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THE REACTION OF GLASS DURING GAMMA IRRADIATION IN A SATURATED TUFF ENVIRONMENT
PART 1: SRL 165 GLASS

by

John K. Bates, Donald F. Fischer,
and Thomas J. Gerding

Chemical Technology Division

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ABSTRACT

The influence of gamma irradiation on the reaction of actinide-doped borosilicate glass (SRL 165) in a saturated tuff environment has been studied in a series of tests lasting up to 56 days. The following conclusions were reached. The reaction of, and subsequent actinide release from, the glass depends on the dynamic interaction between radiolysis effects, which cause the solution pH to become more acidic; glass reaction, which drives the pH more basic; and test component interactions that may extract glass components from solution. The use of large gamma irradiation dose rates to accelerate reactions that may occur in an actual repository radiation field may affect this dynamic balance by unduly influencing the mechanism of the glass-water reaction. Comparisons between the present results and data obtained by reacting similar glasses using MCC-1 and NNWSI rock cup procedures indicate that the irradiation conditions used in the present experiments do not dramatically influence the reaction rate of the glass.

I. INTRODUCTION

The Nevada Nuclear Waste Storage Investigations (NNWSI) project is currently evaluating the volcanic tuff beds of Yucca Mountain, Nevada, as a repository for the permanent storage of nuclear waste. The description of this site is continuously being refined [BALLOU], and currently, although the repository horizon is described as unsaturated, pockets of condensed water may exist for brief interludes. If there were a premature canister failure during the waste containment period (0-300/1000 y), there would then be the potential for standing water to contact the waste form in the presence of a radiation field.

The probability of this sequence of events occurring is extremely low, especially because the heat generated during this period would likely drive any liquid water away from the waste form. However, inasmuch as recent reviews [BURNS-1982A -1982B, McVAY] have indicated that increased reaction between glass waste forms and water can occur under certain circumstances in the presence of gamma radiation, gamma irradiation tests would provide data that may be used in evaluating site suitability.

The current program has been designed to take advantage of information gained in previous leach testing of glasses in gamma fields. These earlier tests, done mainly with simulated waste glasses and deionized water, have indicated that increased leaching from glass can occur in a gamma radiation field as a result of the formation of nitric acid and other radiolysis products [BARKATT, McVAY, NASH, YOKAYAMA], but is not generally attributed to radiation damage of the waste form [BIBL[illegible]-1981].

Additionally, nitric acid, the radiolysis product thought to have the greatest influence in affecting glass reaction, previously has been shown to result mainly from the irradiation of nitrogen-containing gas and not from radiolysis reactions involving the liquid [BURNS-1983, TOKUNAGA]. After formation in the gas, the nitric acid dissolves in the liquid, where a complex series of reactions may occur that result in the formation of NO_x species. The actual reaction products found in solution are dependent on the water composition and on additional components that may be present, but the end result of irradiating an air/water system is that the solution pH becomes more acidic. This creates a condition known to be aggressive toward glass, presumably as a result of the increased solubility of Fe, Al, rare earths, and actinide elements [McVAY]. In basic solutions, these elements are enriched in a layer that forms on the glass surface and may act to retard further reaction. As the pH becomes more acidic, this layer dissolves and leaves the glass more susceptible to attack.

It has also been suggested [BARKATT] that formic and oxalic acids form during gamma radiation of the liquid. These acids would not only serve to drive the solution pH more acidic, but would also increase the solubility of selected elements due to their ability to form complexes.

Finally, NNWSI is conducting corrosion tests using conditions applicable to the NNWSI site. These tests include studies done with gamma radiation [GLASS] and, although focusing mainly on the corrosion of metals, have provided an indication that gamma irradiation increases the oxidizing nature of the aqueous solutions.

The importance of having both nitrogen-containing gas and liquid in the proximity of the irradiation field has thereby been established. This condition is applicable to the NNWSI site because it is located in an unsaturated zone where both air and groundwater will be present. However, a large variability in the ratio of the volume of gas to the volume of liquid (R) could exist, ranging from a thin film of water covering solid surfaces to small amounts of transient standing water. This ratio, R, is an important parameter because it affects the pH and, thus, the solubility and speciation of elements in solution. The greater R becomes, the greater the concentration of radiolysis products in solution, resulting in a more acidic condition. The effect of radiolysis is lessened when the volume of liquid is large compared with that of the gas, i.e., when R is small.

The importance of this factor has generally not been recognized in previous experiments and, thus, has not been controlled. However, Burns et al. [BURNS-1982A] have established a formalism that accounts for R as it relates to the solution pH; the present results [BATES-1985] and those reported by Yokayama et al. [YOKAYAMA] are the first to have been produced by recognizing and controlling this parameter during experimentation.

The effect that the radiation dose rate has on the reaction must also be taken into account. Previous experimenters have been inclined to use large dose rates in an attempt to duplicate the total dose that a nuclear waste glass might encounter during its lifetime in a repository. The advisability of such action might be questioned based on artificial effects that may be introduced into the system; however, it has been demonstrated that the effect of gamma radiation levels off when the dose rate exceeds 1×10^5 rad/h [McVAY].

In the repository, the dose rate that will be important from the standpoint of waste form reaction will depend on when the canister is breached, initiating glass-groundwater contact. Maximum dose rates for either commercial or defense glass will depend on the repository design, but could range downward from upper limits of $\sim 1 \times 10^5$ rad/h for commercial glass and $\sim 1 \times 10^4$ rad/h for defense glass. Gamma, beta, or alpha radiation could initiate ionizing reactions, and may be important, depending on the radiation field present when groundwater contact occurs or on the volume of water present. In the present experiments we have been constrained to use a constant dose rate throughout the experiments. The ramifications of this condition will be examined later.

The present series of experiments has expanded on the available information base by monitoring the behavior of waste package components under unanticipated, but possible, conditions expected in the potential NNWSI repository site. Components included in the tests are defense and commercial glass formulations that contain both uranium and transuranium elements, Type 304 L stainless steel (SS), equilibrated J-13 water, and tuff rock.

The tests provide initial information concerning the degradation of the waste form and the behavior of important waste elements in the presence of tuff, SS, and a gamma radiation field. The results will be compared with similar tests done without the radiation field.

II. EXPERIMENTAL

A. Test Matrix

Interactive testing was done to incorporate waste package and repository components into the procedure. Additionally, tests were done using crushed glass to provide data for different SA/V conditions (surface area of the glass/volume of the liquid). Three test matrices were used:

(1) two glass disks in preequilibrated J-13 water (EJ-13), SA/V = 0.3 cm^{-1};

(2) two glass disks in EJ-13 with crushed tuff, SA/V = 0.3 cm^{-1} with 0.2 g (<100 mesh) of tuff; and

(3) crushed glass (+40 -80 mesh) in EJ-13, SA/V = ~ 0.9 cm^{-1}.

Each matrix was run at a nominal temperature of 90°C for periods of 7, 14, 28, and 56 days. Duplicate samples were run for each time period and, when possible, MCC-1 protocol was followed. Blanks were run for test matrices 1 and 3 using only EJ-13, and for test matrix 2 using EJ-13 in tuff.

Additional tests, without gamma irradiation, were not performed because these types of tests were part of the parametric test program being performed by Bazan and Rego [BAZAN].

