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THE REACTION OF GLASS DURING GAMMA IRRADIATION
IN A SATURATED TUFF ENVIRONMENT
PART 3: LONG-TERM EXPERIMENTS AT 1×10^4 RAD/HOUR

by

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

Chemical Technology Division

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ERRATA FOR ANL-88-14

The following corrections to the original text are noted.

- 1) Page 51, line 19 - Table 9 should be Table 10.
- 2) Page 51, line 5 - Mn should be added to the list of elements that are enriched in the surface layer.
- 3) Page 67, line 1 - The first sentence should read "It is possible to qualitatively estimate ..."
- 4) Page 83, equation (R-6) should read

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ABSTRACT

Savannah River Laboratory 165 type glass was leached with equilibrated J-13 groundwater at 90°C for times up to 182 days. These experiments were performed as part of an effort by the Nevada Nuclear Waste Storage Investigations Project to assess the importance of radiation effects on repository performance and waste glass corrosion. The gamma radiation field used in this work was $1.0 \pm 0.2 \times 10^4$ rad/h.

Glass dissolution is notably incongruent throughout the entire experimental periods and normalized releases follow the sequence $Li \geq Na \geq B \approx U \geq Si$. The normalized leach rates of these elements, as well as the measured growth rates of the reaction layers, decreased with time. The only significant variation observed in the abundance of anions is the systematic decrease in NO_3^-/NO_2^- ratio from the starting EJ-13 groundwater to the EJ-13 blank experiments to the tuff- and glass-containing experiments. A leaching model that is consistent with the observed solution data and depth profiles is presented. The applicability and limitation of the present results in predicting the actual interactions that may occur in the NNWSI repository are discussed.

EXECUTIVE SUMMARY

Savannah River Laboratory 165 type glass was leached with equilibrated J-13 groundwater at 90°C for times up to 182 days. These experiments were performed by the Nevada Nuclear Waste Storage Investigations Project as part of an ongoing effort to assess the importance of radiation effects on repository performance and waste glass corrosion. The gamma radiation field used in this work was $1.0 \pm 0.2 \times 10^4$ rad/h.

In all experiments, including blanks, the final measured pH ranged from 6.7 to 7.5, and a trend of decreasing pH to 56 or 91 days followed by an increase to 182 days was observed. This pH trend was attributed primarily to interplay between acidification by nitric acid production (radiolysis of N_2) and basification by CO_2 loss from solution. In the presence of glass, the exchange of H_3O^+ (or H^+) from solution and mobile cations from the glass promoted further basification. The only significant variation observed in the abundance of anions was the systematic decrease in NO_3^-/NO_2^- ratio from the EJ-13 only to the EJ-13 + tuff to the EJ-13 + tuff + glass experiments. This observation was attributed to the catalytic effect of reduced species present on the tuff and glass surfaces on radiolytic reactions that ultimately lead to the nitrate breakdown.

Glass dissolution was notably incongruent throughout the entire duration of leaching (182 days), and normalized releases followed the sequence $Li \geq Na \geq B \approx U \geq Si$. The normalized leach rates of these elements decreased with time. Depth profiles for H, Li, Na, and B indicated the presence of two distinct regions in the reacted surface layer: (1) gel and (2) transition zone. The following leaching model is consistent with the solution data and observed depth profiles:

- (1) The glass/solution interaction begins with the surface release processes of mobile glass constituents (e.g., Li, Na, B) and H^+ or H_3O^+ from solution. Bulk interdiffusion through the incipient diffusion or transition zone subsequently controls the rate of exchange.
- (2) Behind the diffusion front, a gelation front develops, formed by partial hydrolysis of bridging oxygen bonds. The growth of the zone between these two fronts, i.e., the transition zone, is a

function of their relative rates of advance. Similarly, the growth of the gel layer is determined by the relative rates of etching and gelation. The rates of etching, gelation, and diffusion with respect to the initial glass surface decrease with time.

- (3) Silicon released into solution is primarily derived from etching the solution side of the gel. In contrast, significant release of Li, Na, and B must be attributed to direct leaching of the bulk glass through the gel and transition zones. The release kinetics of Li, Na, and B are largely controlled by the thickness and composition of the transition zone because the gel is a relatively poor barrier to diffusion of these elements (cf. item #4 below).
- (4) Deposition of alteration products in and on the gel layer and reconstitution of the partially hydrolyzed anionic framework may further modify the release rates of some glass constituents.

The measured total normalized concentrations of the actinides Am and Pu, but probably not Np or U are consistent with their release via matrix breakdown, whereas their concentration in solution is controlled by their solubility. Comparison of analyses of filtered and unfiltered solutions suggests that Am, Pu, and Np are present mostly as filterable fraction, although it is unclear if colloids are actually present during the tests.

The release of leachable glass species did not appear to be significantly affected by the presence of tuff, a finding that contrasts with earlier results that used powdered tuff. Together, these results may suggest that the influence of tuff on the aqueous corrosion of glass depends on the total tuff surface available to influence the solution chemistry.

Some preliminary comments are presented on the applicability and limitation of the present results to predicting the actual interactions that may occur in the NNWSI repository. The experiments were not designed to simulate all possible scenarios for waste form-groundwaters interaction, but to assess the importance of radiation for one potential set of conditions. Whereas all test components were relevant to the NNWSI setting, the experimental SA/V ratio, tuff/liquid ratio, and gas/liquid ratio were most likely lower than expected for the repository after waste emplacement. The

compositions of the groundwater and repository atmosphere were chosen based on projected performance of the repository setting; however, both may vary in the experimental and repository systems. Because of the radiation environment and coupled glass dissolution mechanism, SA/V scaling should be applied with caution.

I. INTRODUCTION

The volcanic tuff beds of Yucca Mountain, Nevada, are currently being evaluated by the Nevada Nuclear Waste Storage Investigations (NNWSI) project as a repository for the permanent storage of high-level nuclear waste [BALLOU]. A complete evaluation of the site requires an understanding of the complex physical processes expected to occur in the repository and a description of how the interaction of these physical processes will affect repository performance. In addition, the evaluation must consider changing conditions that will exist as the waste ages and the level of radioactivity decreases.

One issue that has a direct influence on the performance of the repository, especially during the initial 300- to 1000-year containment period, is the effect of penetrating gamma radiation on groundwater chemistry and glass leaching. It is during this period that the radiation levels will be the highest, with the initial dose rate being $\sim 5 \times 10^3$ rad/h for the waste produced by the Defense Waste Processing Facility (DWPF). Radiation will mostly influence the composition of the groundwater via radiolysis reactions. Changes in groundwater chemistry could affect corrosion of the metal components of the waste package, as well as the durability of the waste form in the event of premature failure of the container. Physical damage to the solid components of the waste package as a result of gamma radiation is not expected to adversely affect its performance.

To understand the effect of radiation on groundwater chemistry and waste form durability, NNWSI is performing an extensive set of radiation experiments as a function of dose rate (2×10^5 , 1×10^4 , 1×10^3 , and 0 rad/h). The results of the tests done at 2×10^5 rad/h have been reported [BATES-1], while the 1×10^3 and 0 rad/h tests are in progress

[BATES-2]. This report presents the results of the tests done at 1×10^4 rad/h and discusses the relevance of these tests to repository conditions. A preliminary interpretation of the results is presented with regard to the manner by which the glass waste form corrodes. A more complete discussion of the effect of gamma radiation on groundwater chemistry and waste form durability will be presented when the entire series of experiments are completed.

Background

R. A. Van Konynenburg of Lawrence Livermore National Laboratory (LLNL) has presented a thorough review of the literature pertaining to the irradiation of moist air and liquid water in the presence of components that may be present in a geologic repository [VAN KONYNENBURG]. While most previous studies were not directed specifically to conditions expected in the NNWSI repository (e.g., "open" to exchange with atmosphere, tuff, J-13 water, and 304 L stainless steel), several generic conclusions have been made.

1. When moist air is subjected to gamma radiation, HNO_3 , N_2O , and H_2O_2 are produced.
2. When pure water is subjected to gamma radiation, an equilibrium between free radicals and molecular products is achieved whereby no net decomposition of the water occurs.
3. When moist air is irradiated in the presence of liquid water and waste package components, several competing reactions will occur.

The most important result of these reactions is the increased concentration of nitric acid in solution. The rate of nitric acid production has been quantified 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,
- C_0 = the initial nitrogen concentration,
- $R = \text{vol}_{\text{gas}}/\text{vol}_{\text{liq}}$,
- G = irradiation efficiency of nitrate production,
- D = dose rate, and
- t = time of irradiation

The effect of nitric acid production on groundwater chemistry and glass reaction is more difficult to project. When experiments were done in deionized water, the pH quickly became more acidic and led to accelerated corrosion of the glass [McVAY]. However, in MNWSI groundwater (J-13) in the presence of waste package components, a drift to more acidic pH is counteracted by the buffering effect of the carbonic acid/bicarbonate equilibrium and by the release of alkalis (e.g., Na^+ , Li^+ , Cs^+) from the glass. The net effect of these processes at a dose rate of 2×10^5 rad/h (total dose up to 2.7×10^8 rad) was to retard or have no effect on glass reaction compared with some previously reported non-irradiated experiments [BATES-1].

As the dose rate is lowered to 1×10^4 rad/h (total dose up to 4.4×10^7 rads), the amount of nitric acid produced is expected to decrease. It is of interest to see how this will affect the solution chemistry, i.e., with less acid production, will the effect of alkali release overwhelm that of acid production? Will the resulting "pH excursion" lead to more rapid glass reaction?

II. EXPERIMENTAL

A. Test Matrix

The design of the present experiments was similar to that used previously [BATES-1]. The experimental matrix consisted of one set of experiments in which two glass disks were placed together in individual Type 304 L stainless steel vessels with measured amounts of equilibrated J-13 water (EJ-13). The glass surface area to solution volume (SA/V) ratio for these experiments was nominally set at 0.3 cm^{-1} . A second set of experiments was performed in which a polished tuff core wafer was also added to the vessel, along with the glass. Both sets were run at a nominal temperature of 90°C , a γ -dose rate of $1.0 \pm 0.2 \times 10^4$ rad/h, and with SRL 165 type glass doped with uranium (SRL U) or uranium plus transuranic elements (SRL A). The purpose of these two matrices was to study the effect of radiation on the reaction of glass with groundwater, and to monitor how the released radionuclides interact with the test components.

A third set of experiments was done in which only groundwater, or groundwater plus tuff, were present in the test vessel. These experiments were done to monitor the effect of radiation on groundwater chemistry, and to serve as "blanks" for the glass-containing experiments.

The current set of experiments differed from the previous experiments [BATES-1] in the following manner:

1. The dose rate was reduced from 2×10^5 rad/h to 1×10^4 rad/h.
2. No crushed glass or crushed tuff was included.
3. The duration of the tests extended for 14 to 182 days as opposed to 7 to 56 days.
4. Additional analyses of the solutions and test components were performed.

The complete test matrix is given in Table 1.

B. Test Components

A schematic configuration of the test assembly is shown in Fig. 1. Except that tuff disks are used instead of crushed tuff, all the components shown are identical to those used previously. The tuff disks (from USW-G1, 1235.1-ft and 1232.2-ft levels) were specially prepared for the present experiments by NNWSI. The order of the tuff disks as obtained from NNWSI was retained throughout the testing so that trends attributable to the presence of tuff may be correlated with documented features of the tuff or the position of the tuff in the drill core.

The leachant used in the present experiments (EJ-13 water) was prepared by reacting J-13 groundwater with caliche-free Topopah Spring tuff at 90°C for 14 days [OVERSBY, BATES-3]. The tuff used in this equilibration procedure was supplied by NNWSI (UE-25 h #1, 173.0-ft to 173.6-ft levels) and was from the same batch that had been used to equilibrate J-13 water in the previous tests. Further details of this procedure are described in Appendix I. The solution analysis of the resulting EJ-13 water is shown in Table 2, together with the composition of the EJ-13 water used previously. Although the tuff used in both equilibrations was from the same batch, the final water compositions were slightly different. The 1×10^4 Rad/hr EJ-13 solution has less Si and Al and more Ca than the 2×10^5 Rad/h solution has.

Table 1. Test Matrix for the 1985 Gamma Radiolysis and Leaching Experiment

Test Type	Test #	Sample #	Vessel #	Test Length (days)	Date In	Date Out	Sample Thickness (mm)	Sample Diameter (mm)	Sample SA (cm ²)		Sample Phase (g)		Support Phase (g)		Tuff Mass In (g)	H ₂ O Volume In (mL)	Completed Assembly (g)		Weight Loss (10E-4)
									Total/Vessel	Individual	In	Out	Loss (10E-5)	In	Out	Loss (10E-4)	In	Out	
SRL U • EJ-13	C-201	201	80	14	9/04	9/19	1.80	10.96	447.28	250.66	0.4195	0.41574	21	4.9198	4.9200	-2	303.35	303.35	-
	C-202	202	81	14	9/04	9/19	0.70	10.51	106.62	106.62	0.1527	0.1527	23	4.9052	4.9059	13	303.22	303.22	-
	C-203	203	81	14	9/04	9/19	0.74	10.72	187.14	187.14	0.1502	0.1502	23	4.9052	4.9059	13	303.22	303.22	-
	C-204	204	92	28	9/21	9/19	1.46	10.72	295.69	295.69	0.34474	0.34474	31	4.8505	4.8492	13	302.05	302.05	-
	C-205	205	92	28	9/21	9/19	1.33	10.85	456.34	456.34	0.31750	0.31751	19	4.9090	4.9080	10	304.21	304.17	400
	C-206	206	93	28	9/21	9/19	1.28	10.74	224.38	224.38	0.29517	0.29517	29	4.8937	4.8937	-	303.41	303.35	600
	C-207	207	93	28	9/21	9/19	1.34	10.74	451.54	451.54	0.31668	0.31668	39	4.8937	4.8937	-	303.41	303.35	600
	C-208	208	78	56	6/24	8/19	1.44	10.74	445.71	445.71	0.30777	0.30777	32	4.8937	4.8937	-	303.41	303.35	600
	C-209	209	78	56	6/24	8/19	1.03	10.74	274.77	274.77	0.30777	0.30777	32	4.8937	4.8937	-	303.41	303.35	600
	C-210	210	78	56	6/24	8/19	1.03	10.74	274.77	274.77	0.30777	0.30777	32	4.8937	4.8937	-	303.41	303.35	600
	C-211	211	78	56	6/24	8/19	0.99	10.74	274.77	274.77	0.30777	0.30777	32	4.8937	4.8937	-	303.41	303.35	600
	C-212	212	74	91	5/20	8/19	1.31	10.78	222.75	222.75	0.31326	0.31326	59	4.8768	4.8771	-3	302.51	302.45	600
	C-213	213	74	91	5/20	8/19	1.07	10.67	222.75	222.75	0.31326	0.31326	59	4.8768	4.8771	-3	302.51	302.45	600
	C-214	214	75	91	5/20	8/19	0.95	10.76	213.99	213.99	0.21653	0.21653	198	4.8688	4.8647	41	301.77	301.68	900
	C-215	215	55	182	4/08	10/07	1.28	10.81	227.08	227.08	0.30787	0.30787	228	4.9364	4.9359	5	309.06	308.87	1900
	C-216	216	55	182	4/08	10/07	1.28	10.86	227.08	227.08	0.31261	0.31261	31	4.9122	4.9119	3	311.06	310.94	1200
	C-217	217	65	182	4/08	10/08	1.29	10.72	228.26	228.26	0.30799	0.30799	50	4.8755	4.8751	4	304.24	304.24	-
	C-218	218	82	14	9/04	9/19	1.32	10.77	228.86	228.86	0.30961	0.30961	14	4.8755	4.8751	4	304.24	304.24	-
	C-219	219	83	14	9/04	9/19	1.30	10.91	231.53	231.53	0.31506	0.31506	11	4.9001	4.9001	-	303.16	303.15	100
	C-220	220	94	28	9/21	9/19	1.42	10.75	229.48	229.48	0.34011	0.34011	24	4.9127	4.9123	4	305.51	305.49	200
	C-221	221	96	28	9/21	9/19	1.25	10.70	221.86	221.86	0.30512	0.30484	28	4.9127	4.9123	4	305.51	305.49	200
	C-222	222	96	28	9/21	9/19	1.28	10.70	221.86	221.86	0.30512	0.30512	28	4.9127	4.9123	4	305.51	305.49	200
	C-223	223	76	56	6/24	8/19	1.34	10.78	226.02	226.02	0.32000	0.31964	36	4.9028	4.9025	3	302.37	302.30	700
	C-224	224	77	56	6/24	8/19	1.22	10.72	221.60	221.60	0.32121	0.32121	48	4.9129	4.9127	2	303.77	303.78	400
	C-225	225	77	56	6/24	8/19	1.38	10.85	240.76	240.76	0.32098	0.32098	76	4.9052	4.9052	-	302.60	302.50	1000
	C-226	226	78	91	5/20	8/19	1.53	10.63	227.12	227.12	0.32098	0.32098	76	4.9052	4.9052	-	302.60	302.50	1000
SRL A • EJ-13	C-227	227	78	91	5/20	8/19	1.30	10.78	226.57	226.57	0.31715	0.31702	73	4.8505	4.8505	-	305.34	305.29	500
	C-228	228	79	91	5/20	8/19	1.19	10.77	222.46	222.46	0.31641	0.31641	60	4.9113	4.9109	4	302.02	301.81	2100
	C-229	229	66	182	4/01	10/07	1.32	10.78	225.68	225.68	0.32006	0.32006	60	4.8684	4.8679	5	310.46	310.27	1900
	C-230	230	67	182	4/01	10/07	1.38	10.78	225.68	225.68	0.32006	0.32006	60	4.8684	4.8679	5	310.46	310.27	1900
	C-231	231	84	14	9/04	9/19	1.34	10.78	226.02	226.02	0.31685	0.31685	64	4.8684	4.8679	5	310.46	310.27	1900
	C-232	232	84	14	9/04	9/19	1.30	10.90	226.02	226.02	0.31685	0.31685	64	4.8684	4.8679	5	310.46	310.27	1900
	C-233	233	85	14	9/04	9/19	1.28	10.94	226.02	226.02	0.31685	0.31685	64	4.8684	4.8679	5	310.46	310.27	1900
	C-234	234	85	14	9/04	9/19	1.27	9.94	194.86	194.86	0.25469	0.25469	22	4.8684	4.8679	5	310.46	310.27	1900
	C-235	235	72	28	8/21	9/19	1.35	9.87	194.26	194.26	0.25469	0.25469	22	4.8684	4.8679	5	310.46	310.27	1900
	C-236	236	72	28	8/21	9/19	1.30	9.94	194.74	194.74	0.25469	0.25469	22	4.8684	4.8679	5	310.46	310.27	1900
SRL A • EJ-13	C-237	237	78	28	8/21	9/19	1.30	9.94	194.74	194.74	0.25469	0.25469	22	4.8684	4.8679	5	310.46	310.27	1900
	C-238	238	78	28	8/21	9/19	1.31	9.94	194.74	194.74	0.25469	0.25469	22	4.8684	4.8679	5	310.46	310.27	1900
	C-239	239	80	56	6/24	8/19	1.28	9.94	194.74	194.74	0.25469	0.25469	22	4.8684	4.8679	5	310.46	310.27	1900
	C-240	240	80	56	6/24	8/19	1.28	9.94	194.74	194.74	0.25469	0.25469	22	4.8684	4.8679	5	310.46	310.27	1900
	C-241	241	81	56	6/24	8/19	1.48	9.85	199.63	199.63	0.29481	0.29481	36	4.8755	4.8755	-	303.25	303.20	500
	C-242	242	81	56	6/24	8/19	1.25	9.85	191.06	191.06	0.25449	0.25449	36	4.8755	4.8755	-	303.25	303.20	500

C-226	250	81	56	6/24	8/19	1.43	9.89	199.43	384.95	0.25081	0.29796	36	4.8755	4.8755	-	14.45	303.25	303.20	500
C-227	251	82	91	5/20	8/19	1.25	9.85	191.00	287.11	0.22349	0.25412	37	4.8649	4.8651	-2	14.46	301.91	301.86	500
C-228	252	83	91	5/20	8/19	1.42	9.78	193.87	297.11	0.22362	0.27335	423	4.8821	4.8822	-1	14.00	300.78	300.71	700
C-229	253	83	91	5/20	8/19	1.35	9.83	193.47	358.94	0.27410	0.27446	64	4.8638	4.8637	1	13.27	331.85	331.64	2100
C-230	254	68	182	4/01	10/07	1.44	9.81	191.23	350.88	0.25355	0.25299	21	4.9283	4.9283	-	13.34	329.76	329.51	2500
C-231	255	69	182	4/01	10/07	1.13	9.92	196.80	376.31	0.43571	0.43520	58	4.8734	4.8734	10	2.21	303.20	303.19	100
C-232	256	86	14	9/04	9/19	1.24	9.81	188.36	407.81	0.45372	0.45327	45	4.8822	4.8823	-1	2.35	303.65	303.63	300
C-233	257	87	14	9/04	9/19	1.16	9.84	187.95	407.81	0.41212	0.44178	34	4.9052	4.9052	-	14.10	303.66	303.64	200
C-234	258	74	28	8/21	9/19	1.27	9.96	195.56	399.52	0.25792	0.25724	68	4.8647	4.8644	3	14.12	302.52	302.52	-
C-235	259	76	28	8/21	9/19	1.32	9.90	195.83	399.52	0.27413	0.27435	38	4.9002	4.9001	1	2.14	304.31	304.26	500
C-236	260	84	56	6/24	8/19	1.32	9.92	196.71	399.52	0.26692	0.26945	47	4.9002	4.9001	1	2.28	304.31	304.26	500
C-237	261	85	56	6/24	8/19	1.29	9.85	192.32	384.64	0.26097	0.26033	51	4.8734	4.8734	-	1.96	302.84	302.74	1000
C-238	262	86	91	5/20	8/19	1.31	9.84	192.59	394.44	0.26052	0.25991	61	4.9200	4.9198	2	2.43	303.76	303.68	800
C-239	263	87	91	5/20	8/19	1.26	9.86	191.72	387.89	0.31587	0.31522	65	4.8895	4.8895	-	2.30	326.56	326.39	1700
C-240	264	70	182	4/01	10/07	1.33	9.91	196.67	377.61	0.27553	0.27473	80	4.8729	4.8727	2	2.20	329.75	329.61	1400
C-241	265	71	182	4/01	10/07	1.22	9.82	189.11	376.32	0.44038	0.44038	44	4.9148	4.9148	-	2.30	329.75	329.61	1400
C-242	266	71	182	4/01	10/07	1.22	9.82	189.11	376.32	0.44038	0.44038	44	4.9148	4.9148	-	2.30	329.75	329.61	1400
C-243	267	71	182	4/01	10/07	1.06	9.94	188.30	376.32	0.43260	0.43260	51	4.9148	4.9148	-	2.30	329.75	329.61	1400
C-244	268	75	14	9/04	9/19	1.14	9.86	188.92	376.32	0.43404	0.43555	49	4.9148	4.9148	-	2.30	329.75	329.61	1400
C-245	269	90	14	9/04	9/19	1.27	9.82	212.25	407.81	0.25792	0.25724	68	4.8734	4.8734	10	2.21	303.20	303.19	100
C-246	270	90	14	9/04	9/19	1.27	9.82	212.25	407.81	0.25792	0.25724	68	4.8734	4.8734	10	2.21	303.20	303.19	100
C-247	271	90	14	9/04	9/19	1.33	9.93	196.59	393.08	0.27179	0.27163	16	4.8822	4.8823	-1	2.35	303.65	303.63	300
C-248	272	78	28	8/21	9/19	1.42	9.86	196.70	399.52	0.26857	0.26841	16	4.9052	4.9052	-	14.10	303.66	303.64	200
C-249	273	88	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-250	274	89	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-251	275	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-252	276	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-253	277	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-254	278	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-255	279	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-256	280	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-257	281	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-258	282	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-259	283	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-260	284	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-261	285	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-262	286	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-263	287	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-264	288	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-265	289	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-
C-266	290	90	56	6/24	8/19	1.30	9.93	196.44	399.52	0.26305	0.26277	28	4.8647	4.8644	3	14.12	302.52	302.52	-

Fig. 1. Schematic Configuration of Test Assembly

Table 2. Composition of Tuff-Equilibrated
J-13 (EJ-13) Water

	This Work, (ppm)	[BATES], ppm
Al	<0.10	0.63
B	0.14	0.16
Ca	11.9	9.08
Fe	<0.01	0.01
K	NA*	NA
Li	0.046	0.044
Mg	0.95	0.96
Na	45.4	46.5
Si	30.6	34.4
Sr	0.043	0.045
U	<0.0010	0.0024
F ⁻	2.45	2.40
Cl ⁻	7.70	7.15
HCO ₃ ⁻	NA	NA
NO ₃ ⁻	8.35	7.60
NO ₂ ⁻	<0.5	<0.5
SO ₄ ⁼	18.60	17.30
pH	7.61	8.10

*NA - Not analyzed. EJ-13 water prepared using similar procedures has 6 ppm K and 122 ppm HCO₃⁻ [VAN KONYNENBURG].

Two types of glasses were used in the present experiments:

(1) Savannah River Laboratory (SRL) 165 black frit to which uranium, cesium, and strontium had been added. This glass is referred to as SRL U.

(2) SRL U glass to which ^{237}Np , ^{239}Pu , and ^{241}Am had been added.

This is referred to as SRL A glass.

Table 3 shows the composition of the glasses used in the present and past work. Note that the amount of Am was increased in the present experiments. This was done to obtain better precision in the Am measurements. Details of glass preparation and cleaning procedures have been discussed previously [BATES-1].

The reaction vessels were fabricated by Parr (Parr Instrument Co., Moline, IL) from Type 304 L stainless steel. The vessels have a capacity of 21.4 cm^3 and were sealed with a compression fitting and a silicon rubber gasket. Silicon rubber was chosen as the gasket material because it maintains its integrity for a total dose of $\sim 5 \times 10^8\text{ rad/h}$ [BATES-1], which is about ten times larger than the total dose received in the 182-day tests. Furthermore, silicon rubber was used in the previous tests, and it was felt, for consistency, that the gasket material should not be changed, despite the observation made in the previous tests that the gasket material may have contributed silicon to the test solution.

Water loss for experiments performed for less than 182 days did not exceed 0.10 g, whereas the maximum water loss noted for the 182-day experiment was 0.25 g. These leak rates are generally higher than those observed in the previous experiments [BATES-1]; this, in part, is due to our effort to avoid overtightening the compression fitting. Overtightening the fitting may increase the likelihood of spalling extraneous pieces of rubber gasket into the vessel or contacting the extruding portion of the gasket with the solution, both of which could result in solution contamination.

The experiments were conducted in an oven controlled at a temperature of $90^\circ \pm 0.5^\circ\text{C}$. The temperature was monitored with a data logger that recorded the temperature every eight hours. The heating due to irradiation was expected to be within the error of measurement and was neglected.

Table 3. Composition of SRL Glasses^a

Component	Analysis, wt %	
	SRL 165 U/A (This Work)	SRL 165 U/A [BATES-1]
Al ₂ O ₃	4.08	4.08
B ₂ O ₃	6.76	6.76
BaO	0.06	0.06
CaO	1.62	1.62
Fe ₂ O ₃	11.3	11.3
FeO	0.35	0.35
K ₂ O	NA ^b	NA ^b
Li ₂ O	4.18	4.18
MgO	0.70	0.70
MnO	2.27	2.27
Na ₂ O	10.8	10.8
NiO	0.85	0.85
SiO ₂	52.8	52.8
TiO ₂	0.14	0.14
ZnO	0.04	0.04
ZrO ₂	0.66	0.66
²³⁷ NpO ₂	1.3E-2	0.8E-2
²³⁹ PuO ₂	3.7E-2	2.2E-2
²⁴¹ Am ₂ O ₃	9.5E-4	3.6E-4
U ₃ O ₈	0.960	0.960
Cs ₂ O	0.072	0.072
SrO	0.11	0.11
P ₂ O ₅	0.29	NA ^b

^aGlasses used in [BATES] and this work were prepared from the same frit.

^bNA - Not analyzed.

A ^{60}Co source provided the gamma irradiation. Complete dosimetry of the oven interior was done and the test vessels were positioned in aluminum racks so as to receive the desired dose rate. In addition to the gamma dose, ionizing radiation in the form of alpha emissions from the surface of actinide-doped glasses are present. However, the dose rate from alpha emissions in the present experiments is less than 10^3 rad/h and will only affect a liquid layer ~ 10 μm from the glass surface [e.g., VAN KONYNENBURG]. In the 2×10^5 rad/h tests, there was an indication that the SRL A glass reacted to a slightly larger extent than the SRL U glass, but this could not be directly attributed to an alpha radiolysis effect [BATES-1].

C. Sample Description

All the glass disks were core drilled from cast bars and were then wafered to size. The disks were cleaned ultrasonically three times with ethanol. The SRL A samples were analyzed for loose radioactivity and found to contain less than three times the background level. One of the two disks used in each test had one side ground to 600 grit. Therefore, three different types of glass surfaces were present in each test; both faces of one disk and the bottom side of the other disk are as cut, the top side of the other disk is ground to 600 grit, and the sides of the disks are as cored.

The procedure used for glass preparation was identical to that utilized previously [BATES-1], except that an additional mixing step was added. As a result of this additional step, the glasses synthesized for the present experimental program were more homogeneous than those synthesized in the previous program [BATES-1]. Color variations were notable in a few of the glass disks used in the present experiments, although no corresponding evidence of compositional variations in terms of major oxide components within individual disks were noted when the samples were examined taking EDS profiles. Also notable was the compositional heterogeneity that resulted from the presence of minute crystals of spinel as well as small gas bubbles in virtually all the glass disks. Gamma-ray spectrometry was performed to measure the degree of homogeneity of the actinide distribution in the synthesized SRL A glasses (Table 4). As shown

Table 4. Selected Activities in SRL A Glasses

Sample No.	^{241}Am Normalized, Counts/s•g	^{237}Np Normalized, Counts/s•g	$^{237}\text{Pa}^*$ Normalized, Counts/s•g	$^{152}\text{Eu}^{**}$ Normalized, Counts/s•g
241	358	0.9	1.5	0.13
242	323	0.8	1.2	0.11
243	325	0.7	1.3	0.12
244	321	0.8	1.2	0.13
245	302	0.7	1.2	0.11
246	289	0.6	1.1	0.10
247	392	1.0	1.6	0.14
248	269	0.7	1.0	0.12
249	291	0.2	1.1	0.10
250	312	0.7	1.2	0.12
251	303	0.7	1.2	0.11
252	296	0.7	1.1	0.11
254	288	0.7	1.1	0.10
255	307	0.7	1.3	0.14
256	312	0.7	1.2	0.10
257	322	0.8	1.3	0.27
258	295	0.7	1.1	0.11
259	332	0.7	1.3	0.11
260	290	0.7	1.1	0.10
261	297	0.7	1.1	0.12
262	237	0.6	1.0	0.09
263	284	0.6	1.0	0.10
264	292	0.7	1.1	0.10
265	333	0.8	1.3	0.11
266	307	0.8	1.2	0.11
267	-	1.0	1.5	0.10
268	306	1.2	2.0	0.19
269	331	0.9	1.4	0.13
270	311	0.7	1.2	0.11
271	322	0.7	1.2	0.11
272	311	0.7	1.2	0.10
273	352	0.8	1.3	0.14
274	288	0.7	1.1	0.11
275	352	0.8	1.3	0.14
276	280	0.6	1.1	0.10
277	316	0.8	1.1	0.10
278	283	0.7	1.1	0.10
279	287	0.7	1.1	0.10
280	335	0.8	1.1	0.10
$\bar{X}$	309.24	0.74	1.21	0.118
n	38	39	39	39
S.D.	27.77	0.146	0.188	0.031
%S.D.	8.98%	18%	15%	26%

*Pa is a daughter product resulting from the decay of ^{237}Np .

** ^{152}Eu is a contaminant added to the glass through the reuse of platinum crucibles in the glass melting process.

in Table 3, 1σ variation of Np and Am between glass disks were within 20 and 10 percent of their mean, respectively. The experimentally determined analytical precision of the α -counting facility was less than 10% [BATES].

D. Analyses

The methods used for analyzing the leachates were as follows: inductively coupled plasma (ICP) spectroscopy for cations; ion chromatography for anions; atomic fluorescence spectroscopy for uranium; gamma and alpha spectrometry for Pu, Am, Np; mass spectroscopy and gas chromatography for dissolved gases. Measurements of pH were performed using a Brinkmann Metrohm pH meter and a Beckman combination electrode. The sequence by which samples for each analysis were collected is detailed in Appendix II. In all cases, the solutions were cooled to room temperature before samples were collected. Cation analyses were performed on acidified unfiltered samples, except for additional actinide analyses which were also performed on non-acidified filtered ($0.005\ \mu\text{m}$) and unfiltered samples. Gases were evolved from solution by either stirring in vacuum utilizing a Van Slyke apparatus (for gas chromatography) or freeze-thawing in vacuum (for mass spectrometry). The gas chromatograph setting was optimized for H_2 . An extensive discussion of the Van Slyke apparatus and gas chromatograph system used in the present work can be found in [HART].

Microscopic and SEM/EDS analysis of the reacted glasses were performed using instruments and procedures discussed previously [BATES-1]. Nuclear resonance profiling for hydrogen was performed on selected SRL U glasses by F. Ryerson of LLNL in the laboratory of Professor W. Lanford.* The hydrogen concentration as a function of depth was studied using the nuclear reaction: $^{15}\text{N} + ^1\text{H} \rightarrow ^{12}\text{C} + ^4\text{He} + 4.43\ \text{MeV}$, which has an isolated resonance energy at 6.385 MeV. More extensive discussion of the technique can be found in [LANFORD].

Secondary Ion Mass Spectrometry (SIMS) analyses of the reacted glass surfaces were performed in an effort to obtain depth profiles of various glass components. Analyses were performed on a modified 3M KRATOS SIMS instrument interfaced to an Apple II+ computer. A 2-keV neon ion beam was used as the primary ion beam. The sampled area is of the order of $1\ \text{mm}^2$.

*State University of New York, Albany.

An electron flood gun was positioned near the sample to reduce the build-up of positive charge on the nonconductive glass surfaces. Further details of the SIMS analyses can be found in Appendix III. Some SRL A samples have also been submitted for ion microprobe analysis of actinide distribution, and some SRL U samples have been submitted for Auger and XPS analysis. These results will be presented in a later report.

III. RESULTS

This section summarizes the results of the solution analyses and surface studies on the leached SRL glasses. The as-measured cation concentrations, including blanks, are shown in Table 5; the corresponding blank corrected and normalized concentrations (except for actinides) are presented in Table 6.

Table 7 shows the result of solution analyses for the actinides Am, Pu, and Np. Anion analyses are summarized in Table 8. The test conditions, component weights, and solution volumes are presented in Appendix IV. The results of SEM, SIMS, and nuclear profiling analyses are presented in the subsection on glass surface analyses (III.D). A discussion of the results is presented in Section IV.

A. Precision and Accuracy

To provide a meaningful interpretation of the results, it is imperative to examine the accuracy and precision of the present data set. The overall precision and accuracy of the data presented in Tables 5 to 8 are functions of the accuracy and precision achieved at the experimental and analytical stages of the program. Analytical accuracy and precision are relatively easy to define since these are estimated from repeated analyses of standard samples. The analytical accuracy reported by individual analysts for the present work are as follows: 3-10% for cations, 5% for anions, 5% for U, and 10% for dissolved gases. In each case, the accuracy is based on the total amount present. Measurements of pH are accurate to within 0.02 pH units.

Table 5. As-Measured Cation Concentrations

Test Type	Test #	Test Length (Days)	pH OUT	Cation Concentration (ppm , ug/ml)									
				Al	B	Ca	Fe	Li	Mg	Na	Si	Sr	U
SRLU + EJ-13	G-201	14	7.55	0.57	0.98	11.41	4.47	1.18	1.14	50.08	42.57	0.07	0.453
	G-202	14	8.00	0.39	2.83	10.68	4.08	0.98	1.02	56.33	49.02	0.23	0.984
	G-203	28	7.07	0.73	1.30	11.02	4.97	1.60	1.09	50.62	50.62	0.09	0.620
	G-204	28	7.14	0.80		10.97	5.05	1.53	1.10	49.77	49.06	0.08	0.647
	G-205	56	6.79	1.07	1.36	11.88	10.77	1.88	1.25	53.14	50.64	0.09	0.673
	G-206	56	6.98	1.41	1.78	12.15	12.19	2.20	1.36	54.88	58.18	0.10	0.866
	G-207	91	6.76	1.65	2.12	12.44	11.24	2.51	1.42	55.58	65.80	0.12	1.049
	G-208	91	4.83	1.24	8.70	16.74	29.36	9.30	2.91	82.22	110.90	0.40	1.781
	G-209	182	7.01	0.89	1.51	13.14	8.77	2.57	1.31	52.50	85.50	0.09	0.647
	G-210	182	6.96	1.61	2.81	13.66	19.38	3.41	1.57	56.48	76.86	0.13	1.273
SRLU + EJ-13 + --	G-211	14	7.28	0.24	1.16	10.35	4.11	1.24	0.58	48.93	51.66	0.13	0.386
	G-212	14	6.87	0.33	0.84	9.60	3.77	0.97	0.55	50.08	51.72	0.13	0.290
	G-213	28	6.87	0.18	1.57	10.63	4.94	1.70	0.56	52.15	61.89	0.15	0.491
	G-214	28	6.74	0.27	1.30	10.58	4.49	1.41	0.58	51.79	63.57	0.15	0.418
	G-215	56	6.74	0.74	2.01	12.18	10.91	2.41	0.72	58.17	65.79	0.17	0.625
	G-216	56	6.66	0.58	1.91	12.46	10.23	2.22	0.73	57.42	64.32	0.17	0.592
	G-217	91	6.93	0.88	2.83	12.24	11.81	3.22	0.72	62.74	75.04	0.17	0.703
	G-218	91	6.95	0.70	2.51	12.38	8.01	2.85	0.72	60.63	67.67	0.17	0.678
	G-219	182	7.25	0.84	3.15	14.88	11.54	3.68	0.84	59.82	80.22	0.18	0.762
	G-220	182	7.29	0.76	3.17	15.54	12.06	3.75	0.90	61.04	82.65	0.19	0.771

Test Type	Test #	Test Length (Days)	pH OUT	Cation Concentration (ppm , ug/ml)									
				Al	B	Ca	Fe	Li	Mg	Na	Si	Sr	U
SRLA EJ-13	G-221	14	7.44	0.59	0.72	11.13	4.20	0.96	1.07	48.64	41.46	0.06	0.346
	G-222	14	7.52	0.51	0.81	11.16	4.20	0.99	1.05	48.84	42.41	0.06	0.367
	G-223	28	7.18	0.74	1.26	11.20	5.29	1.46	1.13	49.53	53.04	0.08	0.619
	G-224	28	7.12	0.97	1.21	11.04	5.30	1.38	1.10	48.60	53.55	0.08	0.578
	G-225	56	6.92	1.40	1.53	12.02	11.54	1.79	1.33	53.02	56.70	0.09	0.712
	G-226	56	6.95	1.26	1.44	12.06	11.62	1.68	1.30	52.54	59.29	0.09	0.660
	G-227	91	6.82	1.70	2.13	11.59	10.31	2.44	1.37	53.11	62.10	0.11	1.019
	G-228	91	6.79	1.83	2.18	12.17	11.38	2.59	1.42	56.06	71.61	0.11	0.947
	G-229	182	7.26	1.73	2.73	14.11	22.06	3.29	1.53	55.60	89.09	0.13	1.088
	G-230	182	7.24	1.73	2.57	14.11	21.49	3.16	1.49	54.93	93.93	0.12	1.101
SRLA EJ-13 Tuff	G-231	14	6.85	0.32	0.79	10.28	4.55	0.86	0.58	49.27	52.83	0.15	0.244
	G-232	14	6.86	0.30	0.87	12.80	4.21	0.95	0.72	50.10	51.95	0.17	0.284
	G-233	28	6.75	0.39	1.38	10.67	4.58	1.52	0.58	50.52	61.75	0.16	0.445
	G-234	28	6.72	0.56	1.41	11.11	4.55	1.50	0.59	50.47	64.38	0.17	0.499
	G-235	56	6.92	0.79	1.80	12.82	20.36	2.08	0.76	56.77	80.88	0.18	0.504
	G-236	56	6.88	0.90	1.65	12.88	19.26	1.98	0.75	55.70	73.37	0.18	0.599
	G-237	91	6.85	1.52	2.27	11.99	18.83	2.51	0.75	58.89	84.30	0.16	0.577
	G-238	91	6.87	1.17	2.46	13.04	16.69	2.75	0.79	59.92	71.32	0.18	0.450
	G-239	182	7.16	0.89	3.42	17.66	22.02	3.81	1.01	61.13	95.09	0.22	0.587
	G-240	182	7.09	0.95	3.62	17.42	23.20	3.93	1.01	61.57	88.22	0.22	0.719

Table 5 (Cont'd)

Test Type	Test #	Test Length (Days)	pH OUT	Cation Concentration (ppm, ug/ml)									
				Al	B	Ca	Fe	Li	Mg	Na	Si	Sr	U
EJ-13	G-241	14	7.10	<0.42	<0.13	11.10	4.38	<0.13	0.88	46.30	38.79	<0.04	0.000
	G-242	14	6.89	<0.42	0.12	11.16	2.36	0.06	0.85	44.50	31.59	0.04	0.000
	G-243	28	6.81	<0.43	<0.13	11.06	3.02	<0.13	0.85	44.66	54.02	<0.04	0.000
	G-244	28	6.80	<0.17	0.11	11.06	1.61	0.07	0.85	43.35	38.44	0.04	0.000
	G-245	56	6.73	<0.17	0.14	11.59	4.26	0.06	0.90	46.03	40.40	0.04	0.000
	G-246	56	6.78	<0.17	0.14	11.66	3.37	<0.05	0.92	46.12	38.63	0.04	0.000
	G-247	91	4.35	<0.18	0.13	11.70	32.23	0.08	0.92	45.92	37.58	0.04	0.000
	G-248	91	3.60	<0.18	0.14	11.94	1.12	0.08	1.00	46.96	37.35	0.04	0.000
	G-249	182	6.89	<0.40	0.12	11.94	<0.04	<0.12	0.96	45.13	53.52	<0.08	0.000
	G-250	182	6.93	<0.21	0.16	13.29	3.51	<0.06	1.04	44.87	62.61	0.04	0.000
EJ-13 + Tuff	G-251	14	7.05	<0.74	<0.22	11.26	5.78	<0.22	0.60	48.17	79.29	0.14	<0.007
	G-252	14	6.99	<0.17	0.08	9.27	0.71	0.09	0.51	45.30	45.48	0.12	<0.002
	G-253	28	6.68	<0.70	<0.21	9.31	3.78	0.39	0.53	47.60	58.10	0.13	<0.007
	G-254	28	6.80	<0.17	0.16	9.43	1.29	0.13	0.50	45.07	50.99	0.14	<0.002
	G-255	56	6.48	<0.17	0.14	14.02	4.47	0.16	0.80	49.23	58.48	0.18	<0.002
	G-256	56	6.47	<0.17	0.15	11.12	4.77	0.17	0.61	48.37	57.63	0.15	<0.002
	G-257	91	6.57	<0.18	0.13	10.80	4.36	0.16	0.58	49.06	64.11	0.15	<0.002
	G-258	91	6.48	<0.18	0.16	11.36	4.49	0.20	0.63	51.69	68.03	0.15	<0.002
	G-259	182	6.96	<0.49	<0.15	13.44	<0.05	0.26	0.74	50.04	68.69	0.15	<0.005
	G-260	182	6.90	<0.23	0.15	13.36	<0.02	0.28	0.72	49.68	70.94	0.16	<0.002

Table 6. Normalized Cation Release

Test Type	Test #	Test Length (Days)	pH OUT	Normalized Release (g/m ²)									
				Al	B	Ca	Fe	Li	Mg	Na	Si	Sr	U ^d
SRLU + EJ-13	G-201	14	7.55	0.3	1.3	-0.7	0.7	1.9	1.8	1.9	1.0	1.0	1.78
	G-202	14	8.00	0.1	4.6	-3.0	0.6	1.7	0.9	4.9	2.0	7.5	4.18
	G-203	28	7.07	0.6	1.8	-1.8	0.9	2.6	1.3	2.1	2.0	1.7	2.39
	G-204	28	7.14	0.7	-0.2	-1.9	1.0	2.5	1.5	1.8	1.9	1.5	2.52
	G-205	56	6.79	1.1	1.9	0.7	3.3	3.1	2.7	3.2	1.5	1.8	2.64
	G-206	56	6.98	1.6	2.6	1.4	3.9	3.6	3.5	3.9	2.5	2.2	3.40
	G-207	91	6.76	2.0	3.1	2.3	3.5	4.2	4.0	4.2	3.8	2.8	4.12
	G-208	91	4.83	1.4	13.6	14.7	10.9	15.9	15.8	15.3	9.9	13.4	7.04
	G-209	182	7.01	0.8	2.2	4.3	2.5	4.3	3.2	3.0	3.7	1.8	2.57
	G-210	182	6.96	1.9	4.2	5.8	6.8	5.7	5.2	4.6	2.5	33.3	5.02
SRLU + EJ-13 + Tuff	G-211	14	7.28	0.3	1.5	2.9	0.2	1.7	-0.2	1.0	0.8	-0.4	1.44
	G-212	14	6.87	0.4	1.1	0.9	0.1	1.3	-0.5	1.5	0.8	-0.4	1.13
	G-213	28	6.94	0.3	2.2	3.6	0.6	2.5	-0.4	2.3	1.0	0.1	1.88
	G-214	28	6.74	0.4	1.8	3.4	0.4	2.1	-0.2	2.2	1.2	0.2	1.61
	G-215	56	6.74	1.1	2.8	3.0	2.9	3.7	0.9	3.7	1.0	0.8	2.37
	G-216	56	6.66	0.9	2.7	3.8	2.6	3.3	0.9	3.4	1.0	0.8	2.23
	G-217	91	6.93	1.3	4.2	3.3	3.3	5.1	0.8	5.1	1.2	1.1	2.71
	G-218	91	6.95	1.1	3.7	3.7	1.8	4.5	0.9	4.2	0.2	1.0	2.62
	G-219	182	7.25	1.3	4.8	4.3	3.3	6.1	1.9	4.0	1.4	1.5	3.04
	G-220	182	7.29	1.2	4.8	6.1	3.5	6.1	2.3	4.5	1.7	1.7	3.03
Test Type	Test #	Test Length (Days)	pH OUT	Normalized Release (g/m ²)									
				Al	B	Ca	Fe	Li	Mg	Na	Si	Sr	U ^d
SRLA + EJ-13	G-221	14	7.44	0.4	1.0	-1.6	0.7	1.6	1.3	1.5	0.9	0.8	1.50
	G-222	14	7.52	0.3	1.2	-1.5	0.7	1.7	1.1	1.6	1.1	0.9	1.60
	G-223	28	7.18	0.7	2.0	-1.4	1.2	2.6	1.8	1.9	2.7	1.5	2.69
	G-224	28	7.12	1.1	1.9	-1.9	1.2	2.5	1.6	1.5	2.8	1.4	2.53
	G-225	56	6.92	1.8	2.4	1.2	4.0	3.2	3.6	3.5	2.6	2.0	3.10
	G-226	56	6.95	1.6	2.3	1.3	4.1	3.1	3.4	3.3	3.0	1.9	2.93
	G-227	91	6.82	2.3	3.5	-0.2	3.5	4.5	4.0	3.6	3.4	2.7	4.50
	G-228	91	6.79	2.4	3.4	1.6	3.8	4.5	4.2	4.7	4.6	2.6	3.93
	G-229	182	7.26	2.2	4.3	7.4	8.3	5.7	5.1	4.4	4.4	3.2	4.48
	G-230	182	7.24	2.3	4.1	7.5	8.2	5.6	4.9	4.2	5.1	3.0	4.61
SRLA + EJ-13 + Tuff	G-231	14	6.85	0.5	1.0	3.0	0.4	1.2	-0.2	1.2	1.0	0.0	0.98
	G-232	14	6.86	0.5	1.2	11.0	0.3	1.4	1.0	1.6	0.9	1.0	1.20
	G-233	28	6.75	0.7	2.1	4.1	0.5	2.5	-0.3	1.8	1.1	0.4	1.89
	G-234	28	6.72	0.9	2.2	5.5	0.9	2.5	-0.1	1.8	1.5	0.9	2.13
	G-235	56	6.92	1.3	2.8	5.4	7.4	3.5	1.3	3.5	3.3	1.3	2.12
	G-236	56	6.88	1.5	2.6	5.7	7.1	3.4	1.2	3.1	2.3	1.4	2.58
	G-237	91	6.85	2.5	3.6	2.8	6.7	4.3	1.2	3.9	2.6	0.8	2.43
	G-238	91	6.87	2.0	4.0	6.2	5.9	4.8	1.6	4.4	0.8	1.5	1.94
	G-239	182	7.16	1.4	5.2	12.2	7.6	6.2	3.2	4.5	3.4	2.6	2.30
	G-240	182	7.09	1.5	5.5	11.5	8.0	6.4	3.2	4.7	2.5	2.7	2.81

^d The (HL)₀ values are different than reported previously [BATIS-] because of a computational error. The values presented in this table are correct.

Table 7. As Measured Am, Pu, and Np Activities^a

Experiment Type	Experiment #	Experiment Length (Days)	Plutonium, (dis/sec) ^c			Americium, (dis/sec) ^c			Neptunium, ^b (dis/sec) ^c	
			Unfiltered	Filtered	Acidified ^b	Unfiltered	Filtered	Acidified	Unfiltered	Filtered
SRL A + EJ-13	G-221	14	4.17E-02	2.12E-02	6.69E-01	1.64E-05	0.00E+00	3.87E-02	1.48E-02	
	G-222	14	6.10E-02		8.95E-01	1.30E-03		4.40E-02	NA	
	G-223	28	4.00E-02	4.08E-02	8.87E-01	1.10E-03	1.28E-03	5.66E-02	2.58E-02	3.70E-02
	G-224	28	4.30E-02		8.60E-01	7.94E-04		7.17E-02	1.97E-02	
	G-225	56	5.71E-02	1.40E-01	2.33E+00	8.69E-04	0.00E+00	1.64E-01	3.73E-02	
	G-226	56	6.01E-02		2.86E+00	2.18E-03		2.00E-01	3.92E-02	
	G-227	91	8.58E-02	1.82E-02	3.51E+00	2.30E-03	0.00E+00	2.59E-01	4.15E-02	1.03E-02
	G-228	91	7.14E-02		3.68E+00	1.57E-03		3.74E-01	4.93E-02	
	G-229	182	7.44E-03	7.38E-03	3.22E+00	2.47E-04	0.00E+00	5.76E-01	2.74E-02	1.70E-02
	G-230	182	6.82E-03	5.43E-03	3.05E+00	1.02E-03	0.00E+00	6.93E-01	2.45E-02	3.49E-02
SRL A + EJ-13 + Tuff	G-231	14	3.69E-02	2.09E-02	6.16E-01	2.39E-03	0.00E+00	4.61E-02	9.99E-03	
	G-232	14	3.74E-02		5.33E-01	7.12E-04		3.52E-02	NA	
	G-233	28	1.24E-01	2.37E-02	1.29E+00	1.14E-02	0.00E+00	1.46E-01	NA	2.98E-02
	G-234	28	9.74E-02		1.76E+00	1.42E-02		3.30E-01	2.24E-02	
	G-235	56	1.84E-01	1.11E-02	4.95E+00	1.33E-02	0.00E+00	4.33E-01	4.97E-02	
	G-236	56	9.20E-02		3.38E+00	1.00E-02		4.10E-01	4.74E-02	
	G-237	91	2.64E-01	1.49E-02	5.32E+00	2.03E-02	0.00E+00	1.05E+00	2.69E-02	4.63E-03
	G-238	91	7.42E-01		6.54E+00	2.99E-02		8.59E-01	NA	
	G-239	182	1.22E-02	4.86E-03	4.00E+00	5.56E-04	2.14E-05	1.15E+00	1.87E-02	0.00E+00
	G-240	182	1.81E-02	7.21E-03	4.08E+00	1.23E-03	1.46E-03	1.08E+00	2.56E-02	3.41E-02

^aThis table has been revised and updated compared to that presented in Table 14 of [BATES-2].^bUnresolved Pu + Np counts, all counts were assigned as Pu except those due to Np unfiltered. Np Acidified was set to 0.^cTotal count rate per 100 lambda of solution.

NA = no analysis available.

Table 8. As-Measured Anion Concentrations

Test Type	Test #	Test Length (Days)	pH OUT	Anion Concentration (ppm, ug/ml)									
				F ⁻		Cl ⁻		NO ₂ ⁻		NO ₃ ⁻		SO ₄ ⁼	
				Raw	Corr*	Raw	Corr	Raw	Corr	Raw	Corr	Raw	Corr
SRLU	G-201	14	7.55	2.40	0.00	7.80	-0.08	4.65	1.50	2.75	-1.95	19.95	0.90
EJ-13	G-202	14	8.00	2.40	0.00	7.80	-0.08	4.80	1.65	2.40	-1.80	19.80	0.75
	G-203	28	7.07	2.25	-0.23	7.05	-0.60	4.95	1.95	2.40	-2.25	17.10	-2.62
	G-204	28	7.14	2.40	-0.08	7.50	-0.15	4.95	1.95	2.10	-2.55	39.00	19.28
	G-205	56	6.79	2.20	0.15	21.20	12.95	4.40	1.55	2.40	-0.90	19.70	2.90
	G-206	56	6.98	2.20	0.15	9.10	0.85	4.80	1.95	2.40	-0.90	19.90	3.10
	G-207	91	6.76	2.50	1.30*	18.60	-69.80*	4.20	4.00*	2.80	2.50*	20.90	12.20*
	G-208	91	4.83	5.10	3.90*	287.50	199.10*	0.20	0.00*	0.30	0.00*	10.80	2.10*
	G-209	182	7.01	2.55	0.45	8.85	2.33	0.45	-2.17	0.75	-4.13	21.15	6.23
	G-210	182	6.96	2.55	0.45	8.70	1.68	5.70	3.08	2.70	-2.18	24.90	9.98
SRLU	G-211	14	7.28	2.70	0.15	8.10	0.82	5.10	0.60	2.70	-0.08	21.45	2.40
Tuff	G-212	14	6.87	2.10	-0.45	8.10	0.82	5.25	0.75	2.40	-0.38	21.00	1.95
	G-213	28	6.94	2.10	-0.08	7.80	0.52	5.40	0.90	2.70	0.82	19.65	0.30
	G-214	28	6.74	2.10	-0.08	7.80	0.52	4.80	0.30	3.15	1.27	19.65	0.30
	G-215	56	6.74	2.20	0.40	9.10	-0.55	2.80	-0.50	3.90	1.60	20.20	5.35
	G-216	56	6.66	2.10	0.30	9.10	-0.55	0.20	-3.10	0.30	-2.00	20.20	5.35
	G-217	91	6.93	2.20	0.10	8.70	-6.55	0.20	-4.85	0.30	-2.50	18.50	-1.65
	G-218	91	6.95	2.30	0.20	8.70	-6.55	0.20	-4.85	0.30	-2.50	20.60	0.45
	G-219	182	7.25	2.10	-0.15	6.90	-0.68	4.80	0.30	3.15	-0.07	17.70	0.30
	G-220	182	7.29	1.95	-0.30	6.45	-1.13	4.65	0.15	2.85	-0.23	17.10	-0.30

Test Type	Test #	Test Length (Days)	pH OUT	Anion Concentration (ppm, ug/ml)									
				F ⁻		Cl ⁻		NO ₂ ⁻		NO ₃ ⁻		SO ₄ ⁼	
				Raw	Corr*	Raw	Corr	Raw	Corr	Raw	Corr	Raw	Corr
SRLA	G-221	14	7.44	1.50	-0.90	4.80	-2.92	2.85	-0.30	1.50	-2.70	12.45	-6.60
EJ-13	G-222	14	7.52	2.55	0.15	8.25	0.63	5.10	1.95	2.55	-1.65	21.15	2.10
	G-223	28	7.18	2.40	-0.08	7.95	0.30	6.00	3.00	2.55	-2.10	19.95	0.23
	G-224	28	7.12	1.95	-0.53	5.85	-1.80	4.35	1.35	1.65	-3.00	14.85	-4.87
	G-225	56	6.92	2.20	0.15	8.40	-0.15	4.80	1.95	2.40	-0.90	19.70	2.90
	G-226	56	6.95	2.20	0.15	8.40	-0.15	4.40	1.55	2.10	-1.20	18.40	1.60
	G-227	91	6.82	1.90	0.70*	8.90	-80.50*	3.50	3.30*	2.10	1.80*	15.70	7.00*
	G-228	91	6.79	2.10	0.90*	8.50	-79.10*	3.40	3.20*	2.40	2.10*	17.50	8.80*
	G-229	182	7.26	2.55	0.45	9.15	2.63	6.60	3.98	1.35	-3.53	27.75	12.83
	G-230	182	7.24	1.80	-0.30	6.45	-0.07	4.95	2.33	0.90	-3.98	19.05	4.13
SRLA	G-231	14	6.85	2.25	-0.30	7.95	0.67	5.40	0.90	2.10	-0.68	20.55	1.50
EJ-13	G-232	14	6.86	2.40	-0.15	8.70	1.42	5.25	0.75	2.25	-0.53	22.35	3.30
	G-233	28	6.75	2.25	-0.70	8.55	1.27	5.40	2.60	3.75	1.87	21.00	1.65
	G-234	28	6.72	2.25	-0.70	9.30	2.02	14.85	12.05	6.00	4.12	23.40	4.05
	G-235	56	6.92	2.20	0.40	17.00	7.35	3.80	0.50	3.20	0.90	19.20	4.35
	G-236	56	6.88	2.00	0.20	9.00	-0.65	3.10	-0.20	2.40	0.10	17.30	2.45
	G-237	91	6.85	2.10	0.00	8.90	-6.35	4.80	-0.25	2.80	0.05	21.20	1.05
	G-238	91	6.87	1.80	-0.30	9.20	-6.05	0.20	-4.85	0.30	2.45	17.00	-3.15
	G-239	182	7.16	2.70	0.45	11.55	3.97	2.70	-1.80	0.75	2.33	27.00	9.60
	G-240	182	7.09	2.55	0.33	9.30	1.72	2.10	-2.40	0.75	-2.33	26.10	8.70

* Denotes anomalous result as described in text.

Table 8 (Cont'd)

Test Type	Test #	Test Length (Days)	pH OUT	Anion Concentration (ppm, ug/ml)									
				F ⁻		Cl ⁻		NO ₂ ⁻		NO ₃ ⁻		SO ₄ ⁼	
				Raw	Corr*1	Raw	Corr	Raw	Corr	Raw	Corr	Raw	Corr
EJ-13	G-241	14	7.10	2.40	2.40	7.50	7.72	3.15	3.15	3.90	4.20	18.60	19.05
	G-242	14	6.89	2.40		7.95		3.15		4.50		19.50	
	G-243	28	6.81	2.55	2.48	7.65	7.65	2.85	3.00	4.80	4.65	20.55	19.72
	G-244	28	6.80	2.40		7.65		3.15		4.50		18.90	
	G-245	56	6.73	1.90	2.05	8.40	8.25	2.30	2.85	3.00	3.30	15.10	16.80
	G-246	56	6.78	2.20		8.10		3.40		3.60		18.60	
	G-247	91	4.35	0.80	1.20	103.80	88.40	0.20	0.20	0.30	0.30	3.60	8.70
	G-248	91	3.60	1.60		73.00		0.20		0.30		13.80	
	G-249	182	6.89	2.25	2.10	7.20	6.52	2.70	2.62	5.55	4.88	15.75	14.92
	G-250	182	6.93	1.95		5.85		2.55		4.20		14.10	
EJ-13 + Tuff	G-251	14	7.05	2.55	2.55	7.80	7.72	4.50	4.50	2.55	2.78	19.20	19.05
	G-252	14	6.99	2.55		7.65		4.50		3.00		18.90	
	G-253	28	6.68	2.10	2.17	7.65	7.28	0.75	2.78	0.75	1.88	19.35	19.35
	G-254	28	6.80	2.25		6.90		4.80		3.00		19.35	
	G-255	56	6.48	1.80	1.80	9.30	9.65	2.80	3.30	1.80	2.30	15.70	14.85
	G-256	56	6.47	1.80		10.00		3.80		2.80		14.00	
	G-257	91	6.57	2.10	2.10	9.10	15.25	5.80	5.05	2.90	2.75	20.20	20.15
	G-258	91	6.48	2.10		21.40		4.30		2.60		20.10	
	G-259	182	6.96	1.95	2.25	6.60	7.57	3.90	4.50	2.85	3.08	14.70	17.40
	G-260	182	6.90	2.55		8.55		5.10		3.30		20.10	

Experimental precision and accuracy are much more difficult to quantify. As was pointed out previously [BATES-1], no standard reference materials or norms for leach testing in a gamma radiation field are yet available to ascertain the experimental accuracy. Experimental precision can be estimated from replicate runs as was done previously, although this method is subject to statistical limitations (e.g., numerous replicate runs are required). Such error estimates were not made for the present data; however, several important sources of error that would affect the experimental accuracy as well as the estimated experimental precision can be identified.

One uncertainty is the compositional inhomogeneity of materials used in different experiments. The glass samples, as discussed above, are fairly homogeneous and are not expected to adversely affect the reproducibility of the test results. The tuff disks are clearly compositionally heterogeneous on a millimeter scale and perhaps even on a few-centimeter scale. The effect of this inhomogeneity was not considered in previous experiments because crushed tuff was used. For the present tests, those experiments that contain large inhomogeneous mineral or glass fragments in the tuff will be examined further to see if any anomalous solution results could be correlated with them. Furthermore, the tuff samples are being examined using an ion microprobe to see the particular interactions that have occurred [PHINNEY]. In exceptional instances, the stainless steel surfaces exposed to the solution may also affect the reaction [BATES-2].

Another source of error is the contamination of the solution with Si from the gasket material. Although visible pieces of the gaskets were never observed in the leaching solution upon termination of each experiment, it is possible that extremely small gasket particles could have spalled into the solution or that accidental contact of the leaching solution with the intact gasket has occurred. If Si from the gasket was introduced into the test solutions, it is important to identify the most likely time during the reaction period that this contamination occurred. An increase in the Si concentrations during the early phase of the test could affect the overall glass corrosion process.

The likelihood of gasket particles spalling before the completion of each experiment is small, considering the observed physical integrity of the gasket materials after each run. The unusually high Si values observed in some EJ-13 blank experiments probably are related to contamination that occurred after termination of the run. For example, a strong reverse correlation of the measured Si concentration and total solution volume acidified for cation analysis was noted in the blank experiments. This observation suggests that most of the contamination in these cases may have occurred after the leaching solution had been sampled for anion and dissolved gas analyses, because otherwise no relation is to be expected between Si concentration and volume of leaching solution left for cation analysis. Although the specific mechanism of contamination is still under investigation, one scenario is that refluxing gases vaporized during the 90°C acidification could have condensed on some portions of the Si gasket, reacted with the gasket and dripped back to the solution. A similar process could have conceivably occurred during the progress of the experiments except that the refluxing gases were not as acidic. (It is also possible that the solution could have preferentially leached out some form of Si-bearing inclusion in the stainless steel.)

In our previous report [BATES-1], we estimated the overall precision (i.e., experimental + analytical) to be $\pm 7\%$ for Na, $\pm 4\%$ for B, $\pm 5\%$ for all anions, $\pm 15\%$ for the actinides, and $\pm 10\%$ for all other cations. For the present work, we have instead opted to present the results of duplicate experiments in all tables and figures where they are presented to give the reader a better feel for the experimental uncertainties. However, because the following analyses and interpretations require that experimental results performed under different test conditions be compared, a definition of what constitutes a significant difference between the experimental results has to be adopted. In the following, this difference is defined as that value which exceeds twice the standard deviation of individual elements as analyzed in blank runs. An exception has to be made for silica in the EJ-13 + tuff blank runs, because a clear trend of increased concentration with time is evident. In this case, the standard deviation is defined as the average of the standard deviations of duplicate tests for the 28-, 56-, 91-, and 182-day tests. The 14-day test is excluded because

G-251 yielded an anomalously high Si concentration (see next section). The standard deviation of the pH measurement will be assessed in a manner similar to that of Si.

B. Solution Analysis - Blank

Tables 5 and 8 present the results of cation and anion analyses for the blank runs. Only the EJ-13 water runs truly represent experimental blank runs, so caution is necessary in treating the EJ-13 + tuff runs as blank runs for the SRL glass + EJ-13 + tuff experiments [BATES-1]. Variation of pH with time in both the EJ-13 and EJ-13 + tuff experiments is shown in Fig. 2. In both cases, the trend is one of decreasing pH up to 91 days (56 days in runs with tuff), followed by a subsequent increase. There is no clear indication of an overall difference in pH attained between the two sets of experiments. The pH values for G-247 and G-248 (56 days, EJ-13 only) appear to have been influenced by "anomalous" reactions, as indicated by visual observations (i.e., a thick rusty-colored film was seen on the top surface of solutions) made upon opening the test vessels and by the high Cl^- levels (Table 8) [cf. BATES-2].

Table 8 shows no indication that the concentrations of F^- , Cl^- , NO_2^- , NO_3^- , and $\text{SO}_4^{=}$ varied systematically with time in either the EJ-13 only or EJ-13 + tuff experiments. However, there were several instances where the measured anion concentration deviated significantly from the mean (Table 8). For example, in experiments G-247 and G-248, a reaction occurred whereby the solution pH was more acidic than expected, the chloride levels were elevated, the fixed nitrogen levels were low, and rust-colored precipitates were observed. Also, in some tests, the fixed nitrogen levels were below detection, but all other indications were normal. No explanation for this observation is yet available, but similar results have been obtained by [BIBLER]. Nevertheless, the overall variations in the concentration of these anions are only between 10 to 20 percent (1σ) of their mean values for the EJ-13 only experiments. Greater variations were observed in the concentrations of NO_2^- and NO_3^- for the EJ-13 + tuff experiments, but even these are within 30% of their mean abundances in all the tests. Within a standard deviation of the mean

Fig. 2. Variation of pH with Time in Blank Experiments

concentration of each anion in the EJ-13 and EJ-13 + tuff experiments, the final concentrations of F^- , Cl^- , SO_4^{2-} , and the total fixed nitrogen are identical to the starting EJ-13 water (Table 2).

No systematic difference in the concentrations of Cl^- , F^- , SO_4^{2-} , and total fixed nitrogen exists between the EJ-13 and EJ-13 + tuff experiments. The higher concentrations of total fixed nitrogen in the EJ-13 only experiments observed previously [BATES-1] were not observed in the present work. The only significant difference between the EJ-13 and the EJ-13 + tuff experiments noted in the anion data is the NO_3^-/NO_2^- mole ratio (Fig. 3). This ratio is lower in the EJ-13 + tuff experiments (0.7-1.3) than in the EJ-13 experiments (1.4-2.8) as was observed previously [BATES-1]. The ratio of nitrous to nitric acid showed no significant correlation with pH (Fig. 3) or with time.

Boron showed no significant variation ($\pm 1\sigma < 20\%$, Table 6) in either the EJ-13 or EJ-13 + tuff experiments. Aluminum concentrations are, for the most part, below detection limit. Lithium concentrations are also constant with time but are slightly higher in tuff-containing experiments.

The concentrations of Ca, Sr, and Na remained constant ($\pm 1\sigma < 10\%$) in the EJ-13 only experiments, but showed subtle increases in the EJ-13 + tuff experiments. However, the total variations for EJ-13 + tuff experiments are below 20% of the mean concentration. Magnesium also showed no significant variation with time in both sets of experiments, but its mean abundance in the EJ-13 + tuff experiments tended to be lower than in the EJ-13 experiments. Silicon showed no significant increase to 91 days, but showed a large gain after 182 days in the EJ-13 experiments. Note, however, that both of the 182-day duplicate runs (G-249 and G-250) were sampled for gas chromatographic analysis, and only small amounts of solution (~5 mL) were left for ICP analysis. Thus, Si contamination resulting from acid-soaking the test vessels in the presence of gasket material would disproportionately increase the Si concentration in these tests. Experiments G-241 and G-243 were also sampled for dissolved gases, had reduced solution volumes, and showed increased Si concentration compared to the corresponding duplicate samples.

Fig. 3. Variation of $\text{NO}_3^-/\text{NO}_2^-$ Mole Ratio with Time in Blank Experiments

Silicon concentrations in EJ-13 + tuff experiments showed significant and steady increases with reaction time except for tests G-251 and G-253 which had reduced solution volumes. The mean Si concentration in EJ-13 + tuff experiments was higher than that for the EJ-13 only runs reflecting the Si contribution of the tuff.

Table 9 shows the abundance of dissolved H₂, O₂, and N₂ in several selected blank run solutions. The EJ-13 solution was initially air-saturated and contained no detectable amount of H₂. Respectively, 0.54×10^{-5} and 0.04×10^{-5} M H₂ were detected in the EJ-13 only and EJ-13 + tuff experiments after irradiation for 14 days. More than twice these amounts were measured in the corresponding 28-day experiments. After 182 days, the total dissolved H₂ measured in the EJ-13 experiments was lower than that measured in the 28-day experiment. It is notable that the duplicate EJ-13 + tuff runs--G-259 and G-260 (182 days)--yielded dissolved H₂ values that differed by almost 100%. The concentrations of O₂ and N₂ in the blank experiments were less than or comparable with the levels observed in the starting EJ-13 water.

C. Solution Analyses - SRL Glass

The variations of final solution pH with time for the glass-containing tests are summarized in Figs. 4 and 5. The shaded regions outline the analogous pH variation in the blank experiments. The overall pH trend with time of all runs with SRL glass is similar to that of the corresponding blank runs except for the earlier reversal of the pH trend for the SRL A + EJ-13 + tuff experiments (28 days). Experiments with SRL glass generally had higher final pH's than the corresponding blanks.

As in the blank runs, experiments with SRL glass that contained tuff showed generally lower final pH's than the experiments without tuff. Exceptions to this trend are the 91- and 182-day runs with SRL U glasses. No significant difference was observed in the final pH's of experiments with SRL A and SRL U glasses except for the 182-day experiments, where the final pH of SRL U-containing experiments is about 0.2 pH units more acidic than the SRL A experiment.

Table 9. Dissolved O₂, H₂, and N₂ in Selected Blanks

Test Type	Test No.	Test Length, d	pH Out	Dissolved Gas Concentration, M		
				H ₂	O ₂	N ₂
EJ-13 ^a	Starting				5.3E-4	5.3E-4
EJ-13	G-241	14	7.10	5.4E-6	3.0E-5	3.8E-5
	G-242	14	6.89			
	G-243	28	6.81	1.3E-5	3.2E-5	4.7E-5
	G-244	28	6.80			
	G-245	56	6.73			
	G-246	56	6.78			
	G-247	91	4.25			
	G-248	91	3.60			
	G-249	182	6.89	1.0E-5	4.5E-5	6.1E-5
	G-250	182	6.93	8.8E-6	4.9E-5	8.4E-5
EJ-13 + Tuff	G-251	14	7.05	3.6E-7	2.8E-5	6.0E-5
	G-252	14	6.99			
	G-253	28	6.68	1.4E-5	9.8E-6	4.7E-5
	G-254	28	6.88			
	G-255	56	6.48			
	G-256	56	6.47			
	G-257	91	6.57			
	G-258	91	6.48			
	G-259	182	6.96	2.8E-5	5.2E-5	8.2E-5
	G-260	182	6.90	1.5E-5	5.2E-5	9.6E-5

^aFrom [VAN KONYNENBURG].

Fig. 4. Variation of pH with Time in Experiments with SRL U Glass. The cross-hatched region encompasses the values for the blank experiments.

Fig. 5. Variation of pH with Time in Experiments with SRL A Glass. The cross-hatched region encompasses the values for the blank experiments.

The concentrations of F^- , Cl^- , SO_4^{2-} , and total fixed nitrogen showed no significant difference between the blank runs and those with SRL glasses, although anomalously high concentrations of these anions were noted in several experiments. However, the abundance of nitrate relative to nitrite (Figs. 6a and 6b) clearly is different in SRL + EJ-13 experiments compared with the blank (EJ-13 only) experiments. With one exception (G-209), NO_3^-/NO_2^- is less than 1.3 for experiments with SRL U and SRL A glasses. Note from Figs. 6a and 6b that the observation that NO_3^-/NO_2^- mole ratios are higher in EJ-13 only experiments compared with glass-containing experiments is true even at the same final pH values. The same cannot be said for the tuff-containing experiments wherein the nitrate: nitrite ratios overlap in the glass-containing experiments and the corresponding blanks. Similarly, no significant difference in the NO_3^-/NO_2^- ratio is noted between the SRL U and SRL A experiments with or without tuff.

Because of the nature of the glass matrix used in the present experiments, it is expected that the glass components (e.g., Al, B, Ca, Mg, Si, Na, Li, Sr, Cs, and the actinides, U, Pu, Np, and Am) will become enriched in the leaching solution as the glass reacts. In fact, the release patterns for these elements will, in large part, form the basis for understanding the behavior of nuclear waste glasses in the environments simulated by the experiments. The raw data (Table 5) show that the concentrations of these cations were higher in virtually all glass-containing experiments than the corresponding blank runs or the starting EJ-13 water. As expected, a general trend of increasing concentration with time also is evident. However, because the absolute amounts of Si, Na, and alkali earths added to the leachate from the glass are considerably less than the starting levels in EJ-13 solution, the statistical uncertainty should be reckoned with before the temporal trends for these elements can be established.

In comparing the cation leachate data, it is appropriate to translate the raw data to normalized releases. The normalized release (NL_i) was calculated using standard formulation, $NL_i = C_i V_f^{-1} (SA)^{-1}$, where C_i is the blank corrected solution concentration of species i , V is the volume of solution, f is the mass fraction of i in the glass, and (SA) is the total glass surface area.

Fig. 6. Variation of $\text{NO}_3^-/\text{NO}_2^-$ Mole Ratio with Time in Experiments with Glass. The cross-hatched regions encompass the values of the blank experiments, (\\) EJ-13 only; (///) EJ-13 + tuff.

The values used for V in the present calculations are those of the initial solutions. Actually, the concentrations of cations were determined on acidified solutions that have been previously (prior to acidification) sampled for anions analyses (i.e., about 2 mL less than the initial solution volume). If a significant fraction of the cation released during the test was sorbed onto the vessel walls, the volume of the acidified solution would have been the more appropriate value to use for V . This is done here only for the actinides. Note, however, that even for the other cations where the initial solution volume was used in the estimation of NL_i , no more than about 20% consistent bias (i.e., overestimation) could be introduced even if >99% of the cations were actually sorbed onto the vessel walls.

The variation in the normalized releases of Si, B, Na, and Li for the SRL U and SRL A glass experiments with reaction time are shown in Figs. 7 and 8. For comparison, the normalized mass loss data for individual experiments are also shown. Similar diagrams for Ca, Mg, and Al are presented in Figs. 9 and 10 (not shown in these plots are the negative normalized releases calculated for Ca in short-duration experiments). Variations of normalized releases of U and Sr are shown in Figs. 11 and 12. The relative behavior of Si, B, Na, and Li in all the experiments is consistent with the general normalized release pattern: $Li \geq Na \geq B \geq Si$. Lithium defines the maximum normalized release rate except perhaps at the earliest stages of leaching (<56 days), where normalized release of Li and Na are not significantly different. This observation is in agreement with the results of previous experiments [BATES-1], where up to 56 days Na and Li consistently showed higher normalized release than B. The normalized release of Li, Na, B, and Si in the experiments containing SRL U glasses did not significantly differ from the corresponding experiments with SRL A glasses, except for $(NL)_i$ in the longer term SRL U experiments where the values were somewhat less than for SRL A. Furthermore, the normalized releases of Li, Na, and B are not significantly different in tuff-absent and tuff-containing experiments, although higher releases for all 182-day experiments with tuff were observed. The normalized release of Si appears to be lower in tuff-containing experiments than in the tuff-absent experiments; however, this could be an artifact of the method of blank correcting

Fig. 7. Variation of Normalized Release of Si, B, Na, and Li with Time in Experiments with SRL U Glass (a) EJ-13 Only; (b) EJ-13 + Tuff.

Fig. 8. Variation of Normalized Release of Si, B, Na, and Li with Time in Experiments with SRL A Glass (a) EJ-13 Only; (b) EJ-13 + Tuff.

Fig. 9. Variation of Normalized Release of Ca, Mg, and Al with Time in Experiments with SRL U Glass (a) EJ-13 Only; (b) EJ-13 + Tuff.

Fig. 10. Variation of Normalized Release of Ca, Mg, and Al with Time in Experiments with SRL A Glass (a) EJ-13 Only; (b) EJ-13 + Tuff. Note the 182-day Ca values are off scale being 12.2 and 11.5 g/m².

Fig. 11. Variation of Normalized Release of Sr and U with Time for Experiments with SRL U Glass (a) EJ-13 Only; (b) EJ-13 + Tuff. Note the 91-day experiment # G-208 had an anomalously acidic pH of 4.83.

Fig. 12. Variation of Normalized Release of Sr and U with Time for Experiments with SRL A Glass (a) EJ-13 Only; (b) EJ-13 + Tuff.

Si in the tuff-absent experiments (subtraction of the average Si concentration over the 182-day time period). If a continuously increasing Si correction were done, then the $(NL)_{Si}$ values would be smaller and would approach the values of the tuff-containing experiments. Evidence that a continuously increasing Si correction should be done is presented by [EBERT].

The normalized release of Al is significantly lower than Li, Na, and B. In the experiments without tuff, Mg and Sr have normalized release rates similar to those of Na and B. In the presence of tuff, the normalized release of Mg and Sr are significantly lower than those of Na and B. In the experiments without tuff, the calculated normalized release of Ca is close to that of Mg, but it tends to be irregular in the short-duration experiments (<56 days). In the tuff-containing experiments, the normalized Ca releases are consistently higher than all other elements, perhaps indicating more extensive leaching of tuff. In tuff-containing experiments, U release is consistently lower than the corresponding tuff-absent experiments. For both tuff-containing and tuff-absent experiments, higher normalized U releases were noted in the present experiments compared with those reported previously [BATES-1] for comparable reaction times.

Three actinide fractions were examined following the procedure used previously [BATES-1]. The analysis referred to as acidified (i.e., acid washed, Table 7) is directly comparable with the other cation data because the same solution was analyzed in each case. Figure 13 shows the normalized actinide releases, which were calculated using the nominal mass fractions of the actinides presented in Table 2. The normalized releases of U, Pu, and Am were based on analysis of the acidified solution, whereas the release of Np was based on the amount of Np detected in the non-acidified fraction. There was no evidence that Np interacted strongly with the metal components of the experiment and better precision was available in the measurements of Np in the unfiltered samples. The normalized release of Am is consistently lower (with or without tuff) than that of Si, whereas the values for Np, Pu, and U are not too dissimilar from those of Si. Note that the acidified solution results reported for the experiments with tuff do not include actinides that have sorbed on the tuff surfaces, although the surface actinide activity on the tuff was directly measured by

Fig. 13. Variation of Normalized Release of (a) U, Pu, Am, and Np with Time for Experiments Containing Tuff.

Table 10. Normalized Release of Pu, Am, and Np Plus the Actinide Fraction in Filtered and Unfiltered Aliquots

Experiment Type	Experiment #	Experiment Length (Days)	pH	Plutonium			Americium			Neptunium		
				NL(Pu) ^a (g/m ²)	% Filterable	% Sorbed	NL(Am) ^a (g/m ²)	% Filterable	% Sorbed	NL(Np) ^b (g/m ²)	% Filterable	% Sorbed
SRL A + EJ-13	G-221	14	7.44	2.69E-01	49	100	1.06E-02	100	100	1.47E+00		
	G-222	14	7.52	2.84E-01		100	1.23E-02		100	NA		
	G-223	28	7.18	3.57E-01	0	100	1.56E-02	0	100	2.58E+00	0	
	G-224	28	7.12	3.54E-01		100	2.02E-02		100	2.01E+00		
	G-225	58	6.92	9.41E-01	75	100	4.52E-02	100	100	3.73E+00		
	G-226	58	6.95	1.21E+00		100	5.75E-02		100	4.10E+00		
	G-227	91	6.82	1.67E+00	79	100	8.40E-02	100	100	4.89E+00	75	
	G-228	91	6.79	1.45E+00		100	1.01E-01		100	4.82E+00		
	G-229	182	7.26	1.14E+00	1	100	1.40E-01	100	100	2.41E+00	38	
	G-230	182	7.24	1.10E+00	20	100	1.70E-01	100	100	2.19E+00	0	
SRL A + EJ-13 + Tuff	G-231	14	6.85	2.31E-01	43	100	1.18E-02	100	100	9.27E-01		
	G-232	14	6.86	2.13E-01		100	9.61E-03		100	NA		
	G-233	28	6.75	5.07E-01	81	100	3.90E-02	100	100	NA		
	G-234	28	6.72	7.09E-01		100	9.09E-02		100	2.24E+00		
	G-235	58	6.92	1.23E+00	94	100	7.37E-02	100	100	3.07E+00		
	G-236	58	6.88	8.79E-01		100	7.28E-02		100	3.06E+00		
	G-237	91	6.85	1.35E+00	94	100	1.83E-01	100	100	1.69E+00	83	
	G-238	91	6.87	1.77E+00		100	1.59E-01		100	NA		
	G-239	182	7.16	1.34E+00	60	100	2.63E-01	96	100	1.55E+00	100	
	G-240	182	7.09	1.36E+00	60	100	2.46E-01	0	100	2.11E+00	0	

^aThese values do not include activity associated with tuff. The values would be ~5% larger if the tuff fraction was included.

^bThese values are calculated based on the amount of Np in the unfiltered samples.

NA - no analysis available.

α -spectrometry (ANL) and by ion microprobe analysis (LLNL). Inclusion of the activity associated with tuff would increase $(NL)_{Pu}$ and $(NL)_{Am}$ by approximately 5% [cf. Table 12], and might provide indications that the release of these elements from the glass is slightly higher in the presence of tuff.

Comparison of the acidified solution data with the analyses of filtered and unfiltered fractions should allow an estimate of the percentage of actinides in colloidal and adsorbed forms, respectively. Data shown in Table 7 clearly suggest that well over 90% of Am and Pu recovered in acidified fractions were originally sorbed on the stainless steel surfaces. The normalized Pu and Am release (calculated from acidified solutions) increased gradually, in a nearly linear fashion, from 14 to 91 days, but the Pu release dropped off from this trend in the 182-day tests.

The actinides Am, Np, and Pu generally showed higher concentrations in the unfiltered solutions compared with the filtered solutions. The estimated percentage of actinides present as filterable fraction shows considerable variation, but several general patterns are apparent (Table 9). As a group, the experiments with tuff appear to show a greater tendency for Pu to be filterable. Furthermore, the 91-day experiments, with or without tuff, appear to have the greatest filterable fraction of actinides. It is noteworthy that the 91-day experiments achieved the lowest final pH and maximum concentration of actinides in the unfiltered solutions.

The activities of Am, Pu, and Np in the unfiltered samples [normalized to 100λ ($1000\lambda = 1$ mL)] as a function of pH are shown in Fig. 14. The data used included both the tuff-present and tuff-absent runs. For all these actinides, significantly higher concentrations were noted below pH = 7 in the unfiltered solutions. In contrast, the filtered fraction does not show this pH correlation.

D. Surface Analysis of Glasses

This section describes the data obtained from the analysis of glass surfaces by SEM/EDS, SIMS, and nuclear resonance profiling. The SEM/EDS analyses and nuclear resonance profiling analyses were performed on as-cut surfaces whereas SIMS profiles were done on surfaces that were polished

Fig. 14. Variation of Pu, Am, and Np with pH

prior to the leaching experiments. The NNWSI project is also performing ion microprobe analyses of the tuff wafers, and these results will be presented elsewhere [PHINNEY].

1. SEM/EDS

Figure 15 illustrates the progressive modification of the glass surfaces as a function of leaching time. The initial surfaces are as-cut and, except for the reaction "scales," are very similar in "texture" to the 14-day surface (Fig. 15a). After 14 days of reaction, "scales" about $0.3\text{ }\mu\text{m}$ across were observed to form homogeneously on the surface (bright features in Fig. 15a). On the other extreme, the as-cut surface reacted for 182 days has a surface fabric that has a "woven" or "chain mail-like" appearance. Similar features on altered SRL glass surfaces have been described as "cellular" [BATES-1] or "honey combed" [MENDEL]. Note that because these samples have been dessicated (i.e., removed from solution, dried in air, and exposed to high vacuum conditions) before examination under the SEM, the actual physical appearance of the surface during the leaching experiments may not be the same as that shown in Fig. 15. In fact, the "chain mail-like" morphology is comparable to well-documented dessication textures formed during sol-gel processing [e.g., BRINKER].

All the photomicrographs shown in Fig. 15 were taken from the top surface of glasses in the SRL U + EJ-13 water experiments. Corresponding surface textures of SRL U glasses retrieved from SRL U + EJ-13 + tuff experiments are very similar to those shown in Fig. 15, except that precipitated phases are conspicuously present on the surface of some glasses retrieved from the tuff-containing experiments (EDS spectra show only Si to be present). This is especially true for the 182-day samples, as shown in Fig. 16.

Representative EDS spectra of some of the surfaces shown in Fig. 15 are shown in Fig. 17. We pointed out previously [BATES-1] that, because the excitation depth of the electron beam in these analyses is 1 micron or more and because all layers examined are less than 0.5 microns thick, the spectra presented represent the integrated composition of the hydration layer and the fresh glass underneath. Therefore, the sample spectra are expected to approach the bulk glass spectra as the hydration layer becomes thinner. This is true even if the compositions of the

a. 14 days

b. 28 days

c. 56 days

d. 182 days

Fig. 15. Micrograph of the Surfaces of SRL U Glass

10 μm —

1 μm —

10 μm —

10 μm —

Fig. 16. SEM Comparison of the Surfaces of SRL U Glass from Experiments with and without Tuff

Fig. 17. EDS Spectra of SRL U Glass Surfaces

surface layers are actually the same. The spectra collected from different spots on the same sample surface are identical in almost all cases, which suggests that there are no large differences in hydration layer thicknesses within individual samples (see next section). The EDS spectra clearly indicate the depletion of Na and enrichment of Ca, Fe, and possibly Al in the reacted surface layers (cf. Fig. 21).

The surfaces of the SRL A glasses were also examined with SEM/EDS. Both tuff and non-tuff containing samples were examined with particular emphasis placed on the appearance of the reacted surface and the number and variety of reaction products observed. An ISI Super II SEM was used for examining the transuranic samples, and it was not equipped with a Robinson backscattered electron detector which is particularly useful when searching for alteration products that contain heavy elements.

The surfaces of 28- and 182-day samples are shown in Fig. 18. The main difference between the samples reacted using different experimental conditions is that with tuff present the typical cross-hatched appearance is not evident until 91 days and has not fully developed until 182 days, while without tuff the cross-hatched appearance is present in the 28-day sample.

The photomicrographs (Fig. 18) also show alteration products that were found on the glass surface. These phases were found in more than one place on the surface of an individual sample, but in no sample was the coverage extensive. The phases were not identified because of their limited size and coverage, but EDS spectra were collected (Fig. 19) to provide an indication as to their composition.

Reacted glass samples were also cross-sectioned, mounted in epoxy, polished, and examined using SEM/EDS. A typical cross-section from a 182-day sample without tuff is shown in Fig. 20. Figure 20 was imaged using backscattered electrons which accentuated density differences in the sample. A thin layer covering the bulk glass and filling cracks that penetrate into the glass is evident. The dark region between the layer and the bulk glass is likely an artifact of the mounting and polishing process. A higher resolution image of the same region is shown in Fig. 20b.

The thickness of the layer was determined by measuring the thickness of the reacted regions in several cracks and dividing by two.

Fig. 18. Photomicrographs of Surfaces of SRL A Glass Reacted for (a) 28 day, no tuff; (b) 182 day, no tuff; (c) 28 day, tuff; (d) 182 day, tuff. The marker in each sample represents ~ 4.3 microns

Fig. 19. EDS Spectra of Alteration Phases that Form on the Surface of SRL A Glass

(a)

(b)

Fig. 20. SEM Micrographs of the Cross-Sectioned 182-Day (Without Tuff) Sample. (a) Backscattered electrons, mag = 4000x; (b) secondary electrons, mag = 8000 x.

For the 182-day sample the layer thickness was 0.35 μm . This layer is referred to as the "gel" layer in subsequent discussions and based on the micrographs shown appears to be a region distinct from the bulk glass.

2. SIMS

The objective of this surface study was to describe the distribution of the various glass components (i.e., Li, Na, B, Al, Ca, Mg, Mn, and Fe) in the reacted surface layers. Similarly, the distribution of ^{237}Np , ^{239}Pu , and ^{241}Am on the surface of SRL A glasses was studied using the ion microprobe. Knowledge of the elemental profiles through the reacted surface layers is crucial to the development of a comprehensive aqueous corrosion model for the SRL glasses in the environment considered.

The SRL U glasses from each time period and from experiments with or without tuff were examined with the SIMS. Figure 21 presents a compilation of SIMS profiles collected for samples leached at various times. Intensities were normalized to the Si intensity and to the bulk glass intensity of the particular element.* Sputtering depths were calculated from sputtering times using a gross sputtering rate of 0.93 $\text{\AA}/\text{s}$ estimated

$$^*(\text{NI}_i)_x = \frac{(I_i)_x / (I_{\text{Si}})_x}{(I_i)_B / (I_{\text{Si}})_B}$$

where NI_i is the normalized intensity of species i at a depth x , $(I_i)_x$ is the raw measured intensity of i at a depth x , $(I_{\text{Si}})_x$ is the raw measured intensity of Si ($m/e = 28$) at a depth x , and $(I_i)_B$ and $(I_{\text{Si}})_B$ are the bulk glass raw measured intensities of i and Si, respectively, in the bulk glass. This method of normalization overemphasizes appreciation of an element concentration during sputtering because (1) the range of possible values is $\infty-1$ while for depletion the range is $0-1$ and (2) the effects of sputtering artifacts are more pronounced when an element is enriched in a sample as opposed to being depleted. For these reasons the enrichment curves only indicate that some enrichment has occurred, but may not accurately represent the reaction profile.

Fig. 21. SIMS Profiles for Selected Elements in Reacted SRL U Surfaces (a) 14 Day, (b) 28 Day, (c) 56 Day, (d) 91 Day, and (e) 182 Day. indicates thickness of "gel" layer and indicates the boundary between the interdiffusion zone and the bulk glass.

(c)

(d)

(e)

Fig. 21 (Cont'd)

by surface profilometry (Appendix III). Those features of the SIMS profiles that are useful for the analysis include: enrichment/depletion,* degree of enrichment/depletion,** and profile shape. Before the significance of these features can be realized, several important considerations need to be examined: (1) the Si normalization of elemental profiles assumes that Si concentration is constant with depth, and (2) the relative sputtering rates of Si and the element in question are assumed to be the same throughout the duration of sputtering. The applicability and limitation of the first assumption depends on the corrosion mechanism itself, and will be discussed later. Suffice it to note, at this point, that the measured absolute intensities of Si through the layers did not show any systematic trends and are constant to within 5% of the mean intensity suggesting that this assumption is reasonable. For the second assumption, although the relative sputtering yields are expected to change during the first 10 to 50 nm, steady-state yields are predicted deeper into the reacted surface layers [PANTANO].

The variability of the reaction layer thickness is also critical if an accurate relation between the SIMS profile and the actual elemental distribution is to be established. Although the enrichment or depletion depth is still a useful parameter in characterizing the extent of reaction (i.e., as "average" depth), the shape of the normalized concentration vs. sputtering time profile is highly dependent on the extent and character of the layer thickness variation. Nonuniform surface concentration also has similar effects on the shape of the SIMS profile. These effects must be considered in the interpretation of the SIMS data.

Figure 21a indicates that, after leaching for 14 days in a gamma field, B, Li, and Na are almost totally depleted and Fe, Al, Mn, and Ca are slightly enriched in the near-surface region, relative to the bulk glass. The degree of depletion follow the relation $Li > Na \approx B$, whereas the degree

*Depletion or enrichment depth is defined here as the depth at which the elemental concentration is midway between the depleted and enriched levels, and corresponds to the inflection point in the elemental profile curve.

**The degree of enrichment/depletion of a glass species in the altered surface region is defined in relation to the bulk glass intensity.

of enrichment follows the general relation $\text{Ca} > \text{Fe} > \text{Mn} > \text{Al} > \text{Mg}$. The 28- to 182-day profiles (Fig. 18b-e) show increasingly greater depletion depths for Li, Na, and B and enrichment depths for the enriched glass species. The relative behaviors of all glass species in the near-surface region appeared to have persisted up to 182 days (Figs. 21b-e).

Figure 22 summarizes the extent of elemental depletion of the reaction layers in terms of Li. Figure 23 compares the surface distribution of selected elements for the SRL U glasses leached for 56 days with and without tuff. The thickness of the "gel" layer as measured by SIMS (Fig. 21) is taken as the point where Li shows an increased concentration in the SIMS profile. The "gel" layer thickness as measured by SIMS for the 182-day sample corresponds well with what is observed in the SEM (Fig. 20). The thickness of the interdiffusion is the distance between when the Li profile begins to increase to when it levels off at the bulk glass level (Fig. 21).

3. Nuclear Resonance Profiles

Nuclear resonance profiles for H collected through the reacted surface layers of polished SRL U glasses are shown in Fig. 24. All the glasses analyzed are from experiments without tuff. The hydrogen profiles of the reacted glass surface can be divided into two regions. The boundary of these two regions in each case is marked by the arrow pointing downward in Fig. 24. The region left of the boundary will be referred to as a gel layer and the region right of the boundary as a diffusion or transition zone. The rationale for defining these regions will be discussed fully in the Discussion Section. Enrichment depths are defined as in the previous section. The relative positions of these regions with respect to the leaching configuration are schematically shown in Fig. 25.

The H-profiles in the transition zone for all reacted layers examined are S-shaped. The intensity does not level off to zero when the bulk glass is reached. Instead, the intensity levels off at a non-zero value that appears to correlate with the leaching duration. This observation may be attributed to an analytical artifact arising from the presence of irregular morphology on the reacted glass surfaces. Thus, after the incident nitrogen ion beam has reacted with the last hydrogen atom on the

Fig. 22. Li SIMS Profiles for SRL U Glasses Reacted Without Tuff

Fig. 23. SIMS Profiles of Li, Mg, and Al for 56-Day SRL U Glass, with and without Tuff

Fig. 24. Nuclear Resonance Profiles of Hydration in Reacted SRL U Glass, (a) 14 and 28 Days; (b) 56 and 91 Days; and (c) 182 Days.

Fig. 25. Schematic Interpretation of Glass/Solution Interface Region

thinnest layers, "residual" reactions may still be occurring in the relatively thicker portions of the reacted layers. Note that the existence of reacted cracks perpendicular to the macroscopic surface could also have the same effect on the observed profiles. The agreement between the thickness of the various reacted regions of the glass as measured by SIMS and NRP is fair through 56 days. For the 91- and 182-day samples the "gel" layer thicknesses do not agree well, while no thickness of the interdiffusion zone was determined because the hydrogen level is still decreasing.

The gel layer is characterized by a convex upward hydrogen profile for the glasses leached for 28, 56, 91, and 182 days. In all cases, the intensity dropped very near the surface. This is shown most clearly in the 14-day profile and is presumably due to H_2O loss in the surface due to the vacuum.

Figure 26 summarizes the relation between the enrichment depth and leaching duration. Also shown in the same diagram are the measured positions of the boundary between the gel layer and transition zone.

IV. DISCUSSION

The present experiments were designed to elucidate the effect of radiolysis on interactions that can occur before or after premature containment failure in the NNWSI repository. Interactions before containment failure were simulated by the blank experiments and essentially involve homogeneous reactions occurring in the groundwater as well as reactions of the groundwater with repository components (tuff, Type 304 L stainless steel, air) other than the nuclear waste glass. Interactions after containment failure involve, in addition to the above, the dissolution and hydration of the waste form. Interpretations of the results of pre- and post-containment failure simulations are presented, respectively, in Sections A and B. In order to highlight the synergistic effect of tuff on the interactions involving SRL glasses, the results of tuff-containing experiments are discussed separately in Section C. Finally, we consider the implications and potential relevance of the experimental results to the actual interactions that may occur in the NNWSI repository.

Fig. 26. Variation of Region I and Region II Thicknesses with Square Root of Time for SRL U + EJ-13. Region I + Region II (□), Region I only (Δ) refer to Fig. 25 for region descriptions.

A. Groundwater Interactions

The pH measured on the EJ-13 only and EJ-13 + tuff experiments followed a trend of continued decrease to 91 and 56 days, respectively, followed by an increase to 182 days (Fig. 2). The decrease in pH is expected from the radiolytic production of nitric and nitrous acid from gaseous N_2 in the vessel atmosphere. For the duration and dose rate used in the present experiments, Burns' equation (Eq. 1) [BURNS] for nitric acid production simplifies to:

$$N = 2.9 \times 10^{-5} (C_0 R G D t) \quad (2)$$

Using the values $C_0 = 0.036$ mol/L, $R = 0.33$, $G = 1.9$, and $D = 0.01$ mrad/h appropriate for the present experiments [also see sample calculations in BATES-1 or VAN KONYNENBURG], the total amount of nitric acid produced after 91 days is calculated to be 1.43×10^{-5} mol/L. For a system volume of 22 mL and a total liquid volume of 15 mL, the calculated increase in hydrogen ion concentration is, therefore, 2.10×10^{-5} mol/L. As was pointed out by [VAN KONYNENBURG], the initial bicarbonate concentration of $\sim 2 \times 10^{-3}$ mol/L in EJ-13 water is more than adequate to prevent the pH from becoming more acidic than the carbonic acid-bicarbonate buffer (~ 6.4 at 90°C).

The drift to more basic pH values after 91 days observed in both the EJ-13 only and EJ-13 + tuff experiments (also see Fig. 4 and 5) is both surprising and experimentally significant. In neither set of experiments does there appear to be an obvious mechanism which would drive the pH to more basic values. It should be remembered that whatever mechanism explains the pH trend observed after 91 days must also be able to neutralize the radiolytically produced H^+ . Using the values for the Burns equation given above, the total increase in $[H^+]$ due to HNO_3 production after 182 days should be 4.20×10^{-5} mol/L.

The most likely explanation for the pH increase in the blank experiments is the loss of acid volatiles, specifically CO_2 , and initial air from the experimental system. This pH increase arises from reaction of the type:

It is possible to estimate the total CO_2 and air loss from the total system weight loss data (Table 1) if the "average" composition of the atmosphere above the solution is known. Van Konynenburg [VAN KONYNENBURG] estimated the composition of the gas phase inside a typical reaction vessel used in our previous experiments (system volume = 21.4 mL; liquid/gas volume ratio (R) = 2.7), assuming it was heated from 20°C to 90°C as a closed system. If it is assumed that gases were lost in the molar proportion in which they were present in the initial gas phase (composition similar to that estimated by [VAN KONYNENBURG]), then the N_2 , O_2 , CO_2 , and H_2O mass loss per gram of total weight loss is 0.57, 0.17, 0.003, and 0.24 grams, respectively. The total CO_2 inventory inside a typical reaction vessel can be estimated from the initial HCO_3^- solution concentration ($\sim 2 \times 10^{-3} \text{ M}$) and the initial laboratory air CO_2 content of $\sim 0.0003 \text{ bar}$. This total CO_2 inventory for a vessel with 16 mL of EJ-13 water is $\sim 1.4 \times 10^{-3} \text{ g}$, virtually all in solution initially as bicarbonate.

The above mass loss estimates for N_2 , O_2 , and CO_2 are upper limits because their concentrations in the gas phase are going to be lowered from the close system values [VAN KONYNENBURG] by the leakage itself. If, on the other extreme, it is assumed that H_2O levels are controlled at saturation vapor pressure (0.7 bar at 90°C) and that the total gas pressure inside the vessel is $\sim 1 \text{ bar}$ (i.e., in approximate pressure equilibrium with the surrounding), then the total pressure of $\text{N}_2 + \text{O}_2 + \text{Ar} + \text{CO}_2$ will be $\sim 0.3 \text{ bar}$. If the relative proportions of these gas components are the same as those used in the above calculations, then the partial pressures of N_2 , O_2 , and CO_2 in the vessel are, respectively, 0.23, 0.063, and 0.001 bar. This calculation indicates a total CO_2 mass loss of $\sim 1.9 \times 10^{-3} \text{ g}$ per g of total weight loss. For a total weight loss of 0.2 g (see Table 1), as much as $3.8 \times 10^{-4} \text{ g}$ of CO_2 will have been lost. This value is about 3% of the total CO_2 inventory and represents H^+ loss of $\sim 9 \times 10^{-5} \text{ moles}$. Interestingly, the same calculation also indicates a reduction of N_2 and O_2 concentrations in the gas phase, which is consistent with the measured dissolved N_2 and O_2 levels (Table 9). These results would imply a proportionately lower rate of H^+ accumulation in solution (see Eq. 2). Taken together, the CO_2 and N_2 loss by leakage can explain the pH trends observed. Initially ($< 91 \text{ days}$), the rate of radiolytic production of H^+ is higher than the rate of H^+ consumption by CO_2 loss. As N_2 is depleted in

the gaseous phase due to leakage, the H^+ consumption overcomes the H^+ production. The point where the pH trend reverses depends on the leak rates in individual vessels as well as on other interactions that may affect hydrogen ion concentration. Also, because the production of CO_2 (from dissolved HCO_3) and H_2 (through radiolytic reactions) will serve to increase the relative concentrations of CO_2 and H_2 in the gas phase, a faster approach to the "crossover" of the two rates is to be expected. Observations made when reaction vessels were opened, in fact, indicate that pressure equilibrium with the atmosphere may have been attained in some experiments. For example, the closure nuts for vessels retrieved after 182 days were often loose (although the lids were tightly secured to the vessel body), and no excess pressure was noted.

An alternative mechanism of increasing the final pH of the blank experiments is corrosion of the stainless steel reaction vessel [BOURCIER]. It is possible that dissolution of microgram quantities of stainless steel could consume enough H^+ to neutralize a test solution of pH 4. However, it is not obvious why vessel corrosion, if it was the dominant sink for H^+ , did not overwhelm the radiolytic acidification process early on in the experiments. It is at these early stages of the experiments when corrosion rates of the vessel would have been expected to be highest, unless vessel oxidation rates were also dependent on the concentrations of some radiolytically produced species.

With the exception of the "anomalous" experiments (see below), the only significant variation in the anion data is the decrease in the NO_3^-/NO_2^- ratio from the initial EJ-13 (infinity) to the irradiated EJ-13 (1.4-2.8) to the EJ-13 irradiated in the presence of tuff (0.7-1.3). The relative stability of nitrite relative to nitrate is a function of pH and redox potential. Because of interactions with the stainless steel container and leakage of air out of the vessel (see above), the conditions inside the vessel are likely to be more reducing than those of the starting EJ-13 + air system. The lowered redox potential is expected to favor nitrite over nitrate. We already noted above that all the final pH values measured are lower than the starting EJ-13. Lower pH is expected to favor nitrate over nitrite. Although it may appear that the shift in the NO_3^-/NO_2^- ratio before and after irradiation is due to the more reducing

conditions attained in the vessels during the experiment, similar experiments performed in our laboratory in the absence of γ -radiation [EBERT] did not show any measurable formation of nitrite. This result affirms the role of radiolysis reactions in the formation of nitrite. In spite of the comparable pH, and probably redox potential, EJ-13 experiments showed higher $\text{NO}_3^-/\text{NO}_2^-$ ratios than the corresponding EJ-13 + tuff experiments. We noted previously [BATES-1] that this result may suggest interactions involving the feldspar surfaces in the tuff. More recently, a specific suggestion also was made [VAN KONYNENBURG] that reduced species on the tuff surface may catalyze the decomposition of H_2O_2 which then affects the relative concentrations of radicals that react directly with NO_3^- . The present data cannot clearly distinguish between possible molecular mechanisms that lead to the observed shift in $\text{NO}_3^-/\text{NO}_2^-$ ratio (i.e., beyond that observed in the "blank" experiments). However, the observation of a lowering of the $\text{NO}_3^-/\text{NO}_2^-$ ratio in the glass + EJ-13 experiments (see below) in the absence of tuff suggests that the effect is not specific to mineral or glass surfaces present in the tuff.

No clear trends in cation concentrations were noted in the EJ-13 only experiments as a function of time. The Si concentrations measured in the 182-day duplicate runs and in one 28-day run were noted to be "anomalously" higher than the mean Si concentration in the other experiments, and potential explanations have been presented in the accuracy and precision section. It was argued there that sampling the solutions of G-243, G-249, and G-250 for gas chromatography prior to acidification probably enhanced the contamination effect by concentrating the contaminant to a smaller sample volume. Note that the "anomalously" high Si values were excluded in determining the mean background values used subsequently for blank correction of the glass-containing experiments. If the blank Si concentrations actually increased with time [e.g., EBERT], the present blank correction procedure biases the calculated NL_{Si} to higher values (i.e., over-estimate) and underestimates the decline in Si release rate with time (see below).

Subtle increases in the concentrations of Ca, Sr, and Na, noted in the EJ-13 + tuff experiments, resulted from the interaction of EJ-13 water with tuff. Whereas two weeks were allowed for equilibration of J-13 water with crushed tuff during preparation of EJ-13 solution, the tuff disks used were pre-reacted with EJ-13 water only overnight (Appendix I). It is suggested

that even the two weeks equilibration at 90°C may not be sufficient to "saturate" the EJ-13 solution with all the major secondary phases expected to form in long-term leaching of tuff with EJ-13 water at 90°C [cf. KNAUSS]. The effect of the tuff EJ-13 interaction is best exemplified in the Si solution data (Table 5) where Si concentration clearly increased with time.

No clear trends with time were noted in the dissolved gas concentrations of O₂, N₂, and H₂. Hydrogen gas is a primary product of irradiation of liquid water and significant concentrations of dissolved H₂ were, in fact, observed. Fluctuations in the observed concentration levels may be due in part to H₂ leaking out with the other gases during the experiment or inadvertent gas exsolution prior to gas chromatographic analysis. The O₂ and N₂ concentrations are significantly lower than their expected concentrations in air-saturated liquid water at 90°C [VAN KONYNENBURG]. This again is consistent with the gas leakage during the experiment. In the case of O₂, oxidation of the stainless steel vessel is another potential means of gas loss.

B. Solution Chemistry and SRL Glass Corrosion

1. pH and Anion Trends

The pH trends of the glass-containing experiments, shown in Figs. 4 and 5, follow the pattern observed in the blank runs and may also be explained by the loss of CO₂ due to vessel leakage suggested previously. However, in the presence of glass, an additional mechanism of depleting H⁺ from solution is available, i.e., interdiffusion of hydronium and mobile glass cations, so that the pH values in these experiments are expected to be more basic than the corresponding blank runs. This is, in fact, observed. With the exception of U-208 (see below), the lowest pH's attained by the SRL glass and SRL glass + tuff experiments are 6.75 and 6.65, respectively. When tuff is present, the pH becomes more basic sooner (before 91 days) than when tuff is absent. This pH trend was also noted in the blank experiments. The significance of this observation is unclear, but it may be related to the ability of feldspar surfaces in the tuff to scavenge protons. It should be noted, however, that this explanation is

not consistent with the pH values measured in the tuff-absent and tuff-present experiments performed for 56 days or less (Figs. 4 and 5), where the presence of tuff was seen to promote acidification. The chemical complexity of the tuff matrix, as well as its nebulous role as a catalyst for the formation and decomposition of radicals during γ -irradiation, makes a quantitative relationship difficult to formulate. The main observations regarding solution pH for glass-containing systems are that (1) the general pH trends were not dramatically influenced by the interaction of solution with the glass, (2) the measured pH for all experiments fell within the narrow range of 6.7 to 7.5, and (3) the pH is always more basic than in the blank experiments.

The significance of the anion data will be discussed only briefly, as this is the subject of a more extensive analysis by [VAN KONYNENBURG]. There was no significant difference in F^- , Cl^- , SO_4^{2-} , and total fixed nitrogen concentrations between glass-containing experiments and the corresponding blanks. However, the NO_3^-/NO_2^- ratio in the SRL glass + EJ-13 experiments and the EJ-13 only experiments are significantly different (Fig. 6). This is consistent with the explanation that reduced species in silicate surfaces, whether on the tuff or SRL glass surfaces, act as catalysts in reactions that ultimately favor nitrite over nitrate. In spite of the considerable overlap, the NO_3^-/NO_2^- ratios of the experiments that contain glass only, or glass in addition to tuff, tend to be lower than the same ratio in the experiments that contain tuff only. If catalysis is, in fact, responsible for the shifts in the NO_3^-/NO_2^- ratio, it could be surmised that the SRL glass surfaces are more effective catalysts than the tuff surfaces or that higher pH's enhance the catalytic properties of the silicate surfaces. Alternatively, the lowering of the NO_3^-/NO_2^- ratio can be explained simply by the fact that alkaline solutions tend to favor nitrite over nitrate.

The major effect of gamma radiolysis in the glass-containing systems is again manifested by the production of protons. The drift towards more acid pH seems to have been arrested by the H_2CO_3 -bicarbonate buffer equilibria, CO_2 and N_2 loss from the system, and glass dissolution.

2. Leaching Trends for Li, Na, B, and Si: Mechanisms of Glass Corrosion

The prediction of long-term behavior of SRL glasses in a gamma-irradiated saturated tuff environment will require, in addition to the relatively short-term data collected in this program, a mechanistic understanding of the glass corrosion process. Questions such as the appropriateness of "accelerating" the reaction progress by using large dose rates also could be better answered by understanding the glass corrosion mechanism and its dependence on the different environmental parameters. In the results section, two types of data are presented that will form the basis for the mechanistic interpretation of the results: (1) normalized cation release and mass loss, and (2) glass surface analysis.

The relative behavior of network formers and network modifiers during leaching are of prime importance in analyzing the mechanisms of glass corrosion. The most mobile network modifiers in SRL glasses are the alkalis Li and Na, whereas the key network formers are Si and B. Consequently, the trends in the normalized releases of these elements and their behavior in the surface layers are highlighted in this section. In addition, the nuclear resonance depth profiles of hydrogen across the reacted layers also will be considered to better describe the properties of the reacted layer. In the next section, the behavior of other elements as analyzed in solution and on the glass surface will be compared with those of Li, Na, Si, and B. To simplify the initial analysis, we will concentrate on the experimental systems that did not have tuff present. The effect of the tuff on the leaching kinetics will be considered separately.

The general normalized release pattern of $\text{Li} \geq \text{Na} \geq \text{B} \geq \text{Si}$ was exhibited by the solution data (Figs. 7 and 8). However, as presented, less than 2 g/m^2 separates Li and Si normalized releases in most cases, and the $(\text{NL})_i$ values for Na and Li are not significantly different in the first 91 days of leaching. We emphasize that caution is required in interpreting the normalized Si releases data because of potential experimental problems noted earlier. The normalized leach rates $(\text{LR})_i$ for Li, Na, B, and Si decreased with time and showed no indication of reversing this trend (Figs. 7 and 8). In the case of Li, a parabolic function could be fitted to the data to 182 days (Fig. 27). For Na, the parabolic fit is good to 91 days, whereas release after 182 days for both the SRL U + EJ-13 and SRL A + EJ-13 experiments is lower than predicted by the parabolic fit

(a)

(b)

Fig. 27. Variation of Normalized Concentrations of (a) Li, Na, and Weight Loss with Square Root of Time for Experiment without Tuff; and (b) Li and Na for Experiments with Tuff

(Fig. 27). Figure 28 shows the normalized release of Si and B as a function of $t^{1/2}$. The scatter in the data, especially for Si, is quite considerable, and the parabolic rate constant is less than that of Li. Boron appears to follow a parabolic trend at least to 91 days.

The release of the network formers, Si and possibly B, may be indicative of how fast the glass network dissolves in solution. Two sites of release can be considered: (1) the glass/transition zone interface [e.g., GRAMBOW], and (2) the gel layer/solution interface (Fig. 25). In both cases, the reaction of Si, for example, involves breaking bridging and nonbridging O-Si bonds. Breakage of bridging bonds is likely to be rate-controlling and often is considered to proceed by nucleophilic attack, i.e.,

We will show below that the solution results alone are not adequate for addressing the question of release sites of network formers. The solution release pattern could be made compatible, at least qualitatively, with either site of release (especially when the uncertainty in NL estimates are taken into account). The two release sites noted above, however, are distinguishable from the elemental profile [i.e., the first results in lowering (relatively to the bulk glass) of Si or B concentrations in the gel layer whereas the second one does not].

Indeed, the SIMS profiles through the glass surface showed extreme depletion of B in the gel layer (Fig. 21). Furthermore, B shows depletion in the transition zone that is comparable to Li and Na (see below). Thus, the B profiles for the two reacted surface regions (i.e., gel and transition zone) suggest that B is released primarily in the glass/transition zone interface via a diffusionally controlled process. While it is not expected that B is released by an ion exchange process as are Li and Na, it is possible that enough reorganization of the transition zone occurs during ion exchange that B, after release from the matrix, can diffuse out of the transition zone, albeit at a slightly slower rate than Li and Na.

*In this and similar formulations, the three unreactive bonds joining Si to the anionic network have been omitted for simplicity.

Fig. 28. Variation of Normalized Concentrations of Si and B with Square Root of Time

On the other hand, Si appears to be released primarily from the gel/solution interface. This is indicated by the observation that absolute intensity of sputtered Si is constant across the gel and transition zones. Furthermore, the calculated normalized depths* and collected depth profiles require that considerable release of Si from the gel/solution interface must have occurred. For example, the difference between measured and calculated depletion depths for Li is about 1 μm after 182 days (Table 11), suggestive of an overall etching rate of approximately ~ 5 nm/day. Of course, this rate is an "average" because both the measured and calculated rates decreased with time (see below). Furthermore, underestimation of the total reacted surface area (e.g., because of cracks) by a factor of two will lead to the overestimation of the etching rate by the same order. Although some Si may have been released to the solution from other sites within the gel, the overall contribution of these other release sites are not likely to exceed 10% of the overall release.** We therefore suggest that the normalized release of Si to the leachant was dominated by etching the solution side of the gel, and is distinct from the mechanism of B release. This release mechanism contrasts with the suggestion by Grambow et al. [GRAMBOW] that etching of the outer surface of the glass does not proceed to a significant extent.

The mechanism and control of Si release to solution is extremely important in understanding waste glass corrosion. We noted above that etching the solution side of the gel is the dominant release mechanism of Si. Therefore, the decreased rate of Si release with time must be explained in terms of the parameters that control the etching rate. Two possibilities could be considered in explaining the apparent decrease of

**Normalized depth (ND_i) is defined as:

$$\text{ND}_i = \frac{\text{NL}_i}{\rho} \quad (3)$$

where NL_i is the normalized release of element i and ρ is the density of the unreacted glass ($\rho \approx 2.7$).

**After 182 days, Region I is ~ 0.35 μm thick (Table 11). If 50% of the initial Si present in this region were to go into solution, this source will account for an $(\text{NL})_{\text{Si}}$ of ~ 0.4 g/m². Measured $(\text{NL})_{\text{Si}}$'s are ~ 3.1 and 4.5, respectively, for SRL U and SRL A glass-containing experiments.

Table 11. Measured Thickness of Surface Layers in SRL U Glass

Reaction Period (Days)	Region Thicknesses (μm)						Depletion Depths (μm)	
	Gel		Interdiffusion Zone		Glass Etched		Li ^e (Measured) SIMS	Li ^f (Projected)
	NR ^a	SIMS ^b /SEM	NR ^a	SIMS	Li ^c	Si ^d		
14	0.05	0.04	0.10	0.18	0.36	0.55	0.14	0.50
28	0.08	0.07	0.15	0.25	0.75	0.72	0.19	0.94
56	0.09	0.09	0.17	0.32	0.99	0.74	0.25	1.24
91	0.12	0.28	ND	0.35	1.10	1.40 ^g	0.46	1.56
182	0.16	0.38 (0.35) ^h	ND	0.52	1.21	1.14	0.64	1.85

^aAs measured using nuclear resonance profiles.

^bAs measured using SIMS.

^cAs calculated by taking the difference between the Li depletion depth calculated from $(\text{NL})_{\text{Li}}/\rho$ and the Li depletion depth measured using SIMS profiles (see last two columns).

^dAs calculated from $(\text{NL})_{\text{Si}}/\rho$.

^eActual depletion depth measured from SIMS profiles. Depletion depth is defined as the "gel" layer thickness + 1/2 the thickness of the interdiffusion zone.

^fNormalized depletion depth of Li based on $(\text{NL})_{\text{Li}}/\rho$, this value includes the etched, "gel," and inter-diffusion regions.

^gValue based on one test, all other values based on two tests.

^hValue measured using SEM.

ND - not determined.

etching rate with time: (1) slow precipitation of a supersaturated phase that was not observed under the SEM, or (2) approach to metastable saturation of the gel layer. The first process can be described by an equation of the type [cf. TOLE]:

$$\frac{\partial C_{Si}}{\partial t} = \frac{A}{V} f_{Si}^+ K_+ - \frac{A'}{V} f_{Si}^- K_- (C_{Si} - C_{Si}^{Sat}) \quad (4)$$

where K_+ = the dissolution rate constant of the gel
 K_- = the precipitation rate constant of the precipitating phase
 C_{Si} = silica concentration in solution expressed in mass/unit volume
 C_{Si}^{Sat} = stable or metastable saturation concentration of secondary precipitate
 A and A' = surface area of dissolving and precipitating phase, respectively (if different)
 V = solution volume
 f_{Si}^+ , f_{Si}^- = mass fraction of Si in the dissolving and precipitating phase, respectively
 t = time.

In this form, release of Si from the glass is assumed to be controlled by zeroth-order dissolution, whereas the precipitation rate law is expressed in terms of first order kinetics. The observed leach rate of Si is simply the difference between the linear dissolution rate and the precipitation rate that increases with concentration (and with time). Equation 4 can be integrated from C_{Si}^{Pr} to C_{Si} , where C_{Si}^{Pr} is the concentration of Si at which the alteration product begins to precipitate (t_{ss} is the time when $C_{Si} = C_{Si}^{Pr}$) [cf. TOLE]:

$$C_{Si} = \frac{A f_{Si}^+ K_+}{A' f_{Si}^- K_-} - \left(\frac{A f_{Si}^+ K_+}{A' f_{Si}^- K_-} - (C_{Si}^{Pr} - C_{Si}^{Sat}) \right) \left(e^{-\frac{A'}{V} f_{Si}^- K_- (t - t_{ss})} \right) + C_{Si}^{Sat} \quad (5)$$

The solution concentration of Si achieved in the present experiments lies close to the solubility of α -cristobalite (106 $\mu\text{g/mL}$) and lower than the solubility of amorphous silica (321 $\mu\text{g/mL}$). On the other hand, the possibility also exists that precipitation of analcime or other Si-bearing phase (e.g., Ca-smectite) is responsible for the apparent decrease in the etching rate. For example, an estimate of analcime solubility product based on reaction of the form:

was made from existing thermodynamic data [HELGESON, ROBIE]; this estimate suggests that the leaching solution (EJ-13) is saturated with respect to analcime. Similarly, EQ3/6 simulation of high-temperature reaction of Topopah spring tuff with J-13 water (i.e., solutions similar to EJ-13) suggests control of solution composition by cristobalite, Ca-smectite, and Ca-clinoptilolite [DELANEY]. Inasmuch as none of the above secondary phases were actually observed before 91 days, control of apparent leach rate by precipitation of secondary phases remains speculative.

Approach to metastable saturation of the leached glass surface is viable and does not require assuming the existence of phases that are not actually observed in the leached glasses before 91 days. The problem with treating the leached layer as a distinct phase, however, is the lack of understanding of the thermodynamic properties of leached surface or "gel" layers of nuclear waste glasses. However, if the partially hydrolyzed glass network does indeed approach metastable saturation in the leaching solution, a transition state formulation of the net reaction rate for reaction of the form [cf. GRAMBOW]

where R = Si, H, or a network modifier can be derived as follows:

$$r_+ = \kappa \left(\frac{kT}{h} \right) \exp \left(- \frac{\Delta G_+^*}{RT} \right) \frac{a_{\text{R}_3\text{H}_3\text{Si}_2\text{O}_7} a_{\text{H}_2\text{O}}}{\gamma^*} \quad (6)$$

$$r_- = \kappa \left(\frac{kT}{h} \right) \exp \left(- \frac{\Delta G_-^*}{RT} \right) \frac{a_{\text{R}_3\text{HSiO}_4} a_{\text{H}_4\text{SiO}_4}}{\gamma^*} \quad (7)$$

where r_+, r_- = forward and reverse rates of reaction R-4, respectively

κ = transmission coefficient

k = Boltzman's constant

T = temperature

h = Planck's constant

$\Delta G_+^*, \Delta G_-^*$ = Gibbs free energy of activation of forward and reverse reaction, respectively

a_i = activity of subscripted species, and

γ^* = activity coefficient of the activated complex

By defining the rate coefficients (assuming constant T),

$$K_+ = \kappa \left(\frac{kT}{h} \right) \exp \left(- \frac{\Delta G_+^*}{RT} \right) / \gamma^* \quad \text{and} \quad (8)$$

$$K_- = \kappa \left(\frac{kT}{h} \right) \exp \left(- \frac{\Delta G_-^*}{RT} \right) / \gamma^* \quad (9)$$

*The activated complex, x, has a stoichiometry defined by the sum of the reactant stoichiometry and has been assumed to be in the form of a penta-coordinated silicon complex [MICHALSKE].

and noting that $K_{eq} = K_+/K_-$, the net rate of reaction is

$$r_{net} = r_+ - r_- = K_+ \left(a_{R_3H_3Si_2O_7} a_{H_2O} - \frac{K_-}{K_+} a_{H_4SiO_4} a_{R_3HSiO_4} \right) \quad (10)$$

$$r_{net} = K_+ a_{R_3H_3Si_2O_7} a_{H_2O} \left(1 - \frac{a_{H_4SiO_4} a_{R_3HSiO_4}}{K_{eq} a_{R_3H_3Si_2O_7} a_{H_2O}} \right) \quad (11)$$

The equilibrium constant is simply the ion activity product, Q , at equilibrium, i.e.,

$$K_{eq} = \left(\frac{a_{H_4SiO_4} a_{R_3HSiO_4}}{a_{R_3H_3Si_2O_7} a_{H_2O}} \right)_{eq} = Q_{eq} \quad (12)$$

therefore it can be verified that $r_{net} = 0$ at equilibrium. If we define the degree of saturation $S = (Q/K_{eq})$, we can express the net rate as [cf. RIMSTIDT]

$$r_{net} = K_+ a_{R_3H_3Si_2O_7} a_{H_2O} (1 - S) \quad (13)$$

If we assume that a_{H_2O} and the activity of gel species at the gel surface remain constant as the gel is etched, we can simplify this equation further into

$$r_{net} = K'_+ (1 - S) \quad (14)$$

where

$$K'_+ = K_+ a_{R_3H_3Si_2O_7} a_{H_2O} \quad (15)$$

and

$$S = \frac{a_{H_4SiO_4}}{a_{H_4SiO_4}^{saturation}} \quad (16)$$

The explicit time dependence of $C_{H_4SiO_4}$ can be derived by noting that $r_{net} = (\partial C_{H_4SiO_4} / \partial t) / (V/A \cdot f_{Si})$ and integrating Eq. 14 after rearrangement of terms (assuming ideality), i.e.,

$$\int \frac{1}{K_+'' (C_{H_4SiO_4}^{Sat} - C_{H_4SiO_4})} \partial C_{H_4SiO_4} = \int \partial t \quad (17)$$

$$C_{H_4SiO_4} = C_{H_4SiO_4}^{Sat} - (C_{H_4SiO_4}^{Sat} - C_{H_4SiO_4}^0) e^{-K_+'' t} \quad (18)$$

where
$$K_+'' = K_+ \frac{A}{V} f_{Si} \frac{1}{C_{H_4SiO_4}^{Sat}}, \text{ and}$$

and $C_{H_4SiO_4}^0$ = initial concentration of H_4SiO_4

We see that the etching rate, which is proportional to r_{net} is a simple function of the degree of silica saturation with respect to reaction R-4 and that the growth curve of H_4SiO_4 in solution follows the time dependence shown in Eq. 18. An equation of this form describes the case where the rate of increase of H_4SiO_4 in solution declines with time and can be qualitatively fitted to the observed variation of normalized Si concentration in the present set of experiments.

Note that the two mechanisms discussed above (i.e., precipitation of a supersaturated phase and approach to metastable saturation of the gel) need not operate exclusively. If saturation with respect to the gel surface and a secondary precipitate are both controlling the solution concentration of Si, the net change of Si concentration in solution can be described by:

$$\frac{\partial C_{Si}}{\partial t} = \frac{A}{V} f_{Si}^+ K_+ (C_{Si}^{Sat, gel} - C_{Si}) - \frac{A'}{V} f_{Si}^- K_- (C_{Si} - C_{Si}^{Sat, pr}) \quad (19)$$

where $C_{Si}^{Sat,gel}$ and $C_{Si}^{Sat,Pr}$ distinguish the saturation concentrations of the gel and precipitate, respectively. (Note also that K_+ in Eq. 19 is not identical to that in Eq. 4.)

Equation 19 is analogous to Eq. 14 from $t = 0$ to $t = t_{SS}$ because no Si is precipitated in the secondary phase in this time range. From C_{Si}^{Pr} to C_{Si} , Eq. 19 could be integrated as shown in Appendix IV. The resulting expression again shows a time-dependence of C_{Si} similar to that in Eq. 18 or Eq. 5. The case where multiple secondary phases precipitate can also be evaluated by adding precipitation rate laws for the additional secondary phases to Eq. 19 and following the solution provided in Appendix IV.

This treatment assumes constancy of the surface areas and solution volume. Where these parameters change as a known function of time, a solution to the differential equation can also be formulated.

The normalized release rates of the network modifiers Li and Na indicate the rate at which the mobile cations are leached out of the glass. It is commonly thought that these cations are released from the glass via the following reactions:

where X is a network-modifying ion of valence n . Because of the observed incongruent elemental release, it seems most likely that the solution release patterns exhibited by Na and Li are explained by transport across a growing diffusion barrier. The SIMS profiles are qualitatively consistent with the solution trends and nuclear resonance profiles in that Li and Na

show S-shaped profiles in the transition zone and that measured depletion depths of Na and Li are comparable (though $\text{Li} > \text{Na}$) as may be expected from an interdiffusion process where the diffusion coefficient is concentration-dependent (Fig. 21). Since Li and, in most cases, Na and B profiles in the gel layer are relatively flat compared with those in the transition zone, it appears that the transition zone accounts for most of the retardation effect of the surface layer on Li, Na, and B diffusion. The strong overlap on the solution trend and SIMS depth profile of Na and B appear surprising in lieu of the known difference in the diffusivities of the two elements. The "slow" diffusion of Na may be attributed to the high concentration of Na in EJ-13 solution (i.e., lower diffusion gradient).

The rate of advance of the transition zone into the glass appears to slow down with time when measured from the solution/gel layer boundary (Fig. 26; Table 11). It is also evident from Fig. 26 and Table 11 that, when referred to the solution/gel layer interface, the gel/transition zone boundary moved into the glass at a slower rate than the transition zone/bulk glass interface. This means that the transition zone thickened with time at a rate defined by the difference of the rates of movement of the two interfaces, regardless of the choice of reference frames. This observation is consistent with our suggestion that the transition zone is the diffusion barrier that mainly accounts for the release trend of the alkalis and boron. We caution that, because of the uncertainties involved in making the thickness estimates for the transition zone (i.e., in estimating the slopes of the curves in Fig. 26), the thickness estimates alone do not warrant making the judgment that the transition zone grew parabolically with time.

We designate the transition zone/bulk glass boundary as a diffusion front and the gel/transition zone boundary as a gelation front (Fig. 25). Because we know that the solution/gel boundary also moved into the glass, we designate this boundary as an etching front.

The movement of the diffusion, gelation, and etching fronts with time with respect to a stationary frame (e.g., the initial glass surface) is difficult to evaluate with certainty. With the present data, two methods are available to achieve an estimate of these rates. (1) By assuming that the calculated depletion depth of a strongly depleted glass species actually represents the depth the species was leached with respect

to the original glass surface (see above), the difference between the calculated and measured depletion depths of Li can be used to measure the etching depth. (2) By assuming that all Si released into solution was due to etching, the normalized Si release can also be used directly as a measure of the etching depth. The constant absolute intensity of Si during SIMS profiling supports the suggestion that the calculated Si depletion depth is a good measure of the etching depth.

Both methods of determining the etching depth give reasonable agreement considering the uncertainty in the Si measurements, and the etching depth based on Li is plotted as a function of $t^{1/2}$ in Fig. 29. From this plot, a case can be made that the etching rate also slowed down with time so that the absolute motion of the diffusion and gelation fronts must have also slowed down with time with respect to the initial glass surface. Whereas the decrease of penetration rate of the diffusion front with time is reconciled with the growth of the transition zone, the decreased rate of etching has a completely different origin as already discussed above. However, the decreasing rate of gelation, as indicated by the data, is interesting because this rate has often been assumed to be rate-controlled by the reaction:

It would appear, therefore, that a form of "saturation" effect similar to that used to explain the rate of etching that slowed down with time is again suggested. A transition-state rate formulation for R-2 is

$$r_{\text{net}} = K_+ a_{\text{Si-O-Si}} a_{\text{OH}} - K_- a_{\text{SiOH}} a_{\text{SiO}^-} \quad (20)$$

where K_+ and K_- are defined as in Eqs. 8 and 9, respectively. Noting that a_{OH} is related to a_{SiOH} and a_{SiO^-} via:

where

Fig. 29. Variation of Etching Depth with Square Root of Time

$$a_{OH} = K_{eq(R-7)} \frac{a_{SiO^-} a_{H_2O}}{a_{SiOH}} \quad (21)$$

we can rewrite r_{net} as follows:

$$r_{net} = \left(\frac{K'_+ a_{Si-O-Si} a_{SiO^-} a_{H_2O}}{a_{SiOH}} \right) - K_- a_{SiOH} a_{SiO^-} \quad (22)$$

$$\text{where} \quad K'_+ = K_{eq(R-7)} K_+ \quad (23)$$

At the gel front, $a_{Si-O-Si}$ is constant. The activity of water can also be assumed constant if the gelation process results in opening the gel layer to free diffusion of H_2O , i.e., the solution "buffers" $a_{H_2O}^*$. Therefore, it follows that the parameter a_{SiO^-}/a_{SiOH} controls the net gelation rate: i.e., the higher a_{SiO^-}/a_{SiOH} is at the gel front, the faster the gelation rate is. Therefore, the decrease, with time, of the rate of penetration of the gel into the transition zone is most likely due to the increased degree of hydrolysis of nonbridging oxygens (NBO) at the site of reaction R-2.

This, indeed, is a form of saturation effect where the availability of silanol groups formed from hydrolysis of NBO's increases the rate of condensation of $Si-O-Si$ (i.e., reverse rate of R-2). Actually, (R-2) and (R-7) could have been combined to produce a hydrolysis reaction analogous to (R-4). The point of the above digression is to make the role of OH^- and SiO^- explicit. Note that the exponential decline of H concentration from the gel surface to the transition zone can be interpreted as a reaction profile. However, bulk diffusion of H_2O , as well as condensation reactions in the partially hydrolyzed network, is expected to also influence the shape of the hydrogen profile in the gel layer.

*Note that if a_{H_2O} is not "buffered," it is likely to increase with time in the gel/transition zone boundary as the gel layer opens up to free diffusion of molecular water. This will have the effect of increasing the rate of gelation which is contrary to that observed.

Apart from the potential effect of precipitation discussed above (e.g., Eqs. 4 and 19), precipitation of insoluble phases may further modify the release trends of glass species in other ways. For example, precipitation of alteration phases at the interface of the solution and gel layer may block the effective passageways of leached ions out to the solution and at the same time reduce the effective surface area of etching. The SEM observations do not support such an influence on etching because the gel surface itself appears poorly reconstituted. Nevertheless, precipitation of secondary phases within the gel layer may, in fact, be significant. This influence on NL_1 can be modeled by introducing a tortuosity factor to the transport of leached ions. It is possible that retardation of transport through the gel layer due to this effect may, in part, be responsible for a decrease in the release rate of mobile glass species. Note that the rate of precipitation within the gel may still be described by the second term on the right-hand side of Eq. 4. Reconstitution of the gel layer (e.g., by crystallization) may also introduce similar effects [cf. BUNKER].

To summarize, the elemental release of soluble glass constituents was notably incongruent up to 182 days and followed the sequence $Li \geq Na \geq B \geq Si$. The normalized leach rates for these elements decreased with time following an approximately parabolic release trend, although significant deviation from this trend occurred for some elements after 91 days. Elemental concentration profiles of H, Li, Na and B, and SEM observations indicate the presence of two distinct regions in the reacted surface layer: (1) gel and (2) a diffusion or transition zone. Comparison of calculated and observed depletion depths (e.g., for Li) also suggests that considerable etching has occurred. Measurements of the thickness of the gel and transition zone from the H nuclear resonance profiles and SIMS (Table 11) indicate that both zones thickened at a rate that decreased with time.

The following corrosion model is consistent with the above observations:

- (1) The glass/solution interaction begins with the surface release of mobile glass constituents (e.g., Li, Na, B) and incorporation of H^+ or H_3O^+ from solution into the glass. Bulk interdiffusion through the incipient diffusion or transition

zone subsequently controls the rate of exchange for Li and Na, while diffusion through the disturbed transition zone controls the release of B.

- (2) Behind the diffusion front, a gelation front develops, formed by partial hydrolysis of Si-O-Si bridging bonds. The thickness of the zone between these two fronts (i.e., the transition zone) is a function of their relative rates of advance. Similarly, the growth of the gel layer is determined by the relative rates of etching and gelation. The rates of etching, gelation, and diffusion with respect to the initial glass surface decreased with time.
- (3) Silicon released into solution is primarily derived from etching the solution side of the gel. In contrast, significant release of Li, Na, and B must be attributed to direct leaching of the bulk glass through the gel and transition zones. The release kinetics of Li, Na, and B are largely controlled by the thickness and composition of the transition zone because the gel is a relatively poor barrier to diffusion of these elements (cf. item #4).
- (4) Deposition of alteration products in and on the gel layer or reconstitution of the partially hydrolyzed anionic framework may further modify the release rates of glass constituents.

3. Behavior of Other Glass Species

The interpretation of the normalized release of the alkali earth metals is difficult because of the high initial concentrations in tuff equilibrated EJ-13 solution compared with the total glass contribution. The following is an attempt to qualitatively describe the behavior of these elements in the glass and the interpretation is tempered by the uncertainty of the data.

The measured release rates of Mg and Sr in experiments without tuff are comparable with those of Si. Additionally, the SIMS profile for Mg was essentially constant across the gel layer, the transition zone, and into the bulk glass level (Fig. 21, 23). No large buildup of Mg on the outer surface of the glass was observed, as has in the past been reported

for other SRL glass compositions and reaction conditions [MENDEL]. These observations suggest that Mg and Sr are released into solution as the glass is etched.

Calcium showed more complex release behavior, but as with Mg and Sr the changes in Ca concentration in solution were small when compared to the initial amount of Ca in the EJ-13 leachant. For both the SRL U and SRL A experiments, the concentration of Ca in solution dropped from the initial EJ-13 value in the first 28 days. The normalized release then rose to the 182-day values which in the SRL A experiments even exceeded that of Si. It is suspected that the first 28-day values may have been influenced by precipitation of "calcite", or other Ca-rich phases on the glass surface (Figs. 18 and 19). Such precipitation is possible because of retrograde calcite and CO₂ solubilities, and locally high pH's near the glass surface. Because of the aberrant release behavior and the high initial Ca concentration in solution, it will be difficult to make meaningful interpretations of the release kinetics. Nevertheless, the SIMS profiles showed slight but consistent enrichment of Ca in the surface (gel) layer for all samples analyzed (Fig. 21).

During leaching of SRL glasses, the solution concentrations of Al increased at a rate that slowed down with time to 91 days and then decreased to 182 days. The rate of Al release for the first 91 days is lower than that of Si, possibly indicating etching and back precipitation, as possibly hydroxides or a clay phase, in the gel layer (see Fig. 21). The erratic variation of Fe concentration in solution is related to the corrosion of the stainless steel components of the tests. However, the SIMS profile of Fe is also indicative of minor reprecipitation of Fe released from the glass in the gel layer (Fig. 21).

The release rates of Np and U slowly decreased with time with Np showing a marked reduction at 182 days. The normalized release of Pu and Am in acidified solutions followed approximately linear release kinetics to at least 91 days (to 182 days for Am). However, a significant decrease in the release rate of Pu was noted after 91 days. The normalized release patterns of Pu and Am for the first 91 days may be ascribed to a combination of matrix dissolution and reconstitution in the gel layer as insoluble precipitates. This speculation was based primarily on the known low solubilities of Pu and Am in near-neutral solution pH's. The linear

release kinetics shown by these actinides for the first 91 days may have fortuitously resulted from the pH dependence of actinide solubilities. Preliminary results of ion microprobe analyses of the actinides reveal that Am is consistently enriched on the near-surface region, whereas Pu and Np show more complex behavior. Uranium appears to have been leached out of the altered surface layer, as is consistent with its approximately parabolic release pattern (Figs. 11 and 12).

It was noted in the results section that the unfiltered solution levels of Pu, Am, and Np increased with time in the first 91 days. Furthermore, the filtration experiments indicated that most of the actinides in the unfiltered fraction are filterable and that the percent actinide fraction increased in the first 91 days, at least for Pu. It would appear, therefore, that the actinides are present mostly as colloids in the experimental system studied. The increase in colloidal fraction from 14 to 91 days may possibly reflect aging of the solution. However, the percent filterable fraction may have actually decreased from 91 to 182 days.

An alternative explanation of the results of the filtration experiment is more probable, based on the relation between pH and actinide concentration shown in Fig. 14. Figure 14 mimics the expected solubility behavior of the actinides in this pH range (i.e., higher solubilities below pH = 7), which suggests that the actinide levels in unfiltered solutions may have been controlled by the solubility of actinide-bearing solids (e.g., $\text{PuO}_2 \cdot n\text{H}_2\text{O}$). This explanation assumes that colloids detected in solution are affected by pH in a fashion similar to the actinide fraction actually dissolved in solution. Colloid formation and sorption properties are complexly dependent on numerous environmental parameters and a detailed study of the phenomena beyond the scope of the present work.

C. Effect of Tuff

In an effort to account for physical interaction that may occur in the NNWSI repository, tuff disks were incorporated in several test matrices. The effects of tuff on interactions not involving SRL glasses have already been treated early in this discussion section. Some examples of observed effects include a decrease in the pH and $\text{NO}_3^-/\text{NO}_2^-$ ratio, Si and Ca contribution to solution, and Mg and Sr subtraction from solution. The

present discussion will focus on the effects of tuff on the leaching patterns of SRL glasses.

Lower normalized releases of Si is observed in experiments containing tuff when compared with experiments that do not have tuff (Figs. 7 and 8). Several alternative (but not mutually exclusive) explanations are possible: (1) silicon corrections in experiments done without tuff may result in $(NL)_{Si}$ values that are too large, (2) artifact of normalization procedure, (3) saturation effects on glass dissolution, (4) precipitation of solid phase(s), and (5) preferential silicic acid sorption onto tuff surfaces.

In the non-tuff experiments, the blank Si concentration was assumed to be constant throughout the experimental period. If, instead, slowly increasing values for the Si blank correction were used [EBERT], the $(NL)_{Si}$ values would be less as the experiment period increased. If the calculations were done in this fashion the $(NL)_{Si}$ values for the tuff and non-tuff would be closer in value.

The second and third alternatives are related to the same mechanism, so they will be discussed together. It is recalled that one assumption made in the normalization procedure used for correcting normalized solution concentrations for tuff-containing experiments is that the dissolution of tuff is not affected by the presence of the glass, e.g., tuff will contribute "X" amount of Si after 182 days regardless of the presence or absence of SRL glass in the same solution. Although detailed treatment of this subject is beyond the scope of this report, we suggest that this assumption is not entirely correct [cf. HELGESON-2; LASAGA], i.e., the rate of gross dissolution of tuff is probably dependent on the degree of undersaturation of its component minerals (e.g., K-spar, silica) or glass. Therefore, the release of Si from the glass, for example, will likely influence the release of Si from the tuff. If correct, the normalization procedure will result in overcompensation (through blank subtraction) for the tuff contribution to leachate concentrations and an apparent lower normalized release from the glass. The extent of this effect is difficult to ascertain. The converse relation has been demonstrated above; the trend of decreasing $(NL)_{Si}$ with time was attributed to saturation effects that tended to slow down matrix degradation. This effect also has been demonstrated for other nuclear waste glass formulations by other workers [e.g., PEDERSON] and has been used as the basis for $SA/V \cdot t$ scaling. An important

point not to be overlooked is that the saturation effects involved in the above discussion of Si release kinetics in the tuff-absent experiments involved a variation in Si concentration of 40 to 50 ppm, whereas the difference in Si concentrations of experiments with and without tuff (i.e., for the same leaching times) is of the order of 10 ppm or less. Because the reduction in $(NL)_{Si}$ noted between the tuff-absent and tuff-present systems are significantly smaller than that noted for the saturation effects in the above discussion, we suspect that the saturation effect alone is not an adequate explanation for the observed pattern.

Saturation with respect to secondary product(s) which precipitate(s) either on the glass or on the tuff surface could account for the discrepancy between the $(NL)_{Si}$ in the two sets of experiments. We noted earlier (e.g., Fig. 18) that a greater abundance of "precipitates" were seen on the glass surfaces from tuff-present experiments when compared with tuff-absent experiments. The surfaces of tuff disks are currently being studied at Lawrence Livermore National Laboratory (LLNL) [PHINNEY]. Precipitation of hydrated (amorphous?) silicates or aluminosilicates (with or without alkali earths) could largely account for the observed Si release patterns in the tuff-containing experiments. We again emphasize that this precipitation effect need not be equated to equilibrium solubility, as is often implied. The observed concentrations of Si in solution can result from a dynamic balance between the rate of Si released from the glass (and tuff) and the rate of Si precipitation into secondary phases (see Eq. 4). The raw concentration data presented in Table 4 show that Si actually did not achieve steady-state concentrations.

The last alternative, that of sorption, presumably should have been accounted for by blank subtraction. This, however, is not necessarily the case if the differences in corresponding pH values of the EJ-13 + tuff and SRL glass + EJ-13 + tuff experiments are sufficient to alter the sorption coefficient of, for example, silicic acid onto the tuff surface. However, this scenario is far too speculative to be fully evaluated here.

Figure 27 shows the variation of normalized Li and Na concentrations as a function of $t^{1/2}$ for SRL U + EJ-13 + tuff experiments. Also shown is the parabolic curve fitted to the SRL U + EJ-13 experiments. It is evident that no significant difference exists between the normalized releases measured from the two experiments and that a single parabolic curve can be

fit to both sets of data. This observation is important in that the presence of monolithic tuff did not appear to have significantly altered the release mechanism of Na and Li. Furthermore, the fact that the two data sets could be fit to the same parabolic curve is suggestive of the similar, if not identical, nature (i.e., thickness, composition, and structure) of the transition zones developed in the presence and absence of tuff. This inference is reinforced by the SIMS profiles collected for samples leached for identical lengths of time with and without tuff (e.g., Fig. 23). We note that earlier work that utilized powdered tuff [BATES-1] suggested that tuff may affect the extent of glass corrosion. This result may imply that the relative surface areas of tuff and glass determines whether the presence of tuff will significantly influence glass corrosion.

Perhaps the most important effect of tuff that we had intended to measure is its ability to sorb the actinide elements. In our previous experiments, we noted that crushed tuff appeared to have sorbed significant amounts of Pu but not Am in experiments of short duration (<56 days) [BATES-1]. However, after 56 days the total Pu recovered in the SRL A + EJ-13 and SRL A + EJ-13 + tuff runs in the previous experiments were not significantly different. We therefore suggested that the sorptive capacity of tuff for Pu may be limited. In contrast to the crushed tuff used previously, monolithic tuff with polished surfaces was used in the present experiments. In these experiments, the tuff disks were directly counted in the α spectrometers. The results, summarized in Table 12, suggest that less than 5% of the total Pu release (with one exception) sorbed onto the tuff surface. Note that the levels shown in Table 12 only represent the near-surface activities on the top side of the tuff disks and thus are, at best, minimum estimates.

Normalized Pu releases in experiments with tuff significantly exceeded those of the experiments without tuff, even if the actinides sorbed on the tuff surfaces are not included. The same is true for Am. We attribute these observations to either the pH dependence of Am and Pu solubilities between pH 6 and 7 (Fig. 14) and/or interaction between the actinides and additional Si generated by the tuff. The pH-dependence of solubility may have influenced the total release of Pu and Am in the following manner. At pH values > 7, Am and Pu are enriched in the gel layer together with other

Table 12. Measured Actinide Activities from Tuff Disks

Experiment #	Experiment Length (d)	pH	Total Pu Released (dis/sec)	Total Pu ^c in Tuff (dis/sec)	% Pu in Tuff	Total Am Released (dis/sec)	Total Am ^a in Tuff (dis/sec)	% Am in Tuff
G-231	14	6.85	7.03E+01	2.48E+00	3.4	5.27E+00	1.09E-01	2.0
G-232	14	6.86	6.26E+01	9.70E+00	13.4	4.13E+00	5.69E-01	12.1
G-233	28	6.75	1.48E+02	5.64E+00	3.7	1.66E+01	1.80E-01	1.1
G-234	28	6.72	2.06E+02	3.74E+00	1.8	3.87E+01	1.24E-01	0.3
G-235	56	6.92	3.60E+02	4.33E+00	1.2	3.14E+01	2.10E-01	0.7
G-236	56	6.88	2.53E+02	4.59E+00	1.8	3.06E+01	1.84E-01	0.6
G-237	91	6.85	3.99E+02	2.48E+00	0.6	7.89E+01	1.09E-01	0.1
G-238	91	6.87	5.13E+02	9.70E+00	1.9	6.73E+01	5.69E-01	0.8
G-239	182	7.16	3.78E+02	9.66E+00	2.5	1.09E+02	5.39E-01	0.5
G-240	182	7.09	3.81E+02	9.79E+00	2.5	1.01E+02	5.51E-01	0.5

^aThis total is based on a measurement of activity taken of the polished surface of the tuff wafer which faced upwards during the test. The bottom and side surfaces of the tuff were not counted and activity associated with these surfaces is not included. Also not included in the reported value is activity generated by Pu or Am that had diffused into the tuff.

relatively insoluble elements. When the solution pH dropped below 7, Am and Pu passed to the solution from the gel layer. The Am and Pu thus released then plated onto the vessel walls or onto the stainless steel supports. The presence of tuff disks in the present experiments resulted in lower integrated pH with time, in agreement with the higher total normalized releases of Am and Pu.

The measured Pu, Am, and Np values in the unfiltered (nonacidified) fraction have already been shown to be strongly dependent on solution pH. This effect was noted in the presence or absence of tuff; thus, any sorption effects on the dissolved fraction, if present, were overwhelmed by the pH effect in the present experiments.

In contrast to the behavior of the other actinide elements, normalized U releases are lower in the tuff-containing experiments than in the tuff-absent experiments. Since the lower integrated pH attained in the presence of tuff is not likely to have decreased U solubility, we attribute this observation to the sorption of U by the tuff surface. The results of ion microprobe study of U on the tuff surface will be reported in the future [PHINNEY]. Another possibility, of course, is that the precipitation process alluded to earlier in explaining the normalized Si release pattern also affected the measured U releases. This effect could take the form of discrete precipitation (e.g., weeksite) or scavenging (sorbed/occluded) by other precipitates on the glass or tuff surface.

D. Preliminary Comments on Repository Relevance

After compiling and interpreting the results of the present experimental program, some comments on the relevance of the results to actual repository scenarios are in order. This assessment is not intended to be exhaustive, as there are certain experimental parameters that have been of standard use in NNWSI repository-oriented tests (e.g., use of 90°C static tests, SRL glass formulations, EJ-13 solutions) which are more elaborately discussed elsewhere, e.g., NNWSI Site Characterization Report [LLNL, in prep]. Furthermore, we caution that a thorough analysis of even some of the experimental parameters adapted in the present program may be premature because more experiments are in progress in our laboratory to further understand the interactions which occur in the reaction vessels and to refine the experimental methodologies. Similarly, several experiments

designed to further understand NNWSI repository conditions after waste package emplacement are actively being pursued in other laboratories, foremost of which is LLNL. The following is, therefore, intended only as a guide to understanding the applicability and limitation of the present results to predicting the nature of interactions that will occur in the actual repository. We specifically focus on the possible effects of the choice of test configuration, test component materials, R, γ -dose rate, SA/V ratio, and the nature of the gas phase on the interactions noted.

The NNWSI repository will be located in the unsaturated zone above the water table. During the first 300-1000 years of emplacement, the radiation levels will be most intense, with the initial dose rate being $\sim 5 \times 10^3$ rad/h for waste produced by DWPF. It is expected that liquid water would be prevented from contacting most of the waste packages during this period because of the intense thermal output. The actual temperature will vary with the waste package emplacement design and with space and time (i.e., whatever design would have been adapted). The reduction of repository temperature with time naturally follows the decrease in radiation levels. The probability of availability (as well as total volume that may be available) of liquid water thus also increases with time.

Notwithstanding the probability of occurrence, the conditions we have set to simulate are the interaction of nuclear waste glass with NNWSI groundwater before and after the containment system has been breached prematurely. In distinct contrast to the expected repository scenario, the radiation levels, temperature, and H₂O liquid volume were fixed in the present experiments. Studies, however, have been completed or are in progress in our laboratory to ascertain the effects of these parameters.

Tuff (USW-62, 12.35.1-1232.2 ft level), being the repository host rock, was incorporated in some experiments. No attempt was made to simulate specific configurations except to ensure that the tuff, when present, was not in direct contact with the glass (Fig. 1). Within the time frame of the experiments, we showed that the presence of tuff did not significantly alter the glass corrosion mechanism and kinetics. Because tuff dissolves, the experiments that contained tuff achieved higher solution concentrations of certain glass species and tended to achieve saturation of secondary products sooner than systems that did not contain tuff. Also, small differences in pH values were observed over equivalent

leaching time of tuff-containing and tuff-absent experiments. Neither of these effects appeared to have significantly enhanced the leachability of Li and Na, but they did influence the release of species that are relatively insoluble at higher pH's (e.g., Pu, Np, and Am). Thus, unless the tuff host rocks in the repository are significantly different compositionally and mineralogically from those used in the present experiments, the only significant effect of tuff to consider are its effect on pH and the sorption of actinide elements. (Of course, the very use of tuff-equilibrated J-13 water as leachant already accounted for much of the potential effects of tuff in the system.)

The type 304 L stainless steel vessel and sample supports did not show visible evidence of corrosion. Nevertheless, a few "anomalous" tests (e.g., G-208) showed unusually large amounts of dissolved Fe and thick rust-colored precipitates on the glass. Those anomalous tests indicate that some "irreproducible" interactions may have occurred between the stainless steel materials and the solution. A more extensive treatment of these types of interactions can be found elsewhere [e.g., BATES-2; GLASS]. Another important role of the stainless steel component that cannot be fully addressed by the present work is its effect on redox equilibria in solution. We have suggested above that the $\text{NO}_3^-/\text{NO}_2^-$ ratio and the total release of some multivalent elements (e.g., actinides) may be affected by redox interactions involving the stainless steel. If actual repository conditions are more oxidizing, the normalized release of, e.g., U, may be higher than predicted by these results. Further ramifications of redox conditions on actinide speciation or colloid formation need to be considered in the future.

Another factor that influenced not only the redox but also the pH conditions in the present experimental systems is the composition of the gas phase. We have suggested above that the gas phase in contact with the solution inside the vessels changed composition with time because of leakage. If the gas phase in the NNWSI repository is maintained at ~ 1 atm pressure after nuclear waste emplacement, the bulk composition of the gas phase will depend largely on the relative humidity that is maintained. If $\text{P}_{\text{H}_2\text{O}}$ is maintained at saturation at all temperatures below the boiling point of water, a drastic reduction of the total fraction of air in the gas phase is expected. This scenario will have the effect of, among others,

lower availability of N_2 for nitric acid production and lower O_2 for oxidation. We believe that such conditions may have prevailed in the long-duration experiments, which is consistent with the pH-trend observed. More work is required to understand the quantitative analogy between the gas phase compositions in the experimental and repository systems.

We have previously discussed the importance of R (vol_{gas}/vol_{liq}) in the dynamic interactions in the reaction vessels [BATES-1]. Because the hydrogen ion production rate is an approximate linear function of R (Eq. 2), and because the irradiation effects on the solid waste form are probably negligible, the effect of R could be equated to its effect on solution pH. The magnitude of R in the actual repository is difficult to estimate at present and is expected to vary in different areas in the repository. The value of R will probably be determined entirely by the volume of standing water able to accumulate. In one extreme, conditions could be envisioned where only a small amount of water condenses onto the glass surface, making R a large number. The hydrogen ion production rate from γ -radiolysis will be proportionately high in this case. However, the total pH drift will also depend on the extent of water/glass interactions (at high SA/V) and the availability of buffering species (e.g., HCO_3^-) in solution. The experiments discussed in this paper were not intended to simulate this scenario, but experiments at very high R were completed and will be discussed in the future. The other extreme, that of very low R values, is not likely to occur in the NNWSI repository, but the effect of low R is to diminish the nitric acid production rate per system volume.

In many respects, the overall effect of γ -dose rate on glass corrosion parallels that of R . The nitric acid production rate is an approximate linear function of both R and γ -dose rate, and the influence of γ -dose rate can be mostly attributed to its effect on solution pH. The γ -dose rate used in the present work is higher than the dose rates appropriate for a SRL glass canister breached sometime during the containment period. Most previous experiments involved even higher dose rates [BATES-1 and references cited therein]. Accelerating the effect of γ -radiolysis by increasing the dose rate without accelerating other interactions (e.g., waste glass corrosion) can unduly influence the glass corrosion mechanism and elemental release patterns, e.g., actinides.

Many analyses of the effect of SA/V ratio on the glass corrosion kinetics are available in the literature [e.g., PEDERSON; OVERSBY-2; MACHIELS; MENDEL]. The dependence of leachability on the SA/V ratio depends on the mechanism of corrosion. Obviously, if linear corrosion kinetics prevail regardless of solution composition, LR_i should be independent of SA/V. This kinetic model is to be expected for experiments or actual situations where the leaching solution is kept very dilute, i.e., where SA/V ratio is extremely small or where the solution flushing rate is very high. The SRL glass corrosion patterns in the experimental systems discussed here clearly do not fall in this category. The leachability of Si in the SRL glass described in this report is dependent on its leachate concentration. Leaving everything else constant (e.g., T, initial glass and water compositions, leaching time), the Si concentration in solution is going to be higher in systems with high SA/V ratios compared with systems with low SA/V ratios. Clearly, a general inverse relation between LR_{Si} and SA/V is to be expected in this case. This is exactly what was observed in our previous experiments where some crushed SRL glasses were used [BATES-1].

The question of whether $SA/V \cdot t$ scaling can be used to predict long-term release rates can be addressed here. The applicability of this scaling technique depends on the release mechanism, and it can be used only if LR_i is a function of solution concentration (ΣCi) only. We readily note that because of γ -radiolysis and gas phase interactions noted earlier, the solution pH may be an explicit function of time, so that the scaling cannot strictly apply. However, the solution pH in the present experiments did not seem to have drifted away from neutral values, where leachability is known to be relatively independent of pH [e.g., PLODINEC]. As long as this is the case, it may be possible to assume that this explicit dependence of LR_i on time could be neglected. It is clear from the discussion of the Li, Na, and B release mechanisms that LR_i in the case of these elements depends on $(SA/V \cdot t^{1/2})$ for the time period studied. Therefore, scaling based on $(SA/V \cdot t)$ is not accurate in this case and is, at best, conservative. On the other hand, Si release appears to have been dominated by etching, which we have shown to be a function of degree of saturation only. Therefore, the scaling is likely to apply in the prediction of Si release. We caution, however, that if precipitation of a silicate phase that contains

leached elements (e.g., Na) influences the apparent Si release rate, $SA/V \cdot t$ scaling may not strictly apply, because the saturation level of Si will depend on the concentration levels of the other elements in the phase.

V. SUMMARY AND CONCLUSIONS

This section summarizes the key results and conclusions of the present experimental program. Long-term leaching (up to 182 days) of actinide-doped SRL 165 glass was performed in a gamma radiation field ($D = 1 \pm 0.2 \times 10^4$ rad/h) at 90°C. The leaching solution used was tuff-equilibrated EJ-13 water. The extent of glass reaction was estimated from normalized elemental mass loss data and reaction layer depth measurements. From the correlation of the extent of glass reaction and individual elemental mass loss and depth profiles as a function of leaching time, a model of SRL glass corrosion in EJ-13 water was developed.

The measured pH's in both the blank and actual runs followed a trend of decreasing values to 56 or 91 days and increasing values after 91 days. We attribute this variation to the interplay between acidification by nitric acid production (radiolysis of N_2) and basification by $CO_2(g)$ loss from solution. In the presence of SRL glass, exchange reactions between the hydronium ions or protons from solution and mobile cations (e.g., Li and Na) from the glass further basified the solution. However, the overall effect of glass corrosion on solution pH in the present experiments is not dramatic, and a narrow pH range of 6.7 to 7.5 prevailed for the whole duration of the experiments.

The only significant anion variation observed in the leaching experiments is the systematically lower NO_3^-/NO_2^- ratios from EJ-13 only to EJ-13 + tuff to EJ-13 + tuff + glass experiments. This observation could be attributed to the catalytic effect of reduced species on silicate surfaces upon radiolytic reactions that ultimately lead to nitrate breakdown [VAN KONYENBURG].

The general normalized release pattern, $Li \geq Na \geq B \geq Si$, was exhibited by the solution data. A single parabolic function could be fitted to Li and Na (to 91 days) regardless of the presence or absence of tuff. The release rate of B and Si also slowed down with time.

The nuclear resonance profiles for H and the SIMS profiles for Li, Na, B, Al, Ca, Mg, Mn, and Fe indicated two regions in the reacted layer. The region closer to the unreacted glass, referred to as the transition zone, exhibits well-defined S-shaped profiles for H, Li, Na, and B indicative of concentration-dependent diffusion coefficients for these elements during interdiffusion. The region away from the glass, referred to as the gel layer, exhibits relatively flat profiles for these elements.

Speculations on the mechanisms of release of individual glass species were based on the above information. Lithium and Na are released from the glass via ion-exchange (with proton or hydronium) across the transition zone while B diffuses from the transition zone after pathways for diffusion are established. The transition zone behaves as a transport barrier to these species. On the other hand, the dominant mode of Si release is etching of the gel layer. Some Si may be released from within the gel layer as speculated by [GRAMBOW], but this amount is probably a minor contribution to the overall Si-release. Transport of H, Li, Na, and B across the gel layer is rapid compared with diffusion across the transition zone.

The depth profiles showed that the transition zone grew at a decreasing rate with time, a finding which agrees with the leachate data. Approximate calculations of the rates of gelation and etching suggest that both rates also decrease with time. We attribute these decreased rates with time to saturation effects.

The release of other major glass species were considered within the framework of the mechanism discussed above. The variation of the normalized solution concentrations of Mg and Sr with time is consistent with their release via etching. A similar release mechanism may explain the release pattern of Ca, but some influence of secondary phase precipitation is also indicated. The SIMS profile for Ca and Fe shows an enrichment in the gel layer. Early precipitation of Al phase(s) is indicated by the solution data.

The actinide elements, Pu and Am showed total normalized release patterns that are approximately linear with time to at least 91 days. We tentatively ascribe this release pattern to a combination of matrix breakdown and reconstitution in the gel layer, although preliminary ion microprobe profiles suggest that Pu and Np behavior may be more complex.

The significant correlation between pH with Pu, Np, and Am concentrations in unfiltered nonacidified samples suggests that solubility is the key parameter controlling their concentration levels in solution.

The presence of tuff did not appear to affect the mechanism of release of the major glass species. Because tuff also dissolved in solution, a faster approach to saturation of secondary products was noted where tuff was present. The present data strongly indicate that some sorption of actinides to the tuff surface has occurred. Larger total actinide release was noted in the case of Pu and Am in tuff-containing experiments. This observation is attributed to the lower integrated pH values attained in the tuff-containing experiments in the present program.

Some preliminary comments were made on the applicability and limitations of the present results to predicting the nature of actual interactions in the NNWSI repository. Specific attention was given to test configuration, test component materials, R, γ -dose rate, and SA/V ratio. The present results, together with those of the previous [BATES-1] and ongoing experiments, will be evaluated in the future to provide more definitive assessment of the repository relevance of these experiments.

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APPENDIX I

(This Appendix is a slightly modified version of [BATES] Appendix I)

Preparation of Tuff and Prereacted
(90°C) J-13 Water
(T. A. Abrajano)

The test procedure requires the use of caliche-free tuff and J-13 water that has been pre-reacted at 90°C with tuff. The tuff was prepared using NNWSI-supplied samples of Topopah Spring tuff that had been obtained so as to avoid caliche-containing outcrop material. The J-13 water was also supplied by NNWSI.

The procedure was as follows:

1. Solid preparation (10 g of tuff of <100-mesh per liter of J-13 water).
 - a. Place chunks of rock into plastic bag and hit them with a hammer to obtain about 3/4-inch pieces.
 - b. Place the pieces of rock into a Teflon container with high-purity water (HPW), shake container for two minutes, rinse the pieces with HPW, and let them air dry.
 - c. Crush and grind dried pieces of rock with a stainless steel piston-cylinder apparatus.
 - d. Sieve enough material through a 100-mesh sieve.
2. Equilibration
 - a. Weigh out 10 g of <100-mesh crushed rock per liter of J-13 water into a clean 2-liter Teflon bottle.
 - b. Add 100 mL of J-13 water and shake for two minutes.
 - c. Let stand for one hour. Decant water and discard.
 - d. Fill the bottle near the top with J-13 water (allow some space for expansion), cap tightly, shake for one minute, and place into 90°C oven.
 - e. Twice daily for the first five days, remove the bottle, and shake for one minute. Leave the bottle stationary for the remaining time.

3. Filtering

- a. After two weeks in 90°C oven, remove the bottle and air cool for one hour.
- b. Filter the water through high quality filter paper.
- c. Refilter using a 0.2 μ m Millipore or Nucleopore filter, replacing the filter as required.

4. Storage

- a. Store the filtered water in a dark place in a polypropylene container.
- b. The water should be stable for several months. However, its stability should be checked by ICP analysis before the initiation of a test series.

5. Tuff preparation

- a. Receive tuff cores from LLNL.
- b. Note orientation of cores as related to core depth identification.
- c. Place tuff disks into a 100-mL Teflon container with HPW.
- d. Shake container for two minutes and rinse with HPW.
- e. Refill Teflon container with EJ-13 water and place it in a 90°C oven.
- f. Shake container (for two minutes) after two hours, and then return it to 90°C oven and leave overnight.
- g. Retrieve tuff disks and air-dry them to constant weight.
- h. Store the tuff in marked containers for use in those experiments that require tuff.

APPENDIX II

(This Appendix is excerpted and slightly modified
from [BATES] Appendix II)

Test Procedures

(T. A. Abrajano, J. K. Bates, and T. J. Gerding)

- a. Place the preweighed tuff disks inside designated vessels. Ensure that the polished side of the tuff is facing up.
- b. Place the preweighed sample supports into their designated vessels.
- c. Add the preweighed and measured glass sample disks onto the sample support in the appropriate vessels.
- d. Tare each vessel, add the predetermined amount of pre-equilibrated J-13 water with the use of a wash bottle, and record this vessel water weight.
- e. Zero the empty balance, place the vessel cap on the vessel, and record the "in" weight for the loaded vessel.
- f. Attach the closure fittings to these vessels and tighten according to the type of gasket materials used in the caps. Tightening once is sufficient, and one should not overtighten. When using new Parr bomb fittings, one or two coats of Teflon spray on the threads of the closure fitting will prevent galling and aid in easy assembling and disassembling of these fittings.
- g. The assembled vessels are now ready for the oven. Keep the assembled vessels upright at all times.

OPENING TEST VESSELS

- a. The test vessel assemblies were removed from the oven at the γ -irradiation facility and placed on a bench top to cool. The vessels were sorted into two groups. The first group consisted of the vessels with SRL A samples, and the other consisted of the blank vessels and vessels with SRL U samples. The first group of vessels were opened last because they need special handling and precautionary measures.

- b. All vessel assemblies were removed, and the capped vessels were weighed to determine the "out" weight.
- c. A vise and pipe wrench had to be used to pry the caps from the vessels.
- d. Observations were made of the contents and conditions inside the opened vessels, and notes were taken when warranted.
- e. Any Si gasket particulate which may have fallen into the vessel and/or liquid was carefully removed. Any loose Si gasket material on the cover was removed because the vessel would have to be reassembled at another step in these procedures.
- f. A 5- to 10-mL aliquot sample was collected into Pyrex glass syringe for dissolved gas analysis (only for vessels designated for sampling).
- g. A 2-mL aliquot sample was taken from each vessel for anion analyses.
- h. A 100- λ aliquot sample was taken from all vessels containing SRL A samples and placed onto a premarked stainless steel planchet for actinide counting. Preselected vessels had an additional 200- λ aliquot taken, which was placed into a 0.003 μm filter tube containing 500- λ (1/2-mL) of HPW. The tube was centrifuged, and a 100- λ aliquot was taken and placed onto a premarked stainless steel planchet for actinide counting.
- i. The pH measurements were made in the vessels.
- j. The glass- and tuff-disk samples were carefully removed from the vessels with tweezers, rinsed with HPW, and placed into their respective sample vials, keeping the same sample orientation as the samples were in the vessels. After the disks dried, weights were taken and recorded.
- k. The stainless steel supports were removed, rinsed with HPW, dried, weighed, and the weights were recorded.
- l. The stainless steel supports were placed back into their respective vessels.
- m. Six drops of concentrated nitric acid (Ultrex) were added to each vessel.
- n. The vessels were capped, reassembled with their fittings, swirled to mix the liquid, and placed into a 90° oven overnight.

- o. Next morning, vessel assemblies were removed and cooled to room temperature.
- p. Vessel assemblies were disassembled, and the vessel caps were once again removed.
- q. A 100- λ aliquot was taken from all the vessels which had contained SRL A glass samples; it was placed then onto stainless steel planchets for additional actinide counting.
- r. The stainless steel supports were once again removed, rinsed, placed into prelabeled containers, dried, and eventually reweighed.
- s. The liquids from each vessel were transferred into tared LPE containers, weighed, and sent for analyses.
- t. 19 mL of solution containing 1% HF and 1% HNO₃ by weight was added to each test vessel that contained SRL A samples. The solution was allowed to stand in the vessel for one hour whereupon an aliquot was removed for α -counting.
- u. The vessels from t were rinsed with HPW and smeared for loose activity. The acid wash step was repeated until no measurable activity remained.

APPENDIX III

SIMS Data Analyses System and Depth Calibration
(J. K. Bates, W. L. Ebert, and T. J. Gerding)

For the SIMS analyses, the low-energy sputtered positive ions were electrostatically separated from the negative ions and neutrals and then mass analyzed using a UTI model 100 C quadrupole gas analyzer with a CEM detector. The signal from the CEM was converted to a digital signal by an Interactive System model AI13 12 bit ADC and then read by the computer. A m/e range of 1-150 was scanned over a two-minute period. The CEM signal was sampled 1205 times during a complete scan by the program "AUTOACQUIRE."*

Spectral peaks were identified using the program "AUTOCRUNCHER."* The intensities of the peaks of interest were then divided by the intensity of $m/e = 28$ peak (silicon). The ratios of a given m/e value were then plotted as a function of scan number (sputter time) by the program "RATIOPLOT"* to produce a concentration profile.

Additional data manipulation was done for presentation in the text. The elemental ratios to silicon were further normalized via division of the bulk elemental ratio to silicon for each element. This had the effect of forcing all ratios to equal one when the bulk glass was reached. Elements that were depleted from the glass had ratios between zero and one, while elements that were enriched had ratios greater than one.

An important parameter in using any ratioing scheme to present elemental profiles is the consistency in concentration of the base element throughout the profile. If both the base element and the element of interest change in concentration throughout a profile, the meaning of the profile becomes obscured. For the present data Si was used as the base element. The consistency of Si concentration for the 14- and 182-day samples is shown in Fig. III-A. Here it is seen there may be some enrichment in Si in the first 100-500 Å but that thereafter Si intensity is constant within error of the measurements.

*The computer programs used to process the data (AUTOACQUIRE, AUTOCRUNCHER, SCANPLOT, and RATIOPLOT) were written at Argonne National Laboratory. We would be happy to provide listings to any interested persons.

Fig. III-A. Absolute Intensity of Si as Observed for the 14- and 182-Day Samples

Determination of the sputter rate (the relationship between sputter time and depth) requires additional information. In this work we obtained the approximate sputtering rate for the reacted layer in three ways: (1) by comparing the profiles of the alkali ions (lithium and sodium) with the profile of hydrogen obtained on similar samples using a nuclear profiling technique; (2) by surface profilemetry (Dektac) of glasses sputtered for known periods of time; and (3) by sputtering layers of known thickness as measured by SEM.

In the first method, the relationship between the profiles (H and Li or H and Na) is presumed according to the belief that the alkalis are replaced by a hydronium species (H_3O^+) in the ion exchange reaction. Therefore, we expect that as the native glass is approached, the alkali concentrations should increase with sigmoidal profiles and the hydrogen decrease with a sigmoidal profile.

The second and third methods give absolute measures of the layer thickness based on the measurement of sputtered craters or of regions of known thickness. Sputtering depths measured using both methods 2 and 3 agree within 10% and for 2 keV Ne and standard operating conditions a sputtering rate of $0.33 \mu\text{m/hr}$ results. No difference was found in the sputtering rate of the "gel" layer or the bulk glass.

Depths obtained using nuclear resonance profiling differ from those obtained with SIMS for reasons unknown at this time.

APPENDIX IV

Solution to Equation 19

$$\frac{\partial c_{Si}}{\partial t} = \frac{A}{V} f_{Si}^+ K_+ (c_{Si}^{Sat, gel} - c_{Si}) - \frac{A'}{V} f_{Si}^- K_- (c_{Si} - c_{Si}^{Sat, pr}) \quad (IV-1)$$

$$\text{let } \frac{A}{V} f_{Si}^+ K_+ \equiv K_1$$

$$\frac{A'}{V} f_{Si}^- K_- \equiv K_2$$

$$u \equiv K_1 (c_{Si}^{Sat, gel} - c_{Si}) + K_2 (c_{Si}^{Sat, pr} - c_{Si})$$

$$\therefore du = -(K_1 + K_2) dc \quad (IV-2)$$

$$\text{let } K_3 \equiv -(K_1 + K_2)$$

$$\frac{du}{dt} = K_3 \frac{dc}{dt} \quad (IV-3)$$

$$\frac{du}{dt} = K_3 u \quad (IV-4)$$

$$\frac{du}{u} = K_3 dt \quad (IV-5)$$

Integrating IV-5, we get

$$\ln u + \ln n = K_3 t \quad (IV-6)$$

$$un = e^{K_3 t} \quad (IV-7)$$

If $C = C_{Si}^{Pr}$ at $t = t_{ss}$

$$\frac{1}{h} = [K_1 (C_{Si}^{Sat, gel} - C_{Si}^{Pr}) + K_2 (C_{Si}^{Sat, pr} - C_{Si}^{Pr})] e^{-K_3 t_{ss}} \quad (IV-8)$$

$$K_1 (C_{Si}^{Sat, gel} - C_{Si}) + K_2 (C_{Si}^{Sat, pr} - C_{Si}) =$$

$$[K_1 (C_{Si}^{Sat, gel} - C_{Si}^{Pr}) + K_2 (C_{Si}^{Sat, pr} - C_{Si}^{Pr})] e^{K_3 (t - t_{ss})} \quad (IV-9)$$

$$C_{Si} = \frac{[K_1 (C_{Si}^{Sat, gel} - C_{Si}^{Pr}) + K_2 (C_{Si}^{Sat, pr} - C_{Si}^{Pr})] e^{K_3 (t - t_{ss})}}{K_3} - \frac{K_1 C_{Si}^{Sat, gel}}{K_3} + \frac{K_2 C_{Si}^{Sat, pr}}{K_3} \quad (IV-10)$$

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