batch	N3-3	ANL-51	5	26	7/06/87	1/04/88	204	10.67520				3.16509		
Batch	N3-4	ANL-52	6	26	7/06/87	1/04/88	205	10.46050				3.18516		
Batch	N3-5	ANL-53	7	39	7/06/87	4/04/88	206	10.65264				3.13676		
Batch	N3-6	ANL-54	8	39	7/06/87	4/04/88	211	9.83140				3.14192		
Batch	N3-7	ANL-55	9	52	7/06/87	7/04/88	212	10.72120				3.16627		
Batch	N3-8	ANL-56	10	52	7/06/87	7/04/88	213	10.40990				3.17604		
Continuous	N3-9	ANL-47	1	6.6	8/20/87		214	10.35839				3.17929		
		ANL-		13	8/20/87									
		ANL-		19.5	8/20/87									
		ANL-		26	8/20/87									
		ANL-		32.5	8/20/87									
		ANL-		39	8/20/87									
		ANL-		45.5	8/20/87									
		ANL-		52	8/20/87									
Continuous	N3-10	ANL-48	2	6.6	8/20/87		215	10.57790				3.14283		
		ANL-		13	8/20/87									
		ANL-		19.5	8/20/87									
		ANL-		26	8/20/87									
		ANL-		32.5	8/20/87									
		ANL-		39	8/20/87									
		ANL-		45.5	8/20/87									
		ANL-		52	8/20/87									

Cont'd

Table 7 (Cont'd)

Bottom Canister IN (gm)	Bottom Canister OUT (gm)	Δ Mass	Total Vessel IN (gm)	Total Vessel OUT (gm)	Δ Mass	Water Added During Testing
----------------------------------	-----------------------------------	------------------	-------------------------------	--------------------------------	------------------	-------------------------------------

4.12108

4.12082

4.10002

4.08035

4.10059

4.11724

4.11010

4.10019

4.10150

4.09738

Cont'd

Table 7 (Cont'd)

Description	Test #	Vessel #	Oven Position	Test Period (weeks)	Date Started	Date Stopped	Sample #	Weight Glass IN	Weight Glass OUT	Δ Mass (μ g)	SA Glass	Top Canister IN (gm)	Top Canister OUT (gm)	Δ Mass
Blank	H3-11	ANL-57	11	8.5	8/28/87		none							
				13	8/28/87									
				19.5	8/28/87									
				26	8/28/87									
				32.5	8/28/87									
				39	8/28/87									
				45.5	8/28/87									
				52	8/28/87									
Continuous	H3-12		3	8.5		21g	18.58410							
				13										
				19.5										
				26										
				32.5										
				39										
				45.5										
				52										

Cont'd

Table 7 (Cont'd)

Bottom Canister IN (gm)	Bottom Canister OUT (gm)	Δ Mass	Total Vessel IN (gm)	Total Vessel OUT (gm)	Δ Mass	Water Added During Testing
----------------------------------	-----------------------------------	------------------	-------------------------------	--------------------------------	------------------	-------------------------------------

Since the glass received from the MCC had to be remelted to cast the waste form specimens, the composition and redox state may be different from the reported values [MAUPIN]. The physical properties of the glass are being remeasured, and comparative leach tests are being performed to determine whether there is any difference in reactivity between the as-received and cast glass. A core was taken from bar ATM-10-2 and cut into ten glass disks and a core was taken from sample 20₂ and cored into nine glass disks. MCC-1 type leach tests have been initiated using DIW and 90°C. Tests will be run in duplicate with periods of 56 and 91 days. The test matrix is given in Table 8.

B. NNWSI Parametric Experiments
(QA level III, activity #D-20-29)

Because the NNWSI Unsaturated Test rigidly sets many of the test parameters, the effect that each parameter may have on the final radio-nuclide release needs to be studied. This is being done in parametric experiments. A description, purpose, and status of the parametric experiments in progress are given in Table 9. Each of the ongoing experiments has been discussed in detail previously [STEINDLER, BATES-1, BATES-2] and are continuing as scheduled. Selected parametric experiments are discussed below.

1. P-VI

Unsaturated experiments of unirradiated UO₂ in different configurations have been ongoing. The 6.5-week sampling periods have been extended to 26 weeks in an attempt to smooth out short-term irregularities in U release and to increase the volume of solution available for analysis. The last sampling period was 4/23/87 and the updated results are presented in Tables 10, 11, and 12.

The experiments are sampled in the following manner:

- 1) The UO₂ plus Zircaloy holder are removed from the vessel and placed temporarily in a covered Teflon container;
- 2) the vessel solution is transferred to a liquid polyethylene (LPE) container;
- 3) approximately 10 mL of DIW is added to the vessel (including Teflon stand) and acidified with HNO₃ to ~1% by volume;

Table 8. ATM-18 Comparative MCC-1 Leach Tests

Experiment Type	Expt #	Sample #	Expt Duration (days)	Date In	Date Out	Glass Thickness	Glass Diameter	Glass SA (cm ²)	Total SA Vessel	Glass Mass In (gm)	Glass Mass Out (gm)	Δ Mass
ATM-18 Glass as received ATM-18-2	G-567	1000	56	7/29/87				472.05		0.35128		
		1001								0.35687		
	G-568	1002	56	7/29/87				481.48		0.35968		
		1003								0.36484		
	G-569	1004	91	7/29/87				477.00		0.36289		
		1005								0.35986		
	G-570	1006	91	7/29/87				483.20		0.31144		
		1007								0.36321		
	Archive	1008								0.36893		
	Archive	1009								0.41898		
ATM-18 Glass once cast #28-6	G-571	1010	56	7/29/87				476.94		0.35745		
		1011								0.34722		
	G-572	1012	56	7/29/87				473.48		0.35147		
		1013								0.34045		
	G-573	1014	91	7/29/87				477.59		0.35799		
		1015								0.34364		
	G-574	1016	91	7/29/87				487.01		0.36639		
		1017								0.39253		
	Archive	1018								0.34836		

Table B (Cont'd)

Leachate pH In	Leachate pH Out	Mass EJ-13 In (gm)	Total Mass In	Total Mass Out	Δ Mass	LPE Mass	Surface Analyses			
							Type	Date	Type	Date
5.58		47.17	155.26							
5.58		48.17	156.27							
5.58		47.76	155.13							
5.58		48.37	156.73							
5.58		47.56	155.74							
5.58		47.34	155.49							
5.58		47.76	156.02							
5.58		48.78	156.99							

Table 9. Description, Purpose, and Status of Parametric Experiments

Experiment #	Description	Purpose	Status
P-II	Regular-sized glass waste form, no ss holder, 0.075 mL J-13/ 3.5 days, continuous and batch tests	To study the release from glass only	Initiated 2/20/84. Batch tests completed 2/18/85. Continuous tests in progress
P-III	Half-sized glass waste form, ss holder, 0.075 mL and EJ-13/ 3.5 days, continuous and batch tests	To study the effect of waste form surface area by reducing the as-cast surface area by half	Initiated 12/6/84. Batch tests completed 12/5/85. Continuous tests in progress
P-IV	Half-sized glass waste form, ss holder, 0.0375 mL and EJ-13/ 3.5 days, continuous and batch tests	To study the effect of drop size by reducing the amount of water added and the as-cast surface area by half	Initiated 2/18/85. Batch tests completed through one year. Continuous tests in progress
P-V	Regular-sized glass waste form, ss holder, 0.075 mL and EJ-13/ 14 days, continuous and batch tests	To study the effect of lengthening the time interval between water additions	Initiated 6/10/85. Batch tests completed through one year. Continuous tests in progress
P-VI	Pressed and sintered UO ₂ pellets in various forms, Zircaloy holder, 0.075 mL and EJ-13/ 3.5 days and 0.0375 mL/7 days, continuous tests	To study the release of U from nonreacted fuel pellets under Unsaturated Test conditions	Initiated 4/25/85. Continuous tests in progress
P-VII	UO ₂ pellets soaking in EJ-13 water at ambient temperature, batch tests	To look for reaction product formation	Three- and nine-month batch test terminated

Cont'd

Table 9 (Cont'd)

Experiment #	Description	Purpose	Status
P-VIII	Regular-sized glass waste forms in presensitized ss holders, 0.075 mL EJ-13/3.5 days, continuous and batch tests	To study the effect of presensitizing the ss waste form holder	Initiated 2/27/86. Batch tests completed through six months. Continuous tests in progress
P-IX	A variety of glasses (polished, as-cut, powdered) in a controlled atmosphere chamber	To study the effect of the the degree of water saturation or glass reaction	Initiated. Selected samples terminated after ~five months
P-X	Basaltic and SRL-165 glass vapor hydration tests	To study the use of vapor phase hydration and natural analogues in projecting long-term glass reaction	Review of existing samples and literature initiated
P-XI	SRL 165 U/A glass, WV U/A glass, and ATM-1c/8 hydration	To study the effect of time and temperature on the hydration of nuclear waste glasses under saturated conditions	Sample preparation in progress, preliminary matrix completed

Table 10. Test Conditions for UO₂ Tests

Description	Test No.	Vessel No.	Test Period (weeks)	Date Started	Date Stopped	UO ₂ Weight In	UO ₂ Weight Out	Δ Mass	Total SA	Zircaloy Weight In	Zircaloy Weight Out	Δ Mass	Total Vessel In (gm)	Total Vessel Out (gm)	Δ Mass (gm)
20 sliced discs @ .875 mL/ 3.5 days	1		8.0	4/25/85	6/28/85	29.5228			48.69	2.3858			347.13	NA	
			5.0	6/28/85	7/25/85								355.97	356.18	0.19
			6.5	7/25/85	9/09/85								355.49	356.26	0.77
			6.5	9/09/85	10/24/85								355.36	356.14	0.78
			6.5	10/24/85	12/09/85								356.27	356.94	0.67
			6.5	12/09/85	1/23/86								356.17	356.81	0.64
			6.5	1/23/86	3/10/86								356.18	356.84	0.66
			6.5	3/10/86	4/24/86								356.18	356.92	0.74
			26	4/24/86	10/23/86								356.25	359.46	3.21
			26	10/23/86	4/23/87								356.39	359.42	3.03
Crushed UO ₂ @ .875 mL/ 3.5 days	3		8.0	4/25/85	6/28/85	19.85#2			348	2.3681			337.54	--	--
			5.0	6/28/85	7/25/85								--	--	--
			6.5	7/25/85	9/09/85								346.55	347.34	0.79
			6.5	9/09/85	10/24/85								346.66	347.44	0.78
			6.5	10/24/85	12/09/85								346.79	347.54	0.75
			6.5	12/09/85	1/23/86								346.74	347.56	0.82
			6.5	1/23/86	3/10/86								346.76	347.61	0.85
			6.5	3/10/86	4/24/86								346.80	347.83	0.83
			26	4/24/86	10/23/86								346.84	350.26	3.42
			26	10/23/86	4/23/87								346.82	349.93	3.11
Terminated	4		8.0	4/25/85	6/28/85	18.2584			385	2.3764			334.14	--	--
			5.0	6/28/85	7/25/85								342.86	343.5	0.64
			6.5	7/25/85	9/09/85								343.34	344.17	0.83
			6.5	9/09/85	10/24/85								343.46	344.27	0.81
			6.5	10/24/85	12/09/85								343.43	344.18	0.75
			6.5	12/09/85	1/23/86								343.30	344.17	0.81
			6.5	1/23/86	3/10/86								343.50	344.13	0.63
			6.5	3/10/86	4/24/86								343.25	343.50	0.25
			26	4/24/86	10/23/86								343.68	345.25	1.57

Cont'd

Table 18 (Cont'd)

Description	Test No.	Vessel No.	Test Period (weeks)	Date Started	Date Stopped	UO ₂ Weight In	UO ₂ Weight Out	Δ Mass	Total SA	Zircaloy Weight In	Zircaloy Weight Out	Δ Mass	Total Vessel In (gm)	Total Vessel Out (gm)	Δ Mass (gm)
2 pellets 0.875 mL/ 3.5 days	5		0.0	4/25/85	6/20/85	47.9550			22.10	3.8394			368.47	--	--
			5.0	6/20/85	7/25/85								--	--	--
			6.5	7/25/85	9/09/85								368.76	369.61	0.85
			8.5	9/09/85	10/24/85								368.88	369.64	0.76
			10.5	10/24/85	12/09/85								368.97	369.74	0.77
			12.5	12/09/85	1/23/86								368.75	369.52	0.77
			14.5	1/23/86	3/10/86								368.85	369.92	1.07
			16.5	3/10/86	4/24/86								368.97	369.89	0.92
			20	4/24/86	10/23/86								369.02	372.64	3.62
			26	10/23/86	4/23/87								368.82	372.23	3.41
	6		0.0	4/25/85	6/20/85	48.3599			22.23	5.8539			367.45	--	--
			5.0	6/20/85	7/25/85								--	--	--
			6.5	7/25/85	9/09/85								375.88	376.86	0.98
			8.5	9/09/85	10/24/85								375.88	376.85	0.97
			10.5	10/24/85	12/09/85								375.88	376.76	0.88
			12.5	12/09/85	1/23/86								375.73	376.49	0.76
			14.5	1/23/86	3/10/86								376.84	376.27	0.57
			16.5	3/10/86	4/24/86								375.93	376.16	0.23
			20	4/24/86	10/23/86								376.01	378.90	2.89
			26	10/23/86	4/23/87								376.21	378.76	2.55
2 pellets 0.8375 mL/ 14 days	7		13	4/25/85	7/25/85	47.5955			21.92	3.8485			368.68	--	--
			13	7/25/85	10/24/85								374.89	375.56	0.67
			13	10/24/85	1/23/86								375.17	ND	ND
			13	1/23/86	4/24/86								376.01	375.48	0.53
			20	4/24/86	10/23/86								376.19	376.91	0.72
			26	10/23/86	4/23/87								376.00	376.58	0.58
	8		13	4/25/85	7/25/85	47.7734			22.10	3.8498			368.76	--	--
			13	7/25/85	10/24/85								375.08	375.55	0.51
			13	10/24/85	1/23/86								375.68	376.00	0.39
			13	1/23/86	4/24/86								376.10	376.79	0.63
			20	4/24/86	10/23/86								376.35	376.13	0.22
			26	10/23/86	4/23/87								376.32	376.69	0.37

*The metal closure fitting was wet during weighing.

Table 11. Solution Analysis from UO₂ Parametric Tests Series P-VI

Test #	Analysis #	Solution ^a Vol (mL)	Total Nanogram U
PMP 8U-1	TF-174	-	26,200
	TF-189	0.19	21,600
	TF-214	0.77	449,300
	TF-229	0.78	263,700
	TF-245	0.67	129,300
	TF-260	0.64	74,500
	TF-276	0.66	1,001,000
	TF-294	0.74	2,160,000
	TF-356	3.21	273,700
	TF-432	3.03	168,100
	TOTAL		4,576,000
PMP 8U-2	TF-175	-	11,000
	TF-190	0.64	25,700
	TF-215	1.01	388,100
	TF-230	0.93	201,300
	TF-246	0.81	56,100
	TF-261	0.83	38,300
	TF-277	0.66	46,900
	TF-295	0.80	1,945,000
	TF-357	2.63	1,490,000
	TF-433	3.40	104,800
	TOTAL		4,308,000
PMP 8U-3	TF-176	-	280
	TF-191	-	5,900
	TF-216	0.79	71,300
	TF-231	0.78	126,300
	TF-247	0.75	88,000
	TF-262	0.82	31,100
	TF-278	0.85	194,600
	TF-296	0.83	130,700
	TF-358	3.42	265,800
	TF-434	3.31	138,700
	TOTAL		1,053,000

Cont'd

Table 11 (Cont'd)

Test #	Analysis #	Solution ^a Vol (mL)	Total Nanogram U
PMP 8U-4	TF-177	-	2,680
	TF-192	0.64	7,700
	TF-217	0.83	9,200
	TF-232	0.81	9,670
	TF-248	0.75	193,100
	TF-263	0.81	113,200
	TF-279	0.63	623,800
	TF-297	0.25	967,000
	TF-359	1.57	1,400,000
	Terminated	TOTAL	3,326,000
PMP 8U-5	TF-178	-	2,847
	TF-193	-	1,220
	TF-218	0.85	109,400
	TF-233	0.76	36,100
	TF-249	0.77	33,800
	TF-264	0.77	19,400
	TF-280	1.07	321,700
	TF-298	0.92	71,000
	TF-360	3.62	103,100
	TF-435	3.45	478,000
		TOTAL	1,176,600
PMP 8U-6	TF-179	-	2,610
	TF-194	-	2,947
	TF-219	0.78	30,400
	TF-234	0.77	41,900
	TF-250	0.70	798,000
	TF-265	0.76	1,390,800
	TF-281	0.43	55,800
	TF-299	0.22	593,000
	TF-361	2.95	3,760,000
	TF-436	3.14	389,000
		TOTAL	7,065,000
PMP 8U-7	TF-195	-	1,059
	TF-235	0.67	301,900
	TF-266	-	95,300
	TF-300	0.39	665,000
	TF-362	0.72	1,070,000
	TF-437	0.52	225,000
		TOTAL	2,358,000

Cont'd

Table 11 (Cont'd)

Test #	Analysis #	Solution ^a Vol (mL)	Total Nanogram U
PMP 8U-8	TF-196	-	875
	TF-236	0.51	525,000
	TF-267	0.39	246,600
	TF-301	0.63	264,000
	TF-363	0.78	5,950,000
	TF-438	0.37	2,107,000
		TOTAL	9,093,000

^aThis is the total amount of EJ-13 water added drop-wise during an experimental period. It does not include 0.5 mL of EJ-13 that is added every sampling period before the vessels are sealed.

NOTE - The total nanograms of uranium release is based on an acid strip of the vessel and TeflonTM stand. The concentration of uranium in solution cannot be calculated in the experiment as conducted.

Table 12. Analysis of Solution^a Composition from P-VI Experiments (4/23/87 Sampling Period)

Experiment #	Composition (total nanograms) of Leachate at the 4/23/87 Sampling Period									
	Al	B	Ca	Fe	Li	Mg	Mn	Na	Si	K
1	1500	900	3300	230	200	840	430	177400	53500	10400
2	<1400	860	4800	330	230	1000	200	161700	66000	10600
3	<1300	1400	4000	500	800	3900	600	180000	33000	8400
5	<1300	970	2400	500	200	800	1200	191300	52900	9700
6	2800	1000	5400	360	190	800	240	173600	55600	10500
7	1700	500	6500	570	<150	400	61700	56100	11100	<7900
8	13400	2200	3900	800	<150	440	700	40100	11700	<7900

^aRaw solution compositions, not corrected for addition of EJ-13 water during the experiment. Only the solution collected during the 4/23/87 sampling period has been analyzed for cations other than uranium.

- 4) the vessel is soaked for five minutes and the liquid is transferred to the LPE;
- 5) the vessel is rinsed with DIW and 0.5 mL of EJ-13 is added;
- 6) the UO_2 plus Zircaloy is returned to the vessel;
- 7) the vessel is weighed, sealed, and put back on line.

The uranium detected in the sample solutions represents all of the uranium that has been released from the UO_2 plus Zircaloy except for that which is retained on the Teflon holder after acidification; however, no attempt has been made to determine whether the U is in solution, exists as particulates, or is sorbed to the vessel walls. A yellow precipitate has formed on the top and bottom surfaces of the UO_2 pellets and on the Teflon stand. After acidification some of the yellow precipitate remains on the Teflon stand and thus it is likely that incomplete measurement of all U released from the waste form has been made.

The data (Tables 10 and 11) indicate that in most experiments a fairly constant amount, ~ 0.75 mL, of water accumulates every 6.5 weeks. In some experiments this volume has decreased as the experiments have continued. This is a real effect and results when the inlet lines become plugged. If such plugging is observed, the vessels are supposed to be placed in a new position in the oven. Vessel relocation has been effected in all cases where plugging has been verified, but in some cases several sampling periods have been required to complete the move.

The data also indicate that there is no obvious trend to the release patterns, either between duplicate experiments, or between the different sets of experiments. However, it does seem clear that in experiments 7 and 8, where the water contact has been reduced by a factor of eight and the surface area decreased by a factor of fifteen, the total amount of uranium actually released is not noticeably affected when compared to the other experimental designs used.

Whether these release trends are a function of experimental uncertainties or of different reaction processes, is not known. However, incomplete dissolution of the yellow precipitate from the Teflon stand likely is one cause for the scatter in the data. The yellow precipitate has been identified by XRD as $\text{U}_3\text{O}_8 \cdot 0.8\text{H}_2\text{O}$, and unique spectra have been collected using Raman microprobe.

2. P-VIII

This set of experiments was initiated simultaneously with the N2 Tests and utilized 304 L stainless steel waste form holders that had been heated at ~550°C for 24 hours, ostensibly the same procedure used to sensitize the holders in the N2 Tests. However, the heat treatment was not done at the same time as the N2 Tests and the 304 L steel used in the P-VIII experiments was from a different heat than used in the N2 Tests. The purpose of the P-VIII experiments was to duplicate the N2 Tests using SRL 165 type glass doped only with U (no transuranics). The effective glass composition between the N2 Tests and the P-VIII experiments was the same; however, extensive surface analyses were possible on the P-VIII components, while similar analyses on the N2 components would be difficult due to transuranic contamination.

The results of the P-VIII experiments through 65 weeks are presented in Tables 13, 14, and 15. The appearance of the glass and metal components was strikingly different from that observed in the N2 Tests in that, except for test P-VIII #6, there were no rust-colored precipitates and no evidence for strong interaction between the test components. This observation was reinforced by the solution results which indicate a release commensurate with experiments of minimal ss/glass interaction. The exception was experiment P-VIII #6 where the elemental releases were indicative of a stronger interaction.

The metal test components showed no evidence of sensitization for the experiments P-VIII #s 3-5. Experiment P-VIII #6 has yet to be examined. These results are consistent with those found in the F-1 [BATES-3], N-2, and analog test series in that the extent of glass reaction correlates well with the degree to which the metal is sensitized.

3. P-IX

a. Vapor Hydration Experiments

Parametric experiments are in progress (1) to elucidate the fundamental processes that occur during protracted reaction of silicate and borosilicate glass surfaces (Table 16) with water, and (2) to investigate directly investigate the rate and products of vapor-phase hydration of nuclear waste glasses. These experiments are a continuation of vapor

Table 13. Experimental Matrix and Results from Parametric Experiments (P-VIII Series)

Test No.	Vessel No.	Oven Position	Test Period (weeks)	Date Started	Date Stopped	Sample #	Weight Glass In (gm)	Weight Glass Out (gm)	Δ Mass (μ gm)	SA Glass (cm ²)	Top Canister In (gm)	Top Canister Out (gm)	Δ Mass (μ gm)
P-VIII-1a	96	1	13	2/27/86	5/29/86	1	10.54533			13.86	2.34774		
1b	15	1	13	6/29/86	8/28/86								
1c	96	1	13	8/28/86	11/26/86								
1d	15	1	13	11/26/86	2/26/87								
1e	96	1	13	2/26/87	5/28/87								
1f				5/28/87									
1g													
1h													
1i													
1j													
1k													
1l													
1m													
1n													
1o													
1p													
P-VIII-2a	97	2	13	2/27/86	5/29/86	2	9.99284				2.37578		
2b	36	2	13	6/29/86	8/28/86								
2c	97	2	13	8/28/86	11/26/86								
2d	36	2	13	11/26/86	2/26/87								
2e	97	2	13	2/26/87	5/28/87								
2f	36	2	13	5/28/87									
2g													
2h													
2i													
2j													
2k													
2l													
2m													
2n													
2o													
2p													
P-VIII-3	98	3	13	2/27/86	5/29/86	3	10.23429	10.23450	-210		2.35705	2.35720	150
P-VIII-4	99	4	26	2/27/86	8/28/86	4	10.37222	10.37225	30		2.36451	2.36482	110
P-VIII-5	100	5	39	2/27/86	11/26/86	5	10.17771	10.17515	2560		2.37383	2.37400	170
P-VIII-6	101	6	52	2/27/86	2/26/87	6	10.27582	10.27524	590		2.36734	2.36774	100
P-VIII-7	103	7		2/27/86		7	10.36219				2.35248		
P-VIII-8	104	8		2/27/86		8	10.37649				2.37175		

Table 13 (Cont'd)

Bottom Canister In (gm)	Bottom Canister Out (gm)	Δ Mass (μ gm)	Total Vessel In (gm)	Total Vessel Out (gm)	Δ Mass	Water Added During Testing
3.35091			329.19	321.75	1.56	1.95
			327.34	320.00	1.40	1.95
			328.39	320.15	1.77	1.95
			327.00	329.29	1.54	1.95
			328.00	329.31	1.63	1.95
			327.00			
3.34846			327.34	328.09	1.55	1.95
			334.00	336.47	1.69	1.95
			335.43	337.00	1.57	1.95
			335.22	336.00	1.66	1.95
			335.00	337.40	1.60	1.95
			335.10			
3.36102	3.36102	120	325.59	327.10	1.59	1.95
3.33765	3.33776	110	320.56	323.70	3.14	3.00
3.35271	3.35291	200	324.34	326.95	4.62	5.65
3.39773	3.39823	500	325.02	331.74	5.92	7.00
3.35328			325.71			
3.35672			325.71			

Table 14. Solution Results (Total Nanograms) for P-VIII Experimental Series

Experiment #	Analysis #	Solution Vol (mL)	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	Sr	U
P-VIII-1a	TF 318	21.93	<2200	2800	4200	48000	9000	420	5300	76800	8300	44500	<110	485
1b	TF 342	19.32	<1900	1500	3700	43700	8900	270	3000	107200	8900	103900	<100	253
1c	TF 388	12.10	<1200	<300	2200	60000	4300	260	2600	80700	NA	42000	<61	98
1d	TF 421	14.17	<1400	720	3100	8100	3300	270	570	92100	NA	53100	<70	58
1e	TF 451	13.72	<1400	720	440	9000	4700	410	480	141300	1000	77100	<70	58
P-VIII-2a	TF 319	20.04	<2000	2700	3100	13800	7700	350	1500	73200	3500	52900	<110	391
2b	TF 343	19.23	<1900	2000	6000	79400	5700	1700	8500	94400	15400	87300	<100	172
2c	TF 389	13.40	<1300	<400	1500	22400	<270	150	1100	10500	NA	7000	<70	<11
2d	TF 422	13.00	<1400	775	3100	9500	3300	270	980	108000	NA	59800	<60	52
2e	TF 452	14.37	5000	720	4500	8000	5200	430	370	188200	900	95000	<70	67
P-VIII-3	TF 320	21.42	<2100	2700	4300	9000	11800	450	1300	119000	2800	72000	<110	1101
4	TF 344	18.83	2000	6700	7700	117700	25200	800	4700	290000	13200	220300	94	1105
5	TF 390	14.05	3000	4200	15500	80000	23900	770	6400	323200	NA	150000	155	904
6	TF 423	13.63	6700	34800	12900	39700	54800	845	5700	520700	NA	390500	330	13700

Table 15. Blank Corrected Totals* for Parametric P-VIII Test Series Solutions

		EJ-13 (ng/mL) (after 4/8/87)		710 240	185 160	4500 7140	<10 <10	79 54	400 200	<5 <5	48100 48700	37250 34600	40 35	4.9 21	
Test #	Time Period (weeks)	Water Added (mL)	EJ-13 in Vessel (mL)	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	Sr	U
P-VIII-1a	13	1.95 ± 0.2	2.15		2400	(5500)		9400	(440)		(26500)		(35600)		455
1b	13	1.95 ± 0.2	2.15		1100	(5000)		8700	(500)		3600		23000		243
1c	13	1.95 ± 0.2	2.15		--	(7500)		4100	(500)		(22700)		(37300)		88
1d	13	1.95 ± 0.2	2.15		300	(5500)		3100	(500)		(11300)		(27000)		48
1e	13	1.95 ± 0.2	2.15		300	(5300)		4500	(500)		38300		(3000)		47
P-VIII-2a	13	1.95 ± 0.2	2.15		2700	(5000)		7500	(510)		(30200)		(27200)		381
2b	13	1.95 ± 0.2	2.15		1000	(2000)		5500	800		(9000)		7200		182
2c	13	1.95 ± 0.2	2.15		--	(5200)		--	(700)		(92900)		(73100)		--
2d	13	1.95 ± 0.2	2.15		400	(5500)		3100	(500)		4600		(20300)		42
2e	13	1.95 ± 0.2	2.15		300	(5200)		5000	(400)		65000		15500		56
P-VIII-3	13	1.95 ± 0.2	2.15		3900	(5400)		11000	(410)		15500		(8100)		1090
P-VIII-4	20	3.00 ± 0.2	4.10		5900	(10000)		24900	(800)		92000		67000	(70)	1005
P-VIII-5	39	5.85 ± 0.2	6.05		3100	(11000)		23700	(1700)		32200		(89400)	(90)	954
P-VIII-6	62	7.00 ± 0.2	8.00		33300	(11400)		54500	(2400)		135900		90000	10	13725

*Values are total nanograms, values in parentheses indicate less of an element was detected in solution at the end of an experiment than was initially present in the water.

Table 16. Results^a from the F-1 Unsaturated Test Series

Test No.	Test Description	Weight Change (NL)wt, g/m ²	Total Release, μg Li B	
F-1	13-week batch	0.26	5.9	3.9
F-2	13-week batch	0.25	6.2	5.9
Sum of Two	6.5-week continuous ^b		10.0	3.3
F-3	26-week batch	0.47	10.9	15.1
F-4	26-week batch	0.40	11.1	15.5
Sum of Four	6.5-week continuous ^b		20.8	5.0
F-5	39-week batch	0.71	14.4	22.2
F-6	39-week batch	0.25	10.8	5.4
Sum of Six	6.5-week continuous ^b		27.5	6.3
F-7	52-week batch	0.28	10.5	4.7
F-8	52-week batch	0.06	4.4	7.1
Sum of Eight	6.5-week continuous ^b		37.9	7.1
F-9	52-week continuous	0.05		
F-10	52-week continuous	0.06		
F-11	52-week continuous	0.11		

^aThe release in the batch tests does not account for the amount of Li or B retained by tuff cup and therefore these total releases under represent the total release. No tuff cup was used in the continuous tests so these results are directly comparable to either the results of the N2 tests or of the P-VIII experiments.

^bAverage of tests F-10 and F-11.

hydration experiments involving nuclear waste glasses (SRL 165, SRL 131, PNL 76-68) at temperatures ranging from 80°C to 202°C and relative humidities of 50 to 100% RH. A paper describing the mechanisms of vapor hydration is in preparation.

Present experiments on the above-mentioned nuclear waste glasses at 75°C will be used in confirming/refuting the validity of an Arrhenius-type dependence of reaction rate on temperature. Only a limited number of experiments on monoliths (as opposed to glass powders) were performed at 80°C previously, whereas all the ongoing 75°C experiments (Table 17) use glass monoliths. Nuclear resonance profiles already collected for SRL glasses hydrated for over 150 days (95% RH) (Table 17) appear to show that an Arrhenius relation can predict reaction rates to better than a factor of two even in unsaturated vapor environments [cf. BATES-4].

Hydration experiments on simple silicates, nuclear waste glasses (above), obsidian and basaltic glass at 75°C, and relative humidity of 60, 95, and 100% are in progress for over 270 days. The specific aims of these experiments are (1) to examine the dependence of hydration rate on relative humidity, (2) to determine if the relationship of hydration rate and humidity vary with glass composition, and (3) to compare the rates and products of hydration of the different glass compositions. Preliminary results of H-profiling indicate that the hydration rate of basalt is greater than that of obsidian and that of SRL 131 is greater than that of SRL 165. The hydration rate of obsidian appears to be comparable to that of the SRL glasses. SIMS analyses of these samples are underway.

A new experimental submatrix has been designed to study systematically the effect of glass composition on hydration rates at saturated vapor pressures. A compositional series in the system $\text{Na}_2\text{O}-\text{CaO}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ has been selected that encompasses the optical basicity and structure of nuclear waste glasses. These experiments will be performed at 75°C using deuterated (99.9%) and normal water. Oxide mixtures of all these glasses have been prepared. Crucibles for glass synthesis have been machined from recently acquired high-grade graphite bricks (Union Carbide Stock #TS 1792). Exploratory experiments using simple glasses (soda silicates) and nuclear waste and natural glasses using D_2O are in progress.

Table 17. 1986 Vapor Hydration Experiments for NNWSI

TEST TYPE	TEST#	SAMPLE#	DURATION (d)	% R.H.	DATE IN	DATE OUT	MASS IN (g)	MASS OUT (g)	DIFF. ($\times 10^{-6}$ g)	REMARKS
165-95RH	V-101	101	28	95						
		102	28	95						
		103	58	95						
	V-102	104	58	95						
		105	91	95						
	V-103	106	91	95						
		107	182	95	10/3/86		0.1950			
	V-104	108	182	95	10/3/86	3/9/87	0.1712	0.1712	0	Patch of ppt
		109	365	95	10/3/86		0.1873			
	V-105	110	365	95	10/3/86		0.1870			
		111	INDEF	95	10/3/86		0.1827			
	V-106	112	INDEF	95	10/3/86		0.2018			
131-85RH	V-107	113	91	95						
		114	91	95						
	V-108	115	182	95	10/3/86	3/9/87	0.1952	0.1953	10	Even dist of ppt
		116	182	95	10/3/86		0.1581			
	V-109	117	365	95	10/3/86		0.1892			
		118	365	95	10/3/86		0.2701			
	V-110	119	INDEF	95	10/3/86		0.2466			
7669-95RH	V-111	121	91	95						
		122	91	95						
	V-112	123	182	95	10/3/86	3/9/87	0.2051	0.2037	30	
		124	182	95	10/3/86		0.2034			
	V-113	125	365	95	10/3/86		0.2004			
		126	365	95	10/3/86		0.2066			
	V-114	127	INDEF	95	10/3/86		0.2072			
OBS-95RH	V-115	128	INDEF	95	10/3/86		0.2048			
		129	91	95						
	V-116	130	91	95						
		131	182	95	10/3/86	3/9/87	0.2635	0.2628	0	
	V-117	132	182	95	10/3/86		0.2628			
		133	365	95	10/3/86		0.2605			
	V-118	134	365	95	10/3/86		0.2611			
BAS-95RH	V-119	135	INDEF	95	10/3/86		0.2540			
		136	INDEF	95	10/3/86		0.2525			
	V-120	137	91	95						
		138	91	95						
	V-121	139	182	95	10/3/86	3/9/87	0.1997	0.1998	-10	
		140	182	95	10/3/86		0.3064			
	V-122	141	365	95	10/3/86		0.2313			
		142	365	95	10/3/86		0.2439			
		143	INDEF	95	10/3/86		0.2790			
		144	INDEF	95	10/3/86		0.2311			

Cont'd

Table 17 (Cont'd)

TEST TYPE	TEST#	SAMPLE#	DURATION (d)	% R.H.	DATE IN	DATE OUT	MASS IN (g)	MASS OUT (g)	DIFF. (x10E-6g)	REMARKS
18S-80RH	V-123	145	28	60						
		146	28	60						
		147	58	60						
	V-124	148	58	60						
		149	91	60						
	V-125	150	91	60						
		151	182	60	10/3/86	3/9/87	0.1983	0.1982	-10	
	V-126	152	182	60	10/3/86		0.1832			
		153	365	60	10/3/86		0.2003			
	V-127	154	365	60	10/3/86		0.1876			
		155	INDEF	60	10/3/86		0.1845			
	V-128	156	INDEF	60	10/3/86		0.2042			
131-60RH	V-129	157	182	60	10/3/86		0.1989			
		158	182	60	10/3/86		0.1604			
706S-60RH	V-130	159	182	60	10/3/86		0.1735			
		160	182	60	10/3/86		0.1964			
OBS-60RH	V-131	161	182	60	10/3/86		0.2454			
		162	182	60	10/3/86		0.2246			
BAG-60RH	V-132	163	182	60	10/3/86		0.2556			
		164	182	60	10/3/86		0.2201			
N2S-60RH	V-133	165	91	60						
		166	91	60						
N3S-60RH	V-134	167	91	60						
		168	91	60						
N4S-60RH	V-135	169	91	60						
		170	91	60						
N6S-60RH	V-136	171	91	60						
		172	91	60						
AB-60RH	V-137	173	91	60						
		174	91	60						

Table 17 (Cont'd)

TEST TYPE	TEST#	SAMPLE#	DURATION (d)	% R.H.	DATE IN	DATE OUT	MASS IN (g)	MASS OUT (g)	DIFF. ($\times 10^{-5}$ g)	REMARKS
165-100RH	V-138	175	28	100						
		176	28	100						
		177	56	100						
	V-139	178	56	100						
		179	91	100						
	V-140	180	91	100						
		181	182	100	10/3/86	3/9/87	0.1855	0.1882	270	Cond. H2O
	V-141	182	182	100	10/3/86		0.2047			
		183	365	100	10/3/86		0.1798			
	V-142	184	365	100	10/3/86		0.1828			
131-100RH	V-143	185	INDEF	100	10/3/86		0.1816			
		186	INDEF	100	10/3/86		0.1975			
	V-144	187	182	100	10/3/86		0.2003			
		188	182	100	10/3/86		0.3048			
7668-100RH	V-145	189	182	100	10/3/86		0.2045			
		190	182	100	10/3/86		0.2208			
085-100RH	V-146	191	182	100	10/3/86		0.2416			
		192	182	100	10/3/86		0.2536			
BAS-100RH	V-147	193	182	100	10/3/86		0.3852			
		194	182	100	10/3/86		0.2107			
AB-100RH	V-148	195	182	100						
		196	182	100						

• TOTAL ASSEMBLY MA SS

Water speciation studies of these glasses using step-heating-quadruple mass spectrometry techniques will be performed in collaboration with William Ebert (Section IV.C.).

b. Other Analyses Planned

Compositional (SEM/EDX, SIMS, nuclear reaction techniques) and mineralogical (optical microscopy, XRD, vibrational spectroscopy) characterization of glasses from all hydration runs will be performed. These data will form the basis of the macroscopic description of glass/vapor interaction. The relative abundances of surface precipitated secondary products will also be documented.

X-ray scattering, NMR (^{29}Si , ^{27}Al , ^{11}B , and ^{17}O), IR, and Raman techniques are potential methods that we plan to use to examine the surface structure of the hydration layer(s). The analytical objective here is to detect structural reorganization across the layer(s). These results will be correlated to the macroscopic data collected above. Laser Raman microprobe and IR techniques may also be employed in surface analyses of future in situ runs.

The analytical measurements described above will collectively form the basis of a detailed molecular description of the corrosion process. No comparable comprehensive analytical approach has been attempted by any laboratory for studying vapor corrosion of a glass surface, although individually, each analytical technique has been successfully used by our group and other workers in glass corrosion research for similar applications.

C. Analog Experiment (QA level III, activity #D-20-29)

The purpose of the analog experiment has been described previously [BATES-3]. Two analog experiments were run concurrently with the N-2 Test series. One of these experiments was terminated after approximately one year and the other is ongoing. For each experiment, the solution that is collected after it has passed through the tuff core is analyzed for radionuclides. For the terminated experiment the core was disassembled and the components analyzed. The results are discussed in detail in the topical report, "Application of the NNWSI Unsaturated Test Procedure to

Actinide Doped SRL 165 Type Glass." The conclusions were that the canister sections used in the analog experiment, although heat treated at approximately 550°C for 24 hours, gave no evidence for sensitization and the reaction of the glass, as measured by the release of radioactive tracers ^{121}Eu , ^{133}Ba , and ^{137}Cs , together with the amount of ^{237}Np , ^{239}Pu , and ^{241}Am associated with the metal waste form holder, and the $(\text{NL})_{\text{wt}}$, indicated a reaction after 52 weeks similar to that noted for other tests or experiments run for 52 weeks in which the degree of metal/ss interaction was small.

III. NNWSI GAMMA IRRADIATION TESTING (QA level III, activity #D-20-30)

A. 2×10^5 R/h Experiments

Results of experiments done at 2×10^5 R/h have been discussed previously [BATES-5] relating to the reaction of SRL glass. The results relating to the reaction of ATM-1c and ATM-8 glasses were compiled as an article submitted to the Journal of Materials Research and as a set of data tables to be published as a UCRL document. As a result of reviewer's comments, the article has been revised to incorporate new data. The revised article [BATES-6] and the accompanying data set [BATES-7] have been submitted to NNWSI for review. These reports provide the results and discussion of all experiments done using ATM-1c and ATM-8 glasses to assess the effect of radiation on glass reaction. An overview of these results is given below.

1. Background

One concern that has been raised previously in the literature is the uncertain effects of penetrating radiation on the performance of the waste form when in contact with groundwater. For NNWSI, the conditions anticipated for disposal suggest a priori that radiation should have little effect on the performance of the glass. Specifically, since the waste container is to maintain its integrity during the 300-1000 year containment period, water will contact the glass only after the exposure rate in the repository has dropped to values of less than 50 R/h. Also, since the NNWSI site hydrology is unsaturated, the opportunity for contact between

standing water and glass will be remote. The most likely reactants would be humid air and glass, or small pockets of transient water and glass. The experiments described in this paper address the unlikely, but possible, case where relatively large volumes of liquid water contact glass, and measure the differences that occur in the glass reaction process as a function of exposure rate.

Previous studies [BARKATT, BURNS, McVAY-1] raise several issues that may affect the glass performance. These concerns include:

- (1) What reactions occur when repository groundwater is subjected to gamma radiation in the presence of waste package components, and what is the ultimate effect on glass performance? It has been established [BURNS] that when humid air is subjected to gamma irradiation, nitric acid is produced in the gas phase. When a two-phase air-water system is irradiated, the nitric acid dissolves in the water, and may reduce the pH of the solution, attaining values as low as 3. As the pH changes, if glass is present, the solubilities of glass components change, and the extent of glass reaction may thereby increase. It has been demonstrated [PLODINEC] that glasses are more reactive in high or low pH solutions, but quite resistant to reaction in neutral pH solutions.
- (2) The radiolytic production of nitric acid in an air/water system increases with the exposure rate according to the relationship established by [BURNS],

$$N = 2C_0R [1 - \exp(-1.45 \times 10^{-5} \times GDt)] \quad (1)$$

where

N = the number of moles of nitric acid produced per system volume (moles/L),

C_0 = the initial nitrogen concentration in the gas phase (moles/L),

$R = vol_{gas}/vol_{liq}$,

G = the number of molecules of nitric acid produced when 100 eV of radiation energy is absorbed by the nitrogen gas,

D = exposure rate (R/h), and

t = time of irradiation (h).

Based on this formalism, it is tempting to suggest that if experiments were performed for a short time period using a large exposure rate, more nitric acid would be produced than with a smaller exposure rate, and some indication of projected performance at smaller exposure rates and longer time periods may be expected. It is of interest to determine whether experiments that attain the same total dose yield the same extent of glass reaction.

- (3) According to Eq. (1), the value of R will affect the concentration of nitric acid in solution. Since expected NNWSI repository conditions allow that R may vary considerably, what is the functionality between R and the extent of glass reaction, and can one value of R be used to evaluate successfully repository behavior?

To address these concerns, NNWSI has initiated an extensive series of experiments. These experiments include static leach tests of glasses of different compositions, performed for extended time periods and at different exposure rates (2×10^5 , 1×10^4 , 1×10^3 , and 0 R/h) [BATES-1, -2, -5]. The glasses used in these experiments are based on formulations typical of those to be produced by the Defense Waste Processing Facility at Savannah River Laboratory (SRL), and formulations of a reference composition for reprocessed commercial waste. The reference commercial glasses have compositions similar to Pacific Northwest Laboratory (PNL) 76-68 glass, are designated ATM-1c and ATM-8 glasses, and are made by the Materials Characterization Center (MCC). While no glass from a commercial waste stream, other than that from the West Valley Demonstration Project (composition not similar to ATM-1c or ATM-8), is currently expected to be stored in the first repository, a large data base exists for the leaching of PNL 76-68 and the ATM glasses, and this data base may be useful in interpreting the present results. The rationale for studying different glass types is to determine the effect of radiation over as wide a range of conditions as possible.

The results of the experiments on both SRL and the ATM glasses have been previewed [BATES-8], and the detailed procedures and results on the SRL glass have been reported [BATES-2, -5]. An addendum has also been compiled, which contains the complete set of raw data and experimental conditions [BATES-7].

At exposure rates of 2×10^5 and 1×10^3 R/h, standing water could only come into contact with the glass if there were a premature breach in the containment. However, it was felt that a wide range of exposure rates offered the best opportunity to determine the effects of radiation.

2. Discussion

The experimental data and results are presented in [BATES-6, -7].

In this section the results of the solution and component analyses from each set of experiments are qualitatively compared to assess the effect of radiation on the glass reaction. Additionally, the data are compared to note the effect of varying the experimental parameters (rock/glass types) to the results of other MCC-1 type experiments done with similar glasses. Of the results obtained, the solution pH, behavior of the actinide elements and appearance of the surface and the reacted layer are most affected by varying the exposure rate of gamma irradiation, while the normalized release of cations associated with glass reaction, e.g., the boron group of elements, B, Na, and Mo, and the depth of the reacted layer are nearly unaffected within the range of parameters studied.

a. pH

The pH values of the solutions in the blank experiments are more acidic when radiation is present. In both the 2R and 1R experiments the blank solutions maintained pH levels between 6 and 7 for the duration of the experiments. In the 2R experiment a total dose of 3×10^8 R was reached after 56 days, while in the 1R experiment 7×10^6 R was reached after 278 days. The pH becomes acidic due to the formation of nitrogeous acids, but in both cases the pH did not fall below 6.2 which is the level of the carbonate buffer.

When glass is added, the leachate pH values trend more basic as the exposure rate becomes less. In the 2R experiments the final pH values are about 7.4 after 56 days after ranging between 6.9 and 7.7. While ATM-1c and ATM-8 glasses have different trends (discussed later), the ATM-8 trend is upward from a 7-day value of 6.9. In the 1R experiments the pH values range to the mid-7 level after starting in the high to mid-8 range. Without radiation the leachate pH values continually become more basic. This is a well-established trend in the reaction of nuclear waste glasses and is due to hydrolysis reactions of which the net result is to exchange cations in the glass with hydrogen ions from solution. When radiation is present the final leachate pH is a balance between the rate of formation of nitrogeous acids, the extent of glass reaction, and the buffering capacity of the leachate. The rate of acid formation is essentially constant over the duration of the experiments for each exposure rate. The rate of glass reaction slows eventually in all experiments, although in the 2R experiments the rate actually increases through 14 days before decreasing.

In the present set of experiments the results indicate that at 2R the effect of radiation initially dominates the system and only after continued glass reaction does the pH become slightly more basic. At 1R the effect of radiation is less and the glass reaction initially dominates the leachate pH. Only with continued radiation and slower glass reaction does the solution become more acidic. At 0R the system is dominated by the glass. While the solution pH is affected by the interplay between radiation and glass reaction, it is evident that the extraction of soluble components from the glass and the thickness, although not the composition, of the reaction layer is relatively independent of leachate pH. This is noteworthy because previous studies [PLODINEC] have found that glass reaction is usually less when the leachate is buffered near pH 7 while it is more rapid at higher and lower pH values.

b. Actinide Release

While the extent of glass reaction appears to be unaffected by the exposure rate, the amount of U, Pu, and Np released from the glass and the behavior of these elements in solution is a strong function of exposure rate. The present results indicate that as the exposure rate increases and

the effective solution pH decreases, the normalized release of each actinide element increases, the fraction of Np and Pu that passes through a 50 Å filter increases, the fraction of Np and Pu sorbed to metal, tuff, or glass decreases, and the depletion of U in the reacted glass layer increases. As the pH of the leachate decreases each actinide shows a greater propensity to remain associated with the solution either as a colloidal or non-filterable fraction (Table 18), as opposed to a solid component. This is reasonable in that previous studies [KIM] indicate that the solubility of each of these elements increases with increased acidity in the range 6-10.

c. Reacted Glass

As the exposure rate becomes greater the nature and amount of reaction products on the glass surface and the composition of the reacted layer varies. In the 2R experiments there is no buildup of Si in the region of the reacted layer near the surface and the only reaction products are monazite (established by x-ray diffraction analysis); while in the OR experiments there is a significant increase in Si in the near-surface region and an associated increase in the density of the outer layer. A Sr/Ba phase appears immediately, there are large aggregates of Fe, Ca, Ti, U, Si, and S and the amount of the monazite phase is greatly reduced.

In addition, the relative composition of the reaction layer varies as a function of exposure rate. In the 2R experiments there is less Ca and Al remaining in the reaction layer and the normalized release of these elements is greater than in the OR experiments. The observations made in this section are strongly correlated to the pH of the leachate. When the pH is more acidic, those elements whose solubilities show a strong pH dependence are released from the glass and the reaction layer and are found in solution. When the pH is more basic, these elements either form insoluble aggregates on the reacted surface or are not released from the reacted layer.

Table 10. H₂ and Pu Release^a from ATP-B Glasses

Test Type	Duration (Days)	pH	Radiation Level (R/h)	H ₂						Pu					
				Total ^b Mass Released (μg)	Filtered ^c Fraction %	Solution ^d Fraction %	Metal Fraction %	Metal or Tuff ^e Fraction %	Filtered Concentration (μmoles/L)	Total ^b Mass Released (μg)	Filtered ^c Fraction %	Solution ^d Fraction %	Metal Fraction %	Metal or Tuff ^e Fraction %	Filtered Concentration (μmoles/L)
Glass Disks + EJ-13	7	0.9	2 x 10 ⁵	1.9	100 ^d	100	0	-	0.0	0.03	85	48	58	-	4
	14	7.0		0.2	ND	80	20	-	ND	0.26	ND	48	58	-	ND
	28	7.0		19.1	40	70	30	-	2.0	0.49	32	29	80	-	9
	56	7.4		9.8	78	80	28	-	2.0	0.39	91	58	58	-	5
Glass Disks + EJ-13 + Tuff	7	7.0	2 x 10 ⁵	1.0	100 ^d	100	0	ND	0.5	0.01	89	48	80	ND	2
	14	7.2		5.0	ND	100	0	ND	ND	0.07	ND	20	80	ND	ND
	28	7.2		11.1	100	80	10	ND	5.0	0.23	88	10	90	ND	6
	56	7.8		12.5	80	70	30	ND	2.0	0.22	76	19	90	ND	5
Crushed Glass + EJ-13	7	0.9	2 x 10 ⁵	0.0	100 ^d	80	20	-	0.3	0.03	96	5	95	-	4
	14	7.1		4.1	ND	100	0	-	ND	0.09	ND	5	95	-	ND
	28	7.4		10.9	50	70	30	-	1.0	0.25	48	1	99	-	5
	56	7.7		4.1	65	80	40	-	0.9	0.51	80	1	99	-	6
Glass Disks + EJ-13	20	0.0	1 x 10 ³	9.4	40	100	0	-	0.36	0.09	14	4	98	-	0.16
	56	7.0		5.5	20	90	10	-	0.26	0.21	0	3	97	-	0.11
	91	7.7		10.0	43	60	40	-	0.73	0.42	21	1	99	-	0.10
	182	7.0		9.0	46	90	10	-	0.92	0.54	22	1	99	-	0.14
	270	7.0		10.4	22	80	20	-	0.54	0.00	7	1	99	-	0.09
Glass Disks + EJ-13 + Tuff	20	0.2	1 x 10 ³	5.7	40	100	0	0	0.49	0.00	20	2	90	0	0.09
	56	7.7		0.7	20	100	0	0	0.01	0.20	3	4	91	5	0.05
	91	7.8		11.7	09	70	29	1	0.0	0.26	0	2	94	4	0.00
	182	7.6		13.0	40	90	10	0	1.1	0.39	5	1	94	5	0.05
	270	8.0		11.1	31	100	0	0	0.0	0.49	0	0	90	4	0.00
Glass Disks + EJ-13	14	0.0	0	0.5	30	100	0	-	0.06	0.007	27	5	95	-	0.03
	20	0.0		0.7	ND	100	0	-	ND	0.013	ND	4	90	-	ND
	50	0.0		1.8	40	100	0	-	0.22	0.044	33	2	98	-	0.07
	91	0.2		1.5	40	100	0	-	0.10	0.095	0	1	99	-	0.03
Glass Disks + EJ-13 + Tuff	14	0.1	0	1.0	40	100	0	0	0.12	0.010	54	5	81	14	0.00
	20	0.4		2.1	ND	100	0	0	ND	0.036	ND	2	92	0	ND
	50	0.6		2.3	20	100	0	0	0.18	0.071	17	1	93	0	0.04
	91	0.7		2.3	51	100	0	0	0.31	0.112	22	1	95	4	0.09

^aValues are averages of duplicate experiments, except as noted.^bTotal mass includes two acid soak fractions plus a tuff fraction when applicable.^cFiltered fraction = amount of An passed through 50 A filter/amount of An in unfiltered solution.^d1000 A filters used instead of 50 A.^eAmount of An in unfiltered fraction/total An release.^fAmount of An associated with tuff/total An release.^gTuff water.

ND - Not determined.

d. Parameter Effects and Comparison with Other Results

In all sets of experiments the ATM-8 glass reacts more slowly than the ATM-1c glass, and there is no strong trend for the glass reaction to be retarded in the presence of tuff, despite the observation that Si concentrations are usually slightly larger with tuff present. Both of these observations are unexpected.

The retarded reaction of ATM-8 glass is most likely due to the compositional differences described earlier. Note the release of Al in the ATM-8 experiments is usually decreased substantially more than for the B group of elements. Additionally, in the 2R experiments there could be some effect as a result of the different starting surface texture of the glass, e.g., the ATM-8 glass have fewer fractures which could have resulted in less initial fracture reaction. However, the crushed ATM-8 glass also had slower reaction than ATM-1c glass, which suggests surface texture is not the main contributing effect.

The inclusion of tuff or silicate containing sources in an experimental design often retards the reaction of glass. In the present set of experiments there is no statistical difference in the no-tuff/tuff 2R results, a marked increase in release for the tuff-containing 1R experiments, and small but analytically significant increase in the tuff-containing OR experiments for ATM-8 glass and a small decrease for ATM-1c glass. The most striking difference (no-tuff vs. tuff) in solution compositions and glass reaction is that without tuff Al is extracted from the leachate in all sets of experiments, while with tuff there is a measurable release of Al from the glass. This suggests that Al, in addition to Si, may also play a role in controlling glass reaction.

The present results can be compared only indirectly to other results obtained using glasses of similar compositions because the experimental conditions (SA/V, water composition, experimental components) have not been duplicated between the different groups of experiments. Accordingly, the range of normalized releases obtained in the present experiments fall with the values obtained by [McVAY-2] (90°C, SA/V = 0.1 cm^{-1} , J-13 water, teflon vessels, no radiation) for the boron group (56 days, $(\text{NL})_B \approx 23 \text{ g/m}^2$); are considerably less than observed by [LOKKEN] (90°C, SA/V = 0.1 cm^{-1} , silicate water, teflon vessels, no radiation) where

$(NL)_B \approx 60 \text{ g/m}^2$ after 56 days; and are greater than obtained by [BAZAN] (90°C, EJ-13 water, tuff vessels, no external radiation) where $(NL)_B \approx 1 \text{ g/m}^2$ after 90 days. The range of results obtained by different experimenters emphasizes the importance of the direct comparison of radiation effects made in the present results.

3. Conclusions

A series of leach experiments have been done at various exposure rates of penetrating gamma radiation using saturated NNWSI repository conditions and two different ATM glass types. These experiments demonstrate that the final leachate pH, the behavior of actinide elements in solution, and the nature of the reacted glass surface and associated reaction layer vary as a function of exposure rate, but that for the duration of comparable experiments through 56 days, the release of soluble glass components (B, Mo, Na) is relatively insensitive to the experimental conditions.

These observations suggest that (1) the performance of glass in a repository under conditions of water intrusion will be affected by the exposure rate over the lifetime of the repository, but that the nature of the effect will depend on the temporal interplay between radiolysis, groundwater, and glass reaction products. This interplay cannot be accelerated by simply increasing the exposure rate because, with the other parameters remaining constant, this increases the production of radiolysis products while unnaturally disturbing the balance of the system; and (2) the ratio between the solution volume and the gas available for reaction could be an important factor in affecting glass reaction and the release of radionuclides. This is because as this ratio becomes larger, as is anticipated under unsaturated NNWSI repository conditions, the radiolysis products would become more concentrated. One would project that in a static or nearly static system, if the exposure rate and nitric acid production were large enough, the buffering capacity of the glass and the groundwater would be overcome, the pH would be driven more acidic, and accelerated glass reaction may occur, as has been observed in DIW [BARKATT, McVAY-1]. Additional work to resolve this point is in progress.

B. 1×10^4 R/h Experiments

The topical report describing the FY 1985 results has completed ANL editorial review and has been sent to NNWSI for technical review. Additional effort is being spent analyzing the tests that were done at R values other than ~ 3 to see if the mechanism of reaction is affected by the increased gas volume and decreased liquid in contact with the glass.

C. 1×10^3 and 0 R/h Experiments

Experiments were performed during FY 1986 in radiation fields of $1E3$ R/h and 0 R/h. Glass formulations used included actinide-doped SRL 165 type frit and ATM-1c and ATM-8 glasses. Work this period has centered on analyzing the reacted glass samples generated by these static leaching experiments. The samples are being analyzed with the purpose of identifying secondary products and alteration products on the glass surfaces, determining depletion-depths and concentration profiles normal to the reacted surface, and measuring the extent of reaction using these depletion depths. While many analyses have been completed, a discussion of the results is not ready at this time. An overview of the analyses performed and the results obtained to date including some specific examples and a description of the analyses along with which analyses have been performed on which samples will be presented instead.

An important gauge of the extent of the glass reaction, as measured by changes in the glass itself, has been presented previously as the glass weight change. As the surface of the glass dissolves (etches), or as ion exchange occurs, the glass weight changes. Etching will cause the glass weight to decrease, as will, in most cases, ion exchange. Precipitation of secondary products back onto the glass will cause the glass weight to increase. Only in the unlikely event where products precipitate out of the leachant onto the glass before significant glass reaction occurs will the glass weight increase upon reaction. Typically the glass will lose weight with reaction time as the surface etches and/or ion exchange occurs then gain weight as the leachate becomes saturated and precipitates form on the glass surface. The net weight change is, therefore, a balance between

weight loss due to dissolution and weight gain due to precipitation. A correlation between the leachate data and the presence or absence of precipitates is expected to be found with the net glass weight change results.

Scanning electron microscopy (SEM) with associated energy dispersive x-ray spectroscopy (EDS) was used to locate and analyze the composition of precipitates on the reacted glass surfaces. [Laser Raman microscopy (LRM) is currently being developed in order to characterize these precipitates structurally, as discussed later in the semiannual report, see Section IV.B]. Figure 10 shows a photomicrograph of a precipitate that formed during the nonirradiated leaching of many SRL U glasses. The accompanying EDXS spectrum shows the precipitate to contain calcium, chloride, iron, manganese, and silicon. Some of the reacted glasses had a very large number of these precipitates on the surface. The precipitates are about 10 μm in cross-section and so will be prime candidates for LRM analysis at a later date.

Some of the reacted glass samples were cut into cross-sections using a diamond wafering blade. The cross-sections were polished to a smooth finish using a 0.3 μm alumina slurry. These cross-sections were carbon coated to a uniform thickness of 200 Å to eliminate charging and were examined using the SEM. The region near the reacted surface is depleted in leachable cations, such as sodium, and has a lower density than the unreacted glass. The scattering cross-section in this depletion region is less than that in the unreacted glass and so both backscattered and secondary electron images can distinguish the depleted region as a darker area. The thickness of the depleted region depends on the extent of the glass reaction. Because of the possibility of etching, the depletion region thickness is a lower limit of the extent of reaction. Figure 11 shows a photomicrograph of a typical cross-section image. The darkest area on the right-hand side is the mounting resin. The area on the left-hand side is the unreacted glass and the intermediate region is the depletion region. A thin area between the depletion region and the resin can be seen in some cross-sections which corresponds to the secondary phases and alteration phases on the very surface of the glass. The depletion region is usually much thicker than the surface phases. The depletion region

Fig. 10. Photomicrograph and EDS Spectrum of Precipitate Formed on SRL U Glass. Sample no. 397 reacted 181 d in EJ-13 water at 90°C, 0 R/h. The micrograph was taken using secondary electrons with a magnification of 1000x.

shown in Fig. 11 can be seen to be rather nonuniform in thickness. This is because of the influence of the surface topology. The glasses cross-sectioned were all reacted with "as-cut" surface finishes, which is equivalent to about a 320 grit finish. The glasses often have deep cracks normal to the reacted surfaces. These cracks are highly reactive, often more reactive than the outer surfaces. Their high reactivity may be due to localized pH excursions within the cracks to values higher than are possible at the outer surfaces which are in contact with the buffering leachate. After long reaction times the depletion layer may extend deep enough into the sample to engulf the cracks.

Concentration profiles have been obtained by scanning the electron beam laterally across the depletion zone while monitoring the EDS intensity at energies of interest. The beam may be stepped in very small increments and probe regions from the unreacted interior of the glass, the depleted region, and surface phases, if present. Such "depth profiles" provide information regarding the leaching characteristics of the glass as well as the extent of the reaction. Analysis of precipitates present in the cross-section is semi-quantitative because of the smooth surface finish that can be obtained. (Analysis of secondary phases obtained by analyzing normal to the reacted surface is not quantitative because of the rough surface topology of the sample. Rough surfaces do not generate spectra useful for quantitative analyses, although they are useful as qualitative results.)

The line drawn across the center of the photomicrograph indicates the beam path of the analysis. The line profile of silicon in Fig. 11 shows high concentrations at points in the unreacted glass (left-hand side of spectrum and photomicrograph). The depletion region (center) has a lower silicon concentration than the unreacted glass and the resin has no silicon. Depletion regions generally showed lower silicon concentrations than the unreacted glass. This may result from differing x-ray generating efficiencies in the two regions rather than true concentration difference. The line profile for sodium has been multiplied by a factor of 20 in the figure for convenience in comparing the sodium behavior to that of silicon. Sodium, like silicon, shows a lower concentration in the depletion region than in the unreacted glass. The sodium concentration apparently increases at the interface between the depleted region and the resin. Care must be

Fig. 11. Photomicrograph and EDS Line Profile of Cross Section of ATM-1c Glass. Sample no. 487 reacted 91 d in EJ-13 water at 90°C, 1E3 R/h. The micrograph was obtained using backscattered electron imaging and the magnification is 500x.

taken in evaluating the sodium profile because other elements have x-ray emissions at energies very near that of sodium, for example, copper and zinc. A complete spectrum must be collected to detect the higher energy lines of these other metals in order to identify the low energy peak properly. Further analysis showed the peak to be sodium. Sodium is also notorious for migrating across or into the surface upon exposure to electron or ion beams. Magnesium was also found to be enriched in the surface layer (or precipitate). Notice finally the decrease in intensity of the silicon and sodium lines at the far left edge of their profiles. This results from the electron beam residing longer at the first spot analyzed and burning a small hole in the glass. (This is evident in the actual photo but not in the reproduction.) The x-ray yield in such holes is lower than in the polished flat regions.

As mentioned earlier, the depleted regions near the surface have a lower backscattering density than the unreacted glass. This density difference has been analyzed semi-quantitatively using the "C.A.R.D." system which is integrated with the backscattered electron detector. [CARD is an acronym for Compositional Analysis using the Robinson (backscatter) Detector.] Such analysis is based on the fact that the fraction of the incident electron beam that is backscattered depends on the backscattering cross-section of the region probed, which increases monotonically (though not linearly) with the average atomic number of the sample in that region. For example, pure germanium ($z = 32$) has a higher backscattering cross-section than pure silicon ($z = 14$). Titanium, vanadium, and chromium ($z = 22, 23$, and 24 , respectively) have backscatter cross-sections that are about half way between silicon and germanium. Sodium chloride has a backscatter cross-section about the same as silicon, and has an average atomic number of 14. The CARD analysis technique is useful in identifying elements not directly analyzable using EDS, such as Li, B, and O. By analyzing the sample for EDS detectable elements and for CARD backscatter intensity, one can gauge the amount of nondetectable elements in the sample by the difference between the intensity expected from the detectable elements and the measured intensity. Coupled with other techniques, such as wavelength dispersive x-ray spectroscopy, which is sensitive to boron and oxygen, the amount of nondetectable elements such as lithium may be deduced by difference.

Uncertainties remain in use of the CARD system as a quantitative tool, mainly because the relationship between the backscattered cross-section and the average atomic number is not linear. We do not yet have access to the exact functional dependency, and cannot accurately compute the backscatter cross-sections of complex samples. Nevertheless, the CARD analysis does afford a quantifiable measure of the samples backscattering power.

Another technique that we have used to determine the concentration profiles of the glass constituents normal to the reacted surface is secondary ion mass spectrometry (SIMS). This analysis provides concentration information on all elements, although hydrogen data is nonquantitative because of the high hydrogen gas background in our system, and we analyze only for positive species. SIMS analysis only occurs on species sputtered from the surface at the moment of analysis. By continuously sputtering in the same spot, the sample is eroded and analysis is made on a fresh surface that is progressively deeper into the sample. By monitoring the concentration of a given species as a function of time, a depth profile is generated. Figure 12 shows a typical elemental profile. The ordinate is the elemental intensity normalized to the silicon intensity at nearly the same depth in the sample. By normalizing to an element of assumed constant concentration, instrumental effects are effectively eliminated. The abscissa is in terms of time as data is collected periodically for elements of interest. Assuming a constant sputtering rate (which is an assumption we have yet to verify), the time axis is also proportional to depth. Preliminary determination of the sputter rate using unreacted SRL 165 glass gave a rate of about $200 \text{ \AA min}^{-1}$ at 4 kV acceleration of a Ar^+ primary beam. A one micron thick depletion layer will be sputtered through within one hour at this rate. The layer thickness is defined by the inflection point of the sigmoidal profiles, which occurs after 32 minutes of sputtering (scan #5) in the sample shown in Fig. 12. The layer thickness for this sample is about $0.64 \text{ }\mu\text{m}$.

Glass samples that were doped with transuranic radionuclides have not been analyzed using the SIMS instrument. Instead, they are being analyzed using an ion microprobe instrument (which operates on the same basis as the SIMS instrument) which has been used previously to analyze radioactive samples. No results from these analyses are yet available.

Fig. 12. SIMS Profile of ${}^7\text{Li}^+$ and ${}^{23}\text{Na}^+$ from Sample 423, Experiment Number G-361, SRL U + tuff, 0 R/h, 80 d. The scan numbers shown on the x-axis were obtained at eight minute intervals with scan #1 obtained at time zero.

A separate technique used to analyze the concentration profile of hydrogen in the surface region is resonant nuclear reaction spectroscopy (RNRS). In this technique, the sample is bombarded with a very high energy nitrogen ion beam (>6 MeV). The sample attenuates the beam energy as the beam penetrates the sample. A nuclear reaction occurs between hydrogen atoms and nitrogen ions of a specific energy to produce a photon of energy. This photon has energy in the gamma range and escapes the sample unattenuated. By detecting this gamma photon and calculating the attenuating power of the sample, the concentration of hydrogen as a function of depth in the sample can be obtained. This information, in conjunction with depth profiles of alkali ions (especially sodium and lithium), can be used to characterize further the extent of ion exchange in the depleted region. To date only a few samples have been analyzed (by F. Ryerson, LLNL). An exemplary profile is shown in Fig. 13. The attenuating power of the glass is about $2 \text{ MeV}/\mu\text{m}$ (F. Ryerson, private communication). The depletion region thicknesses suggested by these RNRS results do not agree well with those suggested by the SIMS, SEM, or leachate results. This discrepancy has yet to be resolved.

Table 19 summarizes the analyses performed (or to be performed) on the samples generated by the FY 1986 Gamma Irradiation Experiments. A complete compilation of the surface analytical results will be presented in the near future with a discussion of the entire FY 1986 experimental program.

IV. SURFACE ANALYTICAL SUPPORT (QA level III, activity #D-20-31)

A. SIMS Software

Reprogramming of the data acquisition and data handling codes has been postponed. Plans call for replacing the computer currently used for data acquisition with an Apple IIgs which can collect much more data without the delays necessary with the present computer system. A better representation of the profile will be possible with the greater speed and memory capabilities of the Apple IIgs. The new acquisition computer is expected to be in place by Fall 1987 whereupon a new acquisition code will be written to take advantage of the advanced capabilities.

Fig. 13. Resonant Nuclear Reaction Spectroscopy (RNRS) Result for Sample 400, SRL U, 0 R/h, 180 d. On the x-axis, 1 MeV corresponds to 0.5 μ m (F. Ryerson, private communication)

Table 19. List of Samples Analyzed using Various Surface Analytical Techniques

Exp't Type	Exp't Time (days)	SEM/EDS	SIMS	RNRS*	IMP
SRL U 1E3 R/h	28	301✓	302✓	304	
	56	305✓	306✓	308✓	
	91	311✓	310✓	-	
	181	313✓	314✓	316	
	278	317✓	318✓	320	
SRL U + Tuff 1E3 R/h	28	323✓	324✓	322	
	56	325✓	326✓	328	
	91	331✓	332✓	330	
	181	335✓	336✓	334	
	278	337✓	338✓	340	
SRL A 1E3 R/h	28	343			344
	56	347			348
	91	351			352
	181	353			354
	278	357			358
SRL A + Tuff 1E3 R/h	28	361			362
	56	365			366
	91	369			370
	181	373			374
	278	377			378
SRL U 0 R/h	14	383✓	384✓	384	
	28	385✓	386✓	388	
	56	389✓	390✓	392✓	
	91	393✓	394✓	396	
	181	397✓	398✓	400✓	
	278	403✓	402✓	404✓	
SRL U + Tuff 0 R/h	14	405✓	406✓		
	28	409✓	410✓		
	56	413✓	414✓		
	91	419✓	420		
	181	423✓	424✓		
	278	425✓	428		
SRL A 0 R/h	14	431			432
	28	433			434
	56	439			440
	91	441			442
	181	445			446
	278	449			450

Cont'd

Table 19 (Cont'd)

Exp't Type	Exp't Time (days)	SEM/EDS	SIMS	RNRS*	IMP
SRL A + Tuff 0 R/h	14	453			454
	28	459			460
	56	461			462
	91	465			-
	181	469			-
	278	473			-
ATM-1c 1E3 R/h	28	479✓	480		
	56	483✓	484		
	91	487✓	-		
	181	489✓	-		
	278	493✓	-		
ATM-1c + Tuff 1E3 R/h	28	497✓	500		
	56	501✓	502		
	91	505✓	-		
	181	509✓	-		
	278	513✓	-		
ATM-8 1E3 R/h	28	517			518
	56	521			522
	91	525			-
	181	529			-
	278	533			-
ATM-8 1E3 R/h	28	537			538
	56	541			542
	91	545			-
	181	549			-
	278	553			-

*Analyzed by F. Ryerson (LLNL).

Checked analyses have been completed.

B. Establishment of a Laser Raman Microprobe Facility

The argon ion laser has been repaired and returned. Its performance has been deemed satisfactory and it has been reincorporated into the system. The new photon counter (EG&G model 1109) has been tested and integrated into the system. Presently spectra of known samples are being collected to reoptimize the system. An exemplary spectrum of CaCO_3 is shown in Fig. 14. Notice that the logarithm of the intensity is plotted on the y-axis. The peak at 18363 cm^{-1} is a typical carbonate peak with a Raman shift measured to be 1117 cm^{-1} . The signal-to-noise ratio is very sensitive to the sample topology. Figure 14 shows a worst case, though we feel that there is still room for improvement in the signal-to-noise ratio.

We have also been preparing for computer acquisition and treatment of the data. Students have been hired to operate the LRM and develop the computer software this summer.

C. Development of a Gas Analysis System

A gas analysis system has been developed around a quadrupole mass analyzer (UTI model 100C). Gases may be leaked in directly from a sample ballast, evolved from solution, or desorbed from a solid. The last experiment is referred to as temperature programmable desorption wherein the solid sample is heated at a constant rate while the evolving species are continuously monitored. Current work deals with this technique.

A programmable temperature controller has been assembled and incorporated into the furnace power system. Precise temperature ramps can now be produced for temperature programmed desorption (TPD) experiments. The control unit consists of an Omega programmable temperature controller model CN-2011 coupled to a solid state relay. A simplified schematic of the control unit is shown in Fig. 15. As currently used, the heater power and controller power originate from the same source. It may prove beneficial to alter the connections so the heater power source is separated from the controller power source. This would allow insertion of a variac to reduce the heater power source. The advantage of this change would be that smaller power pulses could be impressed upon the heater so the controller could better regulate the heater temperature. (The controller functions by intermittently closing the relay and allowing the full line power to flow

Sample: CaCO_3 (s)
Sample Size: $\sim 10 \mu\text{m}$
Incident Beam: 19480 cm^{-1} , $\sim 0.25 \text{ watt}/\mu\text{m}^2$
Scan Rate = $0.2 \text{ cm}^{-1}\text{s}^{-1}$
Integration time = 2 s

Fig. 14. Raman Spectrum of CaCO_3 Obtained Using the Laser Raman Microprobe

Fig. 15. Sketch of Temperature Control Unit

through the heater. Presently only very short bursts of power are required to provide sufficiently high temperatures. A lower source power would perhaps allow the controller to operate using more optimal open/close cycles.)

Figure 16 shows the temperature ramps produced by the present control unit arrangement at two different rates. The lower curves represent a heating rate of $10^{\circ}\text{C}/\text{minute}$. The furnace was heated from 50°C to 150°C in ten minutes. The legend in the center of the figure shows the scale of a 5° difference. (The actual y-axis is the thermocouple voltage, mV. For a type K thermocouple in this temperature range, the temperature vs. voltage curve is sufficiently linear for our purposes.) The upper curves were obtained by heating from 100°C to 150°C in ten minutes, or $5^{\circ}\text{C}/\text{min}$.

The dashed lines superimposed on the heating curves show them to be linear over nearly the entire range. Both experimental curves show slight oscillations about this ideal ramp. The higher heating rate shows the greater oscillation, which is typically 1°C different than the ideal value. Both curves deviate from ideality at the start of the experiment, about the first 30-45 seconds. The furnace was heated to near the starting temperatures before the experiments were begun. This may be due to the lag in the heating of the thermocouple by the furnace that has been noted before. It is estimated that the sample inside the crucible may be about 20°C cooler than the thermocouple. Future experiments using samples of well-known desorptive properties will be used to calibrate the actual sample temperature against the thermocouple value of the furnace. Since the lag occurs at the low temperature end of the ramp, it will not interfere with the working range (expected to be above 100°C for most glasses) and so will not be of concern at this point.

These experiments have also shown the furnace to overshoot the final temperature, probably due to the temperature lag associated with the crucible. Again, this should not present any complications in TPD experiments.

Finally, Fig. 17 shows a TPD spectrum of a hydrated glass. The sample, supplied by J. Abrajano (CMT), consisted of a simple soda silica glass hydrated with D_2O . The layer thickness was approximately $1\ \mu\text{m}$. The spectrum shows the $m/e = 19$ peak (HDO^+) as a function of the furnace

Fig. 16. Temperature Ramp Produced using Two Different Heating Rates (Top) 5°C/minute, (Bottom) 10°C/minute.

Fig. 17. TPD Spectra, $m/e = 19$ HDO, of Hydrated Glass

temperature. Familiar bursts were observed up to a temperature near 300°C. These have been postulated to arise from fluid inclusions that ruptured as the pressure inside the inclusion was sufficient to pop the weakened glass and so vaporize the inclusion. The high temperature side of these bursts have exponential-like decay patterns probably reflective of the pumping speed of the chamber pumps. The rise in the background level starting at about 150°C may be due to the buildup of HDO^+ in the chamber due to too slow pumping or may be due to release of HDO^+ through another mechanism, for example, evaporation from the glass structure as opposed to inclusions. Other workers have found a broad desorption peak centered near 400°C for similar samples using thermogravimetric analysis. This latter technique does not distinguish the chemical nature of the desorbing species, but rather measures the weight change of the sample.

At temperatures greater than 300°C the release pattern is somewhat different from the bursts seen earlier. The bursts are much broader and not nearly as peaked. It appears that the pumping speed of HDO is sufficient to prevent appreciable background buildup. It is presently speculated that the surface is melting and water is being driven from hydrated layer. The inclusions are probably all decrepitated at this point.

Minor problems in the temperature control are evident between 300°C and 350°C where the spectrum can be seen to turn back on itself as the furnace radiatively cools before the temperature controller provides another power burst. This can hopefully be remedied by an adjustment in the control unit.

Another experiment using a fresh piece of D_2O hydrated glass is scheduled shortly. This time the TPD spectrum of HDO^+ will be collected for temperatures to near 600°C. A smaller sample size will be used in an effort to reduce further the possibility of too slow pumping speeds contributing to the background level.

V. GLASS ANALOG STUDIES
(QA level III, activity #D-20-31)

The goal of this study has been to develop analytical techniques to investigate how glass changes when reacted in water and to relate reactions that occur in natural glass to those found in nuclear waste glasses. It is generally recognized that when such a reaction occurs a gel layer forms on the surface of unreacted glass. The interest lies in learning:

- (1) How does the gel layer grow with time?
- (2) What is the composition of the gel layer?
- (3) Is the gel layer homogeneous with respect to composition?
- (4) If the layer is heterogeneous, how does the composition change?

The SEM/EDS system described previously allows qualitative analysis to be performed on points or "spots," on small areas, and also allows collection of line profiles, which measure concentration changes along a line. These collected spectra are then converted to quantitative output using the Princeton Gamma Tech (PGT) System 4 software. The software being used consists of a standard library routine, BSTAND, and a sample measurement routine, BSAM. In order to demonstrate the facility of the system and software, and to establish the reproducibility of the technique, a series of exercises were initiated. These exercises consisted of taking a set of glass standards (known concentrations) and using them to analyze each other as unknowns. The effort spent in quantifying the system is necessary because currently the bulk glass is used as a standard when analyzing the reacted layers, and a full understanding of all the processes that affect quantitative measurements will aid in interpreting the results of layer analyses.

The glass standards and samples were mounted in cross-section in epoxy and polished with diamond and/or alumina polish ($0.05\ \mu$). Previously mounted samples [BYERS] were found to have developed cracks between the glass and epoxy, making layer thickness measurements and line profile analysis impossible. It was found that by mounting sample in EpoxideTM resin and hardener (Buehler, Ltd.), allowing at least 24 hours for the mount to set, followed by polishing (several minutes 600 grit carborundum paper followed by an ultrasonic rinse and 3-4 hours of polish in a vibratory polisher, Alumina $0.3\ \mu$) the cracking problem did not develop.

This polishing procedure has been used on all samples and standards subsequently mounted. The polished samples had been coated with carbon in an evaporating coater, previously used primarily for samples only examined in the SEM.

The initial exercise of establishing the reproducibility of the system used three SRL type standard glasses which contained 2%, 5%, and 8% CaO and an NBS standard glass (basalt glass, USNM 111240) Table 20. It was found that the SRL glasses could be used to analyze each other very well (individual elements $\pm 10\%$ of known values, total composition $100 \pm 2\%$). However, these standards were unsuitable for analyzing the basalt glass. Calcium and iron, in particular, were not reliably analyzed. The total composition was $100 \pm 20\%$, although when the total analysis was normalized to 100%, the analysis for individual elements improved. A meeting with a PGT technician suggested that the compositions of the standards were different enough to produce the differences observed. He believed new standards along with careful collection of spectra would eliminate these problems.

New standards were obtained from the Smithsonian Institute. These glass standards consisted of three basaltic glasses. The basalt glass C. Byers used in his analog study was also analyzed by Analytical Chemistry Laboratory (ACL) for later use as a standard. The compositions of these four glasses are given in Table 20. These standards were used to analyze each other. In collecting these spectra it was discovered that the SEM current stabilized after one hour and the area collected was inconsequential. It was also found that samples that had been prepared separately required normalization to obtain comparable results. Such normalization indicated that while the relative amounts of the individual elements were in the correct proportions, the spectra were not being collected under identical conditions. It was decided that this was due to different carbon coatings on each mount. This was tested by coating two different mounts using a carbon evaporator at Northwestern University used in conjunction with their electron microprobe. This higher quality coater produced analyses among the four basalt glass standards that were identical to the known values within the analytical error. A suitable carbon coater has been purchased and is presently being installed.

While the problems of analyzing bulk glass appear to have been solved, the extension of the technique to reacted glass is being made. It appears that shorter collection times may be required because the probe current drifts if left on reacted glass for longer than 100 seconds. Another option is to use a smaller probe current. The x-ray detector is currently being overhauled by PGT after degradation in the energy resolution was noted.

To summarize, sample preparation techniques (sample mounting and polishing) have been developed which meet our analytical needs. A carbon coater suitable for quantitative analysis is being installed. The analytical technique is being extended to analyze reactor glasses.

REFERENCES

BARKATT

A. Barkatt, A. Barkatt, and W. Sousanpour, Nucl. Technol. 60, 218 (1983). NNA.891101.0002

BATES-1

J. K. Bates et al., "NNWSI Waste Form Testing at Argonne National Laboratory, Semiannual Report, January-June 1986," Lawrence Livermore National Laboratory report UCRL-15801-86-1 (1988). NNA.871218.0006

BATES-2

J. K. Bates et al., "NNWSI Waste Form Testing at Argonne National Laboratory, Semiannual Report, July-December 1986," Lawrence Livermore National Laboratory report UCRL-15801-86-2 (1989). NNA.900315.0278

BATES-3

J. K. Bates and T. J. Gerding, "One Year Results of the NNWSI Unsaturated Test Procedure: SRL 165 Glass Application," Argonne National Laboratory report ANL-85-41 (1986). NNA.870903.0081

BATES-4

J. K. Bates and M. J. Steindler, Science 218, 51 (1982). NNA.891101.0005

BATES-5

J. K. Bates, D. F. Fischer, and T. J. Gerding, "The Reaction of Glass in a Gamma Irradiated Saturated Tuff Environment, Part 1: SRL 165 Glass," Argonne National Laboratory report ANL-85-62 (1986). NNA.891101.0008

BATES-6

J. K. Bates, D. F. Fischer, and T. J. Gerding, "The Reaction of Reference Commercial Nuclear Waste Glasses during Gamma Irradiation in a Saturated Tuff Environment," J. Mater. Res. 3(3), 576-579 (May/June 1988). NNA.900125.0073

BATES-7

J. K. Bates, T. J. Gerding, D. F. Fischer, and W. L. Ebert, "The Reaction of Glass in a Gamma Irradiated Saturated Tuff Environment, Part II: Data Package for ATM-1c and ATM-8 Glasses," Lawrence Livermore National Laboratory report UCRL-15991, SANL 610-008 (1988). NNA.871215.0034

BATES-8

J. K. Bates and V. M. Oversby, in Scientific Basis for Nuclear Waste Management VIII, Vol. 44, eds. C. M. Jantzen, J. A. Stone, and R. C. Ewing, Materials Research Society, Pittsburgh, PA, p. 257 (1985). NNA.891101.0010

BAZAN

F. Bazan, J. Rego, and R. D. Aines, in Scientific Basis for Nuclear Waste Management X, Vol. B4, eds. J. K. Bates and W. B. Seefeldt, Materials Research Society, Pittsburgh, PA, p. 447 (1987).
NNA.891108.0048

BURNS

W. G. Burns et al., J. Nucl. Mat. 107, 245 (1982). NNA.891101.0027

BYERS

C. D. Byers, M. J. Jercinovic, and R. C. Ewing, "A Study of Natural Glass Analogues as Applied to Alteration of Nuclear Waste Glass," Argonne National Laboratory report ANL-86-46 (1987). SRX.870720.0172

KIM

J. I. Kim, M. Bernkopf, C. H. Lierse, and F. Kopold, in ACS Symp. Ser. No. 246, eds. G. S. Barney, J. Navratil, and W. Schulz, American Chemical Society, 115-134 (1984).

LOKKEN

R. O. Lokken and D. M. Strachan, in Advances in Ceramics, Vol. 8, Nuclear Waste Management, eds. G. G. Wicks and W. A. Ross, The American Ceramic Society, Inc., Columbus OH, p. 39 (1984).
NNA.891120.0013

MAUPIN

G. D. Maupin, W. M. Bowen, and J. L. Daniel, "Fabrication and Characterization of MCC Approved Testing Material - ATM-10 Glass," Pacific Northwest Laboratory report PNL-5577-10 (1988).

McVAY-1

G. McVay and L. Pederson, J. Am. Ceram. Soc. 64, 154 (1981).
NNA.891109.0053

McVAY-2

G. L. McVay and G. R. Robinson, Pacific Northwest Laboratory report PNL-4897 (1984). HQS.880517.2496

PLODINEC

M. J. Plodinec, G. G. Wicks, and N. E. Bibler, Savannah River Laboratory report DP-1629 (1982). HQ5.880517.2525

STEINDLER

M. J. Steindler et al., "Quarterly Progress Report, Nuclear Fuel Cycle Section," Argonne National Laboratory topical reports ANL-84-37, ANL-84-47, and ANL-84-91 (1984). NNA.900125.0072, NNA.891101.0011, and NNA.891101.0012

**The following number is for Office of Civilian Radioactive
Waste Management Records Management purposes only and
should not be used when ordering this document:**

Accession Number: NNA.891206.0124