B. Test Components

All the tests were done in certified Type 304 L SS Parr reaction vessels (Parr Instrument Co., Moline, IL). The vessels were fabricated by Parr with materials supplied by ANL. These vessels had a capacity of 21.4 cm^3 and were sealed with a compression fitting and a silicone rubber gasket. This combination provided a leak-free system where water losses after 56 days were $\sim$0.01 g. Also used was a simple closure system that maintained its integrity for a total dose of up to 5×10^8 R, as was demonstrated in a short-term test at a dose rate of 2×10^6 R/h.

During testing, each vessel contained $\sim$16 mL of water and at least 4 cm^3 of air. Calculations (see example, Appendix B) based on the theory described by Burns et al. [BURNS-1982A] indicated that this volume of air would not become depleted in nitrogen caused by nitric acid formation throughout the 56-day test period. This was indeed observed, as the amount of NO_3^- and NO_2^- found in solution was near that predicted.

The EJ-13 water used in these tests had been reacted with Topopah Spring tuff for two weeks at 90°C. Extensive testing has shown this procedure sufficient to produce water that, although not completely equilibrated, is more representative of potential repository groundwater than J-13 water [OVERSBY]. The EJ-13 water composition is given in Table 1, and the water equilibration procedure is described in Appendix A.

Table 1. Composition of EJ-13 Water[a] (ppm)

Al	0.63	Mg	0.96	F^-	2.4
B	0.16	Na	46.5	Cl^-	7.15
Ca	9.08	Si	34.4	NO_3^-	7.60
Fe	0.01	Sr	0.045	NO_2^-	ND[b]
Li	0.044	U	0.0024	SO_4^{2-}	17.3

[a] Analysis by inductively coupled plasma spectroscopy, ion chromatography, and atomic fluorescence.

[b] None detected.

In the repository, the water that contacts the waste form will have been exposed to a radiation field prior to reacting with the glass. This may enable radiolytic products to accumulate in the water and, thus, affect the initial water/glass reaction. The degree to which the groundwater would be altered by this irradiation would be variable and would depend on actual repository conditions. These tests addressed this issue in the blank series of tests; however, the water that was used in the tests containing glass was subjected to no radiation pretreatment process.

The experiments were done in an oven whose temperature was controlled at 90 ± 0.5°C and was monitored with a data logger that recorded the temperature every eight hours. The actual temperature of the water contained in the test vessel was not measured during testing, but after the tests were terminated, it was determined that a temperature increase of ∿2°C had likely occurred. This measurement was made by placing separate thermocouples inside and outside a water-containing vessel and monitoring the temperature differential during irradiation. The measurement was done outside the oven at an ambient temperature of 26°C.

The gamma irradiation field was produced by a ^{60}Co source; the dose rate, as measured inside the SS vessels at the beginning of the test period, was $(2 \pm 0.2) \times 10^5$ rad/h. Complete dosimetry of the inside of the oven was done, and the test vessels were positioned in aluminum racks to receive the required dose rate. The entire matrix of 112 tests was completed within one 56-day period.

C. Sample Description

Each test matrix was done with four different glass types. These were:

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

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

(3) Pacific Northwest Laboratory (PNL) 76-68 glass ATM-1c, which contained uranium.

(4) PNL 76-68 glass ATM-8, which contained added ^{237}Np, ^{239}Pu, and ^{99}Tc.

The ATM-8 and ATM-1c glasses were produced by the Materials Characterization Center (MCC) and have somewhat different rare earth compositions, because they were not made from the same base frit. The exact compositions and complete description of the processing conditions used to produce these MCC glasses are currently not available. Details regarding the reaction of these glasses will be reported at a later date, after receipt of the required information from the MCC. The SRL 165 glasses were produced at ANL following procedures documented in Appendix B. The composition of these glasses is given in Table 2.

Table 2. Composition of SRL Glasses Used in Testing

	Analysis (wt %)		
	SRL 165 U/A	Black Frit	
Component	ANL[a]	Ferro[b]	MCC[c]
Al_2O_3	4.08	4.1	4.3
B_2O_3	6.76	6.8	6.8
BaO	0.06		<0.1
CaO	1.62	1.5	1.6
Fe_2O_3	11.35	12.3	11.7
FeO	0.35		
K_2O	NA[d]		0.2
Li_2O	4.18	4.7	4.8
MgO	0.70	0.8	0.6
MnO	2.27	2.9	2.8
Na_2O	10.85	10.3	10.8
NiO	0.85	0.9	0.8
P_2O_5			0.3
SiO_2	52.86	54.1	51.6
TiO_2	0.14		0.2
ZnO	0.04		<0.1
ZrO_2	0.66	1.2	0.7
F	NA	0.06	
Cl	NA	0.05	
Pb	NA	0.05	
$^{237}NpO_2$	0.008		
$^{239}PuO_2$	0.022[e]		
$^{241}Am_2O_3$	0.00036[e]		
U_3O_8	0.96		
Cs_2O	0.072		
SrO	0.11		
Others[f]			

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[a] Composition determined at ANL. Only SRL U glass was analyzed for all components; SRL A glass was analyzed for ^{237}Np, ^{239}Pu, and ^{241}Am. The compositions of both glasses are assumed to be the same except for actinide elements.

[b] Black frit supplied to ANL by SRL, composition as determined by Ferro Corp.

[c] Black frit supplied by SRL to the MCC, composition as determined by MCC.

[d] Not analyzed.

[e] Analysis by alpha spectrometry.

[f] La_2O_3, Nd_2O_3, and $CeO_2 < 0.05$; $MoO_3 < 0.01$; and $Cr_2O_3 < 0.01$ wt %.

All the glass disks were core drilled from cast bars and cut to size. All surfaces of the glass were, therefore, as-cut and had a surface finish of ∿250 grit. The glass disks were supported on perforated Type 304 L SS stands, and the crushed glass and crushed tuff were on the bottom of the vessel. A complete description of the experimental procedures is given in Appendix B, and the characterization of the glass is described in Appendix C.

D. Analyses

At the completion of each test, the solutions were cooled to room temperature and analyzed for pH, cations (inductively coupled plasma spectroscopy, ICP), anions (ion chromatography, IC), uranium (atomic fluorescence, AF), cesium (atomic absorption spectroscopy, AA), and radionuclides (γ and α counting). The solid test components were measured for weight change and were analyzed by scanning electron microscopy and associated energy dispersive X-ray analysis (SEM/EDS) and secondary ion mass spectroscopy (SIMS). A complete description of the procedures used to obtain and prepare the solutions/samples for analysis is given Appendix B.

III. RESULTS

These tests have resulted in an extensive collection of data. The test conditions, component weights, and solution volumes are presented in detail in Appendix D. The results are summarized for the cation analyses of the blanks and SRL glass tests in Tables 3 and 4, respectively; radionuclide analyses in Table 5; and anion analyses of the blanks and SRL glass tests in Tables 6 and 7, respectively. These results are discussed in Sections III.B and C, and details of all analyses are given in Appendix E. Surface analyses using SEM/EDS and SIMS have been conducted, and these results are presented in Section III.D. The results of solution and glass analyses are then discussed, as a whole, in Section IV.

A. Precision and Accuracy

It is important to quantify the precision of the data to enable one to judge whether observed trends are significant. Data precision is reflective of error introduced during the test procedure and of error in the individual analytical measurements. In the current tests, the pH and anion results have been affected by dissolved gas in the test solutions. In collecting the pH data, some instability existed in the test solution. An acceptable pH measurement was one in which the pH quickly dropped (became more acidic) to a certain stable value. However, outgassing frequently caused the pH values to slowly rise (become more basic) after the quick drop from their initial readings. This made it difficult to judge which pH value should be recorded; for consistency, the lowest value was always selected. Stirring the solution, which was the standard procedure used in the 7-, 14-, and 28-day tests, seemed to promote this instability and was discontinued for the 56-day tests. The 28-day results were most affected by the instability.

Table 3. pH and Cation Analyses - Blank Samples

Test	Test No.	Duration (days)	pH	Elemental Concentration (ppm, µg/mL)																
				Al	B	Ba	Ca	Mo	Na	Si	Sr	Ti	Zn	Li	Ce	Nd	La	Mg	Cs	U
Analytical Sensitivity[a]				0.2	0.08	0.09	0.1	0.09	0.3	0.5	0.03	0.01	0.02	0.08	0.4	0.3	0.1	0.03	0.1	0.0005
Blanks	99	7	6.76	0.70	0.18	<0.09	8.92	<0.09	47.3	41.9	0.06	<0.01	0.06	<0.08	<0.4	<0.3	<0.1	1.00	<0.1	0.003
	100	7	6.66	0.75	0.17	<0.09	8.79	<0.09	47.2	45.3	0.06	<0.01	0.05	<0.08	<0.4	<0.3	<0.1	0.96	<0.1	0.002
	97	14	6.31	0.69	0.16	<0.09	8.53	<0.09	47.0	50.2	0.05	<0.01	0.02	<0.08	<0.4	<0.3	<0.1	0.96	<0.1	0.002
Vessel	98	14	6.48	0.69	0.17	<0.09	8.60	<0.09	46.7	52.6	0.05	<0.01	0.02	<0.08	<0.4	<0.3	<0.1	0.99	<0.1	0.002
+	101	28	7.05	0.74	0.31	<0.09	8.63	<0.09	46.4	55.0	0.07	<0.01	0.05	<0.08	<0.4	<0.3	<0.1	0.98	<0.1	0.003
EJ-13	102	28	7.15	0.76	0.26	<0.09	8.67	<0.09	46.8	48.6	0.06	<0.01	-	<0.08	<0.4	<0.3	<0.1	0.98	<0.1	0.003
	103	56	6.56	0.81	0.24	<0.09	8.97	<0.09	44.7	48.6	0.07	0.01	0.05	<0.08	<0.4	<0.3	<0.1	1.01	<0.1	0.003
	104	56	6.81	0.78	0.23	<0.09	8.91	<0.09	44.6	45.1	0.07	0.01	-	<0.08	<0.4	<0.3	<0.1	1.01	<0.1	0.003
Blanks	107	7	6.88	0.54	0.18	<0.09	19.76	<0.09	47.6	44.7	0.10	-	0.03	<0.08	<0.4	<0.3	<0.1	1.38	<0.1	0.005
	108	7	6.94	0.56	0.18	<0.09	18.89	<0.09	46.2	42.9	0.10	-	0.06	<0.08	<0.4	<0.3	<0.1	1.32	<0.1	0.005
Vessel	105	14	6.94	1.46	0.19	<0.09	24.36	<0.09	47.5	49.1	0.10	0.02	0.04	<0.08	<0.4	<0.3	<0.1	1.52	<0.1	0.008
+	106	14	6.84	0.85	0.19	<0.09	23.69	<0.09	47.4	46.0	0.11	0.02	0.07	<0.08	<0.4	<0.3	<0.1	1.51	<0.1	0.008
EJ-13	109	28	7.27	0.48	0.29	<0.09	31.14	<0.09	47.5	51.2	0.12	0.02	0.03	<0.08	<0.4	<0.3	<0.1	1.61	<0.1	0.014
+	110	28	7.45	1.20	0.26	<0.09	29.18	<0.09	45.9	55.0	0.13	0.02	0.05	<0.08	<0.4	<0.3	<0.1	1.60	<0.1	0.011
Tuff	111	56	6.71	0.51	0.28	<0.09	31.45	<0.09	46.0	52.4	0.15	0.02	-	<0.08	<0.4	<0.3	<0.1	1.71	<0.1	0.023
	112	56	6.61	0.41	0.28	<0.09	39.03	<0.09	45.2	55.5	0.17	0.02	0.03	<0.08	<0.4	<0.3	<0.1	1.86	<0.1	0.039

[a] Analytical sensitivity is defined as three times the detection limit for each element.

Table 4. Normalized Elemental Mass Loss (Cations) from SRL Glasses U and A

Test Type	Test Duration (days)	pH		Normalized Release (g/m^2)									
				B		Li		Na		Si		Cs	
		U	A	U	A	U	A	U	A	U	A	U	A
Glass	7	6.97	6.83	0.1	0.2	0.6	0.9	0.4	0.8	0.8	2.1	0.0	0.0
Disks	7	6.72	6.96	0.1	0.2	0.5	0.9	0.2	0.8	0.8	1.6	0.0	0.0
+	14	6.98	6.96	0.3	0.2	0.9	1.1	1.1	0.9	(0.3)[a]	0.2	0.0	0.0
EJ-13	14	6.40	6.71	0.3	0.3	0.9	1.1	0.8	0.9	(0.4)	0.0	0.0	0.0
	28	6.84	6.57	0.2	0.3	1.4	1.9	1.4	1.8	(0.3)	0.0	0.0	0.0
	28	6.74	6.64	0.2	0.6	1.3	1.8	1.4	1.9	(0.3)	0.3	0.0	0.0
	56	6.31	6.64	1.3	1.6	2.0	2.5	2.5	2.3	1.8	2.5	0.0	0.0
	56	6.38	6.61	1.3	1.7	2.0	2.5	2.5	2.5	1.9	2.0	0.0	0.0
Glass	7	7.15	7.01	0.1	0.2	0.6	0.9	0.8	1.5	1.2	2.3	0.0	0.0
Disks	7	7.23	6.91	0.1	0.1	0.6	0.8	0.3	1.3	1.2	3.3	0.0	0.0
+	14	7.12	7.02	0.2	0.2	0.7	0.9	0.9	0.3	0.4	1.4	0.0	0.0
EJ-13	14	7.00	6.89	0.2	0.3	0.8	1.1	0.7	0.3	0.3	0.0	0.0	0.0
+	28	7.12	6.88	0.2	0.4	1.0	1.5	(1.5)	1.9	(1.0)	0.5	0.0	0.0
Tuff	28	7.15	6.84	0.4	0.5	1.3	1.6	1.8	1.9	0.1	0.9	0.0	0.0
	56	6.58	6.70	1.4	1.5	2.1	2.3	3.2	2.4	2.4	2.1	0.0	0.0
	56	6.70	6.73	1.3	1.4	2.0	2.3	3.1	2.3	2.1	1.7	0.0	0.0
Crushed	7	7.02	7.02	0.0	0.1	0.3	0.3	0.0	0.1	0.1	0.3	0.0	0.0
Glass	7	7.01	7.01	0.0	0.1	0.3	0.3	(0.1)	0.2	0.2	0.4	0.0	0.0
+	14	6.63	6.77	0.1	0.1	0.4	0.4	0.3	0.1	(0.3)	(0.2)	0.0	0.0
EJ-13	14	6.71	6.77	0.1	0.1	0.4	0.4	0.2	0.2	(0.1)	(0.1)	0.0	0.0
	28	6.68	6.69	0.2	0.2	0.9	0.9	0.8	0.4	0.0	0.0	0.0	0.0
	28	6.56	6.65	0.2	0.2	0.7	0.7	0.7	0.7	0.0	0.2	0.0	0.0
	56	6.58	6.35	0.8	0.8	1.2	1.2	1.2	1.0	0.7	1.7	0.0	0.0
	56	6.47	6.68	0.7	0.9	1.1	1.1	1.2	1.2	0.7	0.9	0.0	0.0

(contd)

Table 4 (contd)

Test Type	Test Duration (days)	Normalized Release (g/m^2)											
		Al		Ca		Mg		Sr		U		Weight Loss	
		U	A	U	A	U	A	U	A	U	A	U	A
Glass	7	0.5	0.5	0.6	0.1	2.1	0.8	0.0	0.0	0.06	0.15	0	0.08
Disks	7	0.5	0.4	(0.2)[a]	0.6	1.7	0.9	0.0	0.1	0.05	0.15		
+	14	0.7	0.2	1.0	0.3	1.0	0.3	0.2	0.1	0.24	0.13	0.2	0.06
EJ-13	14	0.6	0.2	0.5	0.3	0.8	0.3	0.2	0.1	0.23	0.25		
	28	0.2	(0.1)	0.4	(0.2)	0.6	0.3	0.0	0.1	0.30	0.29	0.44	0.68
	28	0.2	0.2	0.3	(0.1)	0.4	0.5	0.1	0.1	0.35	0.67		
	56	1.1	1.4	1.2	2.6			0.4	0.6	1.47	1.77	1.10	1.04
	56	1.2	1.3	1.5	1.2			0.4	0.6	1.53	1.82		
Glass	7	3.6	2.0	1.1	(0.4)	1.7	0.3	0.0	0.0	0.08	0.09		
Disks	7	2.7	3.6	(2.5)	0.7	1.4	1.0	0.0	0.0	0.05	0.09		
+	14	1.0	1.4	(4.0)	(6.2)	0.7	1.4	(0.1)	0.1	0.18	0.16		
EJ-13	14	1.0	1.0	(4.5)	0.5	0.4	1.7	0.0	0.0	0.19	0.22		
+	28	0.0	1.3	(17.1)	(8.2)	(0.9)	0.1	(0.3)	0.0	0.32	0.34		
Tuff	28	1.3	1.1	(5.6)	(0.4)	0.5	0.6	0.1	0.1	0.37	0.42		
	56	5.5	3.0	33.3	21.7			0.5	0.4	1.61	1.71		
	56	6.3	3.4	32.6	14.6			0.5	0.4	1.37	1.61		
Crushed	7	0.0	0.0	(0.4)	(0.1)	0.0	0.0	0.0	0.0	0.03	0.04		
Glass	7	0.0	0.0	(0.4)	(0.1)	0.0	0.0	0.0	0.0	0.03	0.04		
+	14	0.0	(0.1)	(0.1)	(0.1)	0.1	0.0	0.1	0.2	0.11	0.10		
EJ-13	14	0.0	0.0	(0.1)	(0.1)	0.0	0.1	0.1	0.1	0.08	0.12		
	28	(0.1)	(0.1)	0.0	(0.4)	0.2	0.0	0.2	0.1	0.30	0.20		
	28	0.0	(0.1)	0.1	(0.2)	0.2	0.1	0.1	0.1	0.26	0.23		
	56	0.0	(0.1)	0.2	0.3			0.7	0.8	0.87	0.76		
	56	0.0	0.0	0.3	0.1			0.7	0.7	0.79	0.44		

[a] Parenthetical entries are negative values.

Table 5. Actinide Release from SRL A Glass

Np Analyses:

Test Duration (days)	SRL Disks					SRL Disks + Tuff					SRL Crushed				
		Count Rate[a] (cps)					Count Rate[a] (cps)					Count Rate[a] (cps)			
	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (ng)	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (ng)	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (ng)
7	6.83	ND		ND		7.01	ND		ND		7.02	ND			ND
7	6.96	ND		ND		6.91	ND		ND		7.01	ND			ND
14	6.96	ND		ND		7.02	ND		ND		6.77	ND			ND
14	6.71	ND		ND		6.89	ND		ND		6.77	ND			ND
28	6.57	ND		ND		6.88	ND		ND		6.69	ND			ND
28	6.64	ND		ND		6.84	2 E-3		ND		6.65	ND			ND
56	6.64	ND		ND		6.70	5 E-3		ND		6.35	ND			ND
56	6.61	6 E-3		ND		6.73	5 E-3		ND		6.68	ND			ND

Pu Analyses:

Test Duration (days)	SRL Disks					SRL Disks + Tuff					SRL Crushed				
		Count Rate[a] (cps)					Count Rate[a] (cps)					Count Rate[a] (cps)			
	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (ng)	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (ng)	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (ng)
7	6.83	1.7E-2	9 E-3	5.3E-2	14.6	7.01	5 E-3	5 E-3	9 E-3	2.7	7.02	1.3E-2	1.3E-2	2.5E-2	7.6
7	6.96	1.2E-2		4.8E-2	13.0	6.91	6 E-3		1.1E-2	3.3	7.01	1.2E-2		2.7E-2	10.9
14	6.96	1.2E-2		3.7E-2	10.2	7.02	5 E-3		2.1E-2	5.6	6.77	2.3E-2		6.2E-2	18.3
14	6.71	1.2E-2		4.7E-2	12.6	6.89	8 E-3		3.6E-2	9.5	6.77	2.4E-2		6.2E-2	21.0
28	6.57	2.9E-2	1.8E-2	1.7E-1	50.6	6.88	2.3E-2	2.3E-2	1.1E-1	33.6	6.69	4.0E-2	2.0E-2	1.3E-1	42.2
28	6.64	3.3E-2		2.2E-1	64.2	6.84	2.8E-2		1.1E-1	33.1	6.65	4.2E-2		1.2E-1	39.2
56	6.64	5.1E-2	4.6E-2	2.5E-1	72.9	6.70	4.8E-2	5.2E-2	2.3E-1	68.8	6.35	1.1E-1	1.3E-1	3.4E-1	110.0
56	6.61	6.2E-2		2.7E-1	78.2	6.73	4.1E-2		1.9E-1	56.6	6.68	6.6E-2		2.1E-1	68.4

Am Analyses:

Test Duration (days)	SRL Disks					SRL Disks + Tuff					SRL Crushed				
		Count Rate[a] (cps)					Count Rate[a] (cps)					Count Rate[a] (cps)			
	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (pg)	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (pg)	pH	(non-filtered)	(filtered)	(acid soak)	Total Release (pg)
7	6.83	9 E-4	0	7 E-3	33.7	7.01	0	0	3 E-3	13.5	7.02	0	2 E-4	1.1E-2	51.3
7	6.96	5 E-4		ND	ND	6.91	6 E-4		4 E-3	18.4	7.01	3 E-4		1.0E-2	48.0
14	6.96	0		8 E-3	35.6	7.02	0		1.3E-2	57.0	6.77	0		1.2E-2	56.2
14	6.71	2 E-4		6 E-3	27.0	6.89	1 E-4		1.5E-2	66.7	6.77	2 E-4		2.4E-2	130
28	6.57	0	0	2.4E-2	127	6.88	2 E-4	3 E-4	5.2E-2	270	6.69	3 E-4	0	2.8E-2	156
28	6.64	2 E-4		2.6E-2	135	6.84	5 E-4		5.6E-2	289	6.65	4 E-4		3.0E-2	168
56	6.64	2 E-4	0	4.1E-2	213	6.70	3 E-4	0	8.2E-2	420	6.35	6 E-4	0	7.6E-2	422
56	6.61	2 E-4		2.7E-2	139	6.73	4.1E-4		6.2E-2	322	6.68	6 E-4		4.8E-2	268

[a] Counts per second per 100 λ of solution, not corrected for detector efficiency, which is 21%.

[b] Not determined.

Table 6. pH and Anion Analyses - Blank Samples

Test Type	Test No.	Duration (days)	pH Out	Concentration (ppm, μg/mL)					Total Fixed Nitrogen, μmol/mL
				F^-	Cl^-	SO_4^{2-}	NO_3^-	NO_2^-	
Blank, No Tuff	99	7	6.76	2.65	7.10	18.6	6.35	3.30	0.17
	100	7	6.66	2.65	7.35	19.7	7.80	3.10	0.19
	97	14	6.31	2.65	7.60	20.9	8.25	2.05	0.18
	98	14	6.48	2.60	7.40	20.1	8.70	2.65	0.20
	101	28	7.05	2.80	7.15	18.7	11.6	3.45	0.26
	102	28	7.15	2.80	7.65	19.7	9.15	4.35	0.24
	103	56	6.56	3.10	8.35	20.4	13.6	5.50	0.34
	104	56	6.81	3.05	8.05	20.6	12.6	6.65	0.35
Blank, Tuff	107	7	6.88	2.60	7.10	19.4	4.65	4.45	0.17
	108	7	6.94	2.60	7.10	19.6	4.15	4.20	0.16
	105	14	6.94	2.60	7.45	20.9	5.00	5.10	0.19
	106	14	6.84	2.60	7.55	20.9	3.95	4.20	0.16
	109	28	7.27	2.75	7.40	19.4	6.15	7.00	0.22
	110	28	7.45	2.75	7.70	19.7	4.80	6.85	0.23
	111	56	6.71	3.10	7.85	21.1	8.15	9.90	0.35
	112	56	6.61	3.00	7.45	20.1	8.10	8.40	0.31
Average:									
No Tuff		7		2.65	7.25	19.2			0.18
		14		2.65	7.50	20.5			0.19
		28		2.80	7.40	19.2			0.25
		56		3.10	8.20	20.5			0.35
Tuff		7		2.60	7.10	19.5			0.17
		14		2.60	7.50	20.9			0.18
		28		2.75	7.55	19.6			0.23
		56		3.05	7.65	20.6			0.33

Table 7. Anion Analyses - SRL Glass

Test Type	Test No.	Duration (days)	pH Out	Concentration (ppm, μg/mL)									
				F^-		Cl^-		SO_4^{2-}					
					Blank Corrected		Blank Corrected		Blank Corrected	NO_3^-	NO_2^-	Total Fixed Nitrogen	Blank Corrected
SRL U	3	7	6.97	2.75	0.10	8.15	0.90	20.8	1.6	5.75	3.10	0.16	(0.03)[a]
+	4	7	6.72	2.70	0.05	8.65	1.40	21.7	2.5	7.15	3.25	0.18	(0.01)
J-13	1	14	6.98	2.50	(0.15)	7.45	(0.05)	19.6	(0.90)	6.80	3.25	0.18	(0.01)
	2	14	6.40	2.45	(0.20)	7.45	(0.05)	19.0	(1.5)	6.30	3.55	0.18	(0.01)
	5	28	6.84	2.35	(0.45)	6.35	(1.05)	15.4	(3.8)	7.75	2.75	0.18	(0.07)
	6	28	6.74	NA		NA		NA		NA	NA	NA	
	7	56	6.31	3.00	(0.10)	7.70	(0.50)	19.1	(0.10)	11.9	3.70	0.27	(0.08)
	8	56	6.38	2.95	(0.15)	10.70	2.5	19.7	0.50	11.6	4.30	0.28	(0.07)
SRL U	11	7	7.15	2.65	0.05	7.90	0.80	24.2	4.7	4.05	3.95	0.15	(0.02)
+	12	7	7.23	2.60	0 0	7.80	0.70	19.7	0.2	4.15	3.84	0.15	(0.02)
J-13	9	14	7.12	2.40	(0.20)	7.40	(0.10)	19.7	(1.20)	4.90	4.75	0.18	(0.02)
+	10	14	7.00	2.45	(0.15)	7.50	0.0	19.9	(1.00)	5.85	4.35	0.19	0.01
Tuff	13	28	7.12	2.70	(0.05)	7.40	(0.15)	18.7	(0.90)	6.00	5.90	0.23	0.0
	14	28	7.15	2.70	(0.05)	7.20	(0.35)	18.8	(0.80)	5.75	6.75	0.24	0.01
	15	56	6.85	3.00	(0.05)	7.95	0.30	19.8	(0.80)	8.10	7.15	0.33	0.0
	16	56	6.70	2.80	(0.25)	7.55	0.10	19.5	(1.1)	7.20	6.95	0.27	(0.06)
Crushed	19	7	7.02	2.60	(0.05)	7.80	0.65	19.7	0.5	2.60	4.30	0.14	(0.05)
SRL U	20	7	7.01	2.65	0.0	7.80	0.65	20.5	1.3	3.15	3.90	0.14	(0.05)
+	17	14	6.63	2.45	(0.20)	7.45	(0.05)	18.8	(1.7)	7.35	3.10	0.19	0.0
J-13	18	14	6.71	2.45	(0.20)	7.40	(0.10)	18.3	(2.2)	2.95	7.55	0.17	(0.02)
	21	28	6.68	2.75	(0.05)	7.20	(0.20)	18.3	(0.9)	6.50	5.75	0.23	(0.02)
	22	28	6.56	2.70	(0.10)	7.40	0.0	17.9	(1.3)	5.90	5.60	0.22	(0.03)
	23	56	6.58	3.05	(0.05)	7.90	(0.30)	19.9	(0.6)	7.40	7.10	0.27	(0.08)
	24	56	6.47	2.90	(0.20)	7.85	(0.35)	19.5	(1.0)	6.85	7.25	0.27	(0.08)

Table 7 (contd)

				Concentration (ppm, μg/mL)									
				F^-		Cl^-		SO_4^{2-}					
Test Type	Test No.	Duration (days)	pH Out		Blank Corrected		Blank Corrected		Blank Corrected	NO_3^-	NO_2^-	Total Fixed Nitrogen	Blank Corrected
SRL A	27	7	6.83	2.50	(0.15)	7.20	(0.05)	20.2	1.0	5.80	3.75	0.18	(0.01)
+	28	7	6.96	2.55	(0.10)	7.15	(0.10)	20.1	0.9	5.25	4.30	0.18	(0.01)
J-13	25	14	6.96	2.50	(0.15)	7.00	(0.50)	18.1	(1.1)	4.40	5.00	0.18	(0.01)
	26	14	6.71	2.70	(0.05)	7.70	0.20	19.4	0.2	6.80	3.85	0.19	0.0
	29	28	6.57	2.75	(0.05)	7.65	0.25	20.2	1.0	10.1	3.45	0.24	(0.01)
	30	28	6.64	2.80	0.0	7.75	0.35	19.3	0.1	9.7	3.75	0.24	(0.01)
	31	56	6.64	3.05	(0.05)	8.15	(0.05)	20.7	0.2	11.7	5.20	0.30	(0.05)
	32	56	6.61	2.75	(0.35)	8.40	0.20	19.4	(0.9)	11.4	5.40	0.30	(0.05)
SRL A	35	7	7.01	2.35	(0.05)	7.30	0.20	19.5	0.0	6.05	3.95	0.18	0.01
+	36	7	6.91	2.55	(0.05)	7.30	0.20	19.6	0.1	6.05	4.00	0.18	0.01
J-13	33	14	7.02	2.60	0.0	7.25	(0.25)	17.8	(3.1)	6.30	4.10	0.19	0.01
+	34	14	6.89	2.60	0.0	7.00	(0.50)	17.9	(3.0)	4.95	4.50	0.18	0.0
Tuff	37	28	6.88	2.75	0.0	7.35	(0.20)	18.9	(0.70)	6.85	6.00	0.24	(0.01)
	38	28	6.84	2.75	0.0	8.00	0.45	18.5	(1.1)	5.80	6.70	0.24	(0.01)
	39	56	6.70	2.85	(0.20)	7.95	0.30	21.4	1.2	8.65	7.40	0.30	(0.05)
	40	56	6.73	2.85	(0.20)	7.50	0.15	19.8	(0.8)	9.00	7.10	0.30	(0.05)
Crushed	43	7	7.02	2.60	(0.05)	7.05		18.4	(0.8)	5.10	4.35	0.18	(0.01)
SRL A	44	7	7.01	2.55	(0.10)	7.20		19.9	(0.2)	5.65	4.10	0.18	(0.01)
+	41	14	6.77	2.75	0.10	8.40		20.0	(0.5)	6.15	4.35	0.19	0.0
J-13	42	14	6.77	2.65	0.0	7.70		19.5	(1.0)	6.15	5.05	0.21	0.02
	45	28	6.69	2.75	(0.05)	7.50		18.2	(1.0(	6.15	5.65	0.22	(0.03)
	46	28	6.65	2.75	(0.05)	7.45		18.3	(0.9)	5.30	6.50	0.23	(0.02)
	47	56	6.35	2.95	(0.15)	7.60		19.2	(0.4)	11.0	6.50	0.32	(0.03)
	58	56	6.68	2.85	(0.25)	7.60		18.9	(0.7)	6.78	9.10	0.31	(0.04)

[a] Parenthetical entries are negative values.

Anion measurements were affected when trapped gas was introduced, or formed, during the measurement process. The trapped gas displaced liquid in the ion chromatograph, thereby reducing the actual volume of liquid analyzed. This caused all anion values to be proportionally lowered by the amount of liquid displacement. Samples in which the effects of trapped gas were observed were rerun, if possible, or the values were corrected to compensate for the gas formation.

Two potential sources of error exist for Si test results. Silicon gaskets were used to seal the test vessels. The gaskets lost some elasticity during the longer experiments and, in some cases, small pieces of gasket material were found in the solution when the vessels were opened. These pieces could have been introduced when the vessel was opened. Additional contact between the gasket and water may have been possible due to extrusion of the gasket that occurred when the vessels were sealed. Secondly, errors in Si analysis may have been caused by difficulties encountered in using ICP to analyze for Si. Both sources of error were compounded because changes in Si concentration were small compared with the amount of Si in the EJ-13 water.

In the tests with tuff present, there was inadvertent dispersal of tuff onto the glass disks. The amount of tuff on the glass varied between samples and resulted from turbulence in the solution, which occurred when the EJ-13 water was added to the test vessel. The tuff was difficult (or impossible) to completely rinse from the glass surface at the end of the experiment; thus, the weight change values for glass disks in the experiments with tuff present are not indicative of glass reaction. Other effects of tuff coverage on the glass are difficult to assess, but it was noted that the glass surfaces from equivalent tuff and no-tuff experiments had the same appearance when examined at high magnification using scanning electron microscopy.

Some error (difficulty in data interpretation) is introduced due to the inhomogeneity of the actinide composition in SRL A. This problem is described in Appendix C and discussed in the analysis of the actinide data.

Finally, the degree of reaction is likely to vary between tests because the tests were based on a specific SA/V ratio, which necessitated that the R ratio vary slightly between tests. This variance in R may have resulted in the formation of different amounts of nitric acid in each test and may have affected the degree of reaction.

The precision of the data was determined extensively for Na, B, actinide elements, and anions using the results of all duplicate tests, and for other EJ-13 elements using the data from the blank tests. The extensive deviation measurements were done by taking the percentage standard deviation from identical tests (duplicates) and averaging the values. This resulted in over 50 values being used to determine the percentage deviation. For Na, an element for which the effect due to leaching was small compared with the amount of Na present in the EJ-13 water, the precision was ±7%. For B, which results mainly from glass dissolution, the precision was ±4%. Values for the precision of anion and actinide measurements, determined in the same fashion, were ±5% and ±15%, respectively.

Standard deviations for other cations, based on duplicate measurements from the blank tests, were less than ±10%.

The accuracy of the measurements depends on the analytical methods and on the experimental procedures. The analysts provided an estimate of accuracy based on the analysis of standards; these are 3-10% for ICP, 5% for anions, 10% for Cs, and 5% for U. In each case, the accuracy is based on the amount of an element present in the sample.

Some measure of the accuracy of the experimental method could have been obtained by having the experimenters periodically run standard reference forms and compare results with established norms. In the present case, this was not practical because no standard reference forms are available and no norms have been established for leach testing in gamma radiation conditions. For the present tests, the experimenters had several years experience performing standard (MCC-1) leach tests on nuclear waste materials, but had not performed any tests in a gamma radiation field. However, the tests were planned and run only after extensive review of reported past procedures used in gamma radiation testing.

B. Solution Analyses - Blank

Several radiation tests were run in which only water, or water plus tuff, was present in the test vessel. These tests provide data necessary to evaluate repository performance by providing an indication as to how EJ-13 water will react under potential repository conditions. The tests also provide data to be used in adjusting the glass-containing test samples so that the degree of glass reaction can be ascertained. For the latter purpose, the tests can be referred to as blanks, but only in the water-only tests is this actually true. The tests involving tuff plus water are not actually blanks because the influence of the tuff may not be the same as when glass is also present in the system. For example, a tuff/water system may attain a pH of 7 after a period of irradiation, but with glass present the same system may attain a pH of 6.5. Thus, using a "blank" based on a pH of 7 may not correctly account for the influence of tuff on the system.

The pH, cation, and anion data for blank samples are presented in Tables 3 and 6. The major anticipated radiolytic reactions are the production of nitric and nitrous acids, and these reactions are indicated by the increase in the amount of fixed nitrogen in solution. The amount of fixed nitrogen increased from 0.12 μmol/mL (NO_3^-) in EJ-13 water to 0.35 μmol/mL ($NO_3^- + NO_2^-$) in 56-day irradiated EJ-13 water with no tuff. The amount formed with tuff present, 0.33 μmol/mL, is slightly less. This amount of nitrogen fixation (∿11 ppm NO_3^-) corresponds well with that predicted using the formalism proposed by Burns et al. [BURNS-1982A] if G[*] for the production of nitric acid is 1.3. Calculations of the maximum amount of nitric acid that can be produced with the current test conditions also indicate that, after 56 days, only 0.1% of the nitrogen in the air has been fixed.

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[*] The number of molecules produced for each 100 eV of energy absorbed.

Two clear trends are observed: (1) slightly less total fixed nitrogen is observed in the tuff-containing system and (2) the NO_3^-:NO_2^- ratio shifts from 2:1 to 1:1 with tuff present in the system. The amount of fixed nitrogen should be dependent only on the volume of air present, which was essentially unchanged between the tuff and no-tuff experiments. No obvious explanation for either of these observations can be advanced.

Of the other anions in EJ-13 water, Cl^- and SO_4^{2-} remain constant throughout the duration of the test, whereas F^- may be slightly increasing. Oxalic or formic acids, which may be produced and could influence the degree of glass reaction and actinide solubility, were not directly analyzed, but there was no indirect evidence in the IC runs of their formation.

The pH of the solution was difficult to measure. This was especially true for the 28-day series, where stirring the solutions during measurement resulted in instability. The 56-day solutions were not stirred, but the pH measurements were not as stable as those in the 7- and 14-day tests. It is difficult, therefore, to assess trends in the pH measurements. It is possible that the 28-day values are too high. However, in all cases the final solution pH is more acidic than that of the initial EJ-13 water.

Several potential trends were observed for cations. In the water-only tests, there is an increase of ∿0.1 μg/mL in the amount of B detected in the 28- and 56-day samples compared with that in the 7- and 14-day samples, e.g., 0.17 to 0.26 μg/mL, but no gradual increase from 7 to 56 days is observed. This lack of continuity, plus the fact that there is no known source of B in the system, suggests that an analytical bias exists in the 28- and 56-day results. This possible bias is also observed in the tuff/water tests.

The amount of Na in solution is possibly decreasing with time, but the total change is only ∿5%, which is less than the precision of the Na measurements. The concentration of other elements is constant with time.

In the tuff/water tests, the concentrations of alkaline earths, Ca, Mg, and Sr, in addition to U, show a ∿100% increase after 7 days, followed by continued increase through 56 days. This is evidence for a gradual reequilibration of the system, responding to the formation of radiolytic products and a gradual decrease in solution pH. All these elements have a higher solubility as the solution pH becomes more acidic.

The concentration of Na behaves similarly to what was observed in the water-only tests, showing a slight decrease after 56 days. The Si appears to increase gradually, but these results are tempered by the large uncertainty associated with Si measurements. The remaining elements are either below their detection limits or remain constant throughout the test.

C. Solution Analyses - SRL Glass

The compositions of SRL U and SRL A glasses differ because of the ^{237}Np, ^{239}Pu, and ^{241}Am that have been added to the SRL A glass. The small change in matrix element composition would not likely have a measurable effect on the reaction of the glass, but there may be a radiolysis effect mainly due to alpha decay. Therefore, comparison between the reaction of SRL U and SRL A glasses is important. Also, comparisons between tuff/no-tuff and disk/crushed-glass experiments may be useful.

1. pH

The trends in pH observed for SRL U and SRL A disks are identical within the error of the measurements (Fig. 1). After 7 days, the pH dropped from its pretest value of 8.1 to ∿7. There is a small decrease (0.1 pH units) through 28 days, followed by a further drop of 0.3 pH units after 56 days. The trends for both the tuff and no-tuff tests are similar, but the pH in the tuff tests is consistently ∿0.2-0.3 units higher than for the tests without tuff. The values for crushed glass are similar to those observed for glass disks.

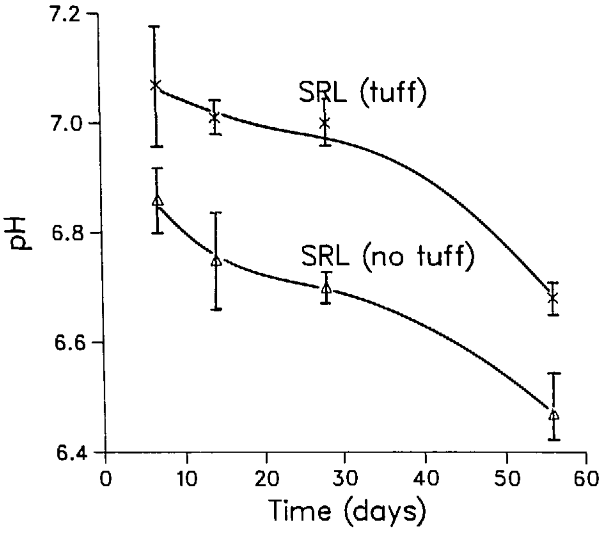


Fig. 1.

pH Trends Observed for SRL A and SRL U Glass

2. Cations

The accumulation of cations in solution follows two distinct trends. The cations of Li and Na show a gradual increase of normalized elemental mass loss, $(NL)_i$, through 56 days (Fig. 2), indicating that these elements are continuously released from the glass. However, B, Ca, Mg, Sr, and U show very little release through 28 days, followed by a significant increase in concentration after 56 days. This behavior correlates well with the trend observed for pH and, in part, may result from increased solubility for these elements as the solution becomes more acidic. This is expected for Ca, Mg, Sr, and U, but is surprising for B. The cations Al and Si have U-shaped profiles, decreasing in concentration through 28 days and having the highest concentrations at 56 days.

It is likely that the release of Na and Li is relatively unaffected by constraints imposed by pH or secondary mineral formation and provides an indication of the degree of glass reaction (hydration). This observation will be correlated with SIMS results presented later.

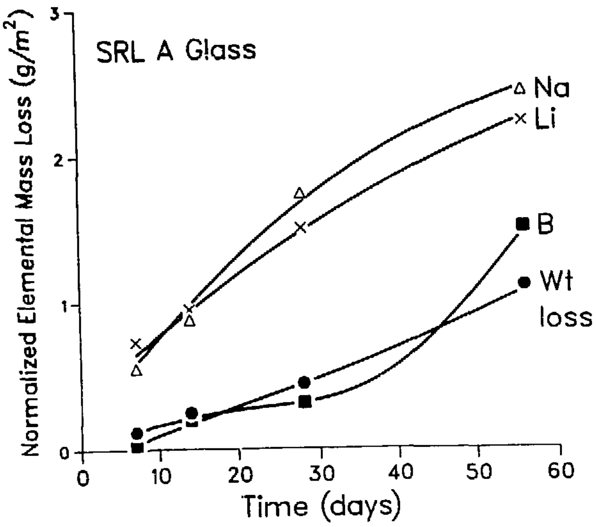


Fig. 2.

Average Cation Trends Observed for SRL Glass

When tuff is present in the system, the amount of an element in solution may not be representative solely of glass reaction. One effect that tuff could have would be to sorb elements from solution, thus lowering their concentrations. However, no elements show lower concentrations when tuff is present. Most elements show the same release both with and without tuff. The exceptions are Al and Ca, which have greater concentrations when tuff is present. For Al, an increase exists for all time periods, whereas for Ca an increase is particularly evident in the 56-day tests.

The release results for B, Li, and U indicate that SRL A glass reacts to a slightly greater degree than SRL U glass. There is good analytical sensitivity and precision for B, Li, and U, which show low interference due to tuff or EJ-13 water; however, because the difference in release is only ∿15% after 56 days, it may not be significant.

3. Anions

The concentrations of F^-, Cl^-, and SO_4^{2-} stay constant throughout the test period. The amount of fixed nitrogen in solution after 56 days is, in all cases, less than was observed in the blanks. This occurs in all test series and the difference increases with time. Because it is unlikely that insoluble nitrate phases are forming, this difference suggests less nitrogen is being fixed. In both the crushed-glass and disk experiments, R is ∿30% smaller than in the blanks. Under these conditions, 30% less fixed nitrogen would be formed, thereby accounting for about 2.5 ppm of the difference after 56 days. This accounts for some, but not all, of the discrepancy. The remainder is unexplained.

It is also interesting that in the disk experiments, the NO_3^-:NO_2^- ratio ranges from two to three, increasing with time, whereas in the tuff and crushed-glass experiments, this ratio remains at one for the duration of the tests. The NO_3:NO_2 ratio is governed by interaction of radiolysis products with the test components; H_2O_2, which forms during radiation, is catalytically decomposed by reactions with the tuff and crushed glass. Although H_2O_2

does not interact directly to oxidized NO_2^-, it does affect the e^-_{aq} and OH^- equilibria, which in turn can affect the nitrate-nitrite balance [VANKONYNENBURG].

4. Actinides

The interpretation of the actinide results is complicated by the inhomogeneity of the glass. The glass samples were chosen as described in Appendix C. The Am concentrations in the samples used in the disk-only and crushed-glass experiments were equal and reasonably constant. The Am concentrations in the disk + tuff experiments, while constant for experiments of the same time period, varied by up to a factor of four between time periods. For all but the 14-day tests, the Am concentrations were higher in the disk + tuff tests than in either the disk or crushed-glass tests.

The Np in the disk-only and disk + tuff tests fluctuated considerably, but because Np was generally not detected in the solutions, Np inhomogeneity did not matter. The amount of Pu in each sample was not determined. The Pu concentration in the glass is based on the analysis of crushed samples. Nevertheless, the trends observed for actinide release are quite regular and do not seem to be radically affected by the initial actinide composition of the SRL glass.

Three different actinide analyses were done: filtered, nonfiltered, and acid soak. All solutions were sampled immediately upon opening the reaction vessel. These were unfiltered. Aliquots from one-half of the 7-day samples were filtered through a 1000-Å filter, whereas one-half of the 28- and 56-day samples were filtered through a ∿50-Å filter. Finally, an aliquot from each sample was taken after the acid rinse step and should represent the total amount of each radionuclide released from the glass, other than what was adsorbed onto the tuff. These results are tabulated in Table 5.

The data analysis below includes a discussion of trends observed in actinide release, trends observed in actinide concentrations in solution, differences between actinide release in the three test types, the effect of filtering, and the amount of actinide plate-out.

The trends for total Am and Pu release are shown in Fig. 3. In general, the total release of each actinide increases with time, with the largest relative increase occurring between the 14- and 28-day time intervals. An exception is the 14-day results for the disk-only test, where the Pu and Am release is the same as in the 7-day experiment. It is tempting to relate this observation to a ∿35% decrease in the amount of actinide (Am) in the 14-day samples, but in the glass-tuff test series, the Am concentration in the glass fluctuates by 400%, yet the total Am released increases steadily. It does not seem possible to draw a positive relationship between the amount of an actinide in solution, or released from the glass, and the amount initially present in the glass. This is further indicated by the results of the crushed-glass series, where the total surface area of glass available for reaction is three times that in the disk experiments, yet the total amount of Pu and Am released is similar to that for the disk experiments. Within the limits of the current tests, the amount of Pu and Am in solution is governed more by the properties of the solution than by the reaction (hydration) of the glass.

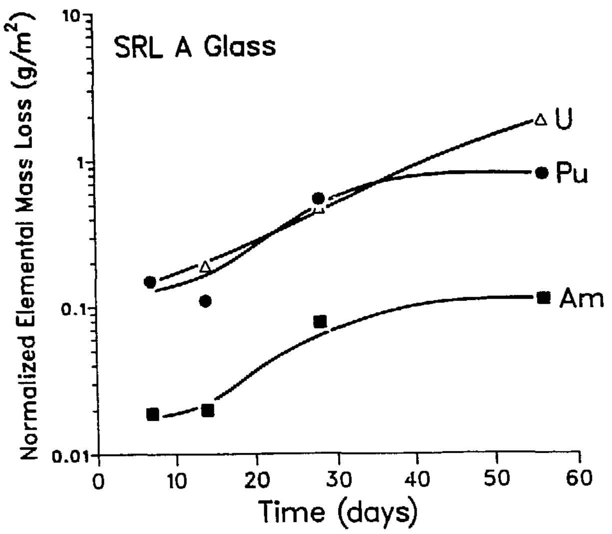


Fig. 3.

Total Am, Pu, and U Release from SRL A Glass, Disk-Only Test

The total amount of each actinide released can be used to calculate a normalized elemental release. This must be done under the compositional constraints described previously and in Appendix B. Based upon the Am and Pu concentrations measured for the crushed glass, $(NL)_i$ values are given for the 56-day experiments in Table 8. These values are compared with results from other tests of similar glass in Section IV.

Table 8. Normalized Elemental Release of Actinides after 56 Days

Test Type	Normalized Release (g/m^2) Am	Pu	U
Disk Only	0.11	0.82	1.8
Disk + Tuff	0.24	0.67	1.7
Crushed Glass	0.08	0.36	0.6

Actinide concentrations in solution can be determined based on the amount of each actinide in solutions that were passed through the 50-Å filter. This method assumes that no actinide was absorbed onto the filter, because the residual activity on the filter was not determined. After 28 days, the concentration of Pu is $\sim 2 \times 10^{-9}$ mol/L and is the same for each test series (glass disks, glass disks + tuff, crushed glass). After 56 days, the value has doubled to $\sim 4 \times 10^{-9}$ mol/L and is the same in the disk-only and disk + tuff experiments, but is substantially larger ($\sim 8 \times 10^{-9}$ mol/L) in the crushed-glass experiment. This latter observation may be due to the relatively acidic pH measured for this crushed-glass experiment.

Although Pu solubility limits in EJ-13 type waters, as a function of pH, have not been reported, Pu solubility measurements have been made at a pH of 7 [AINES] in J-13 water. Solubility measurements of Pu have also been made in other solutions [KIM] under controlled conditions. These measurements indicate (1) that the Pu solubility limit may change quite rapidly in near-neutral solutions, up to 100 times as the pH varies from 7 to 6; (2) that the Pu solubility depends on the Pu species in solution; and (3) that the concentration of Pu polymers, $(PuO_2)_2(OH)_2^{2+}$, in deionized water (DIW) with a pH of 7 is $\sim$1 x 10^{-7} mol/L.

In the present experiments, it is possible that the Pu in solution is governed by solubility constraints. In the experiments done with glass disks, the amount of Pu in solution increases as the pH becomes slightly more acidic. With crushed glass, the amount of Pu in solution also increases as the pH becomes more acidic. However, in the 28-day tests, the amount of Pu in solution and the total amount of Pu released are the same for both the glass disks and the crushed glass. This occurs despite the fact that the crushed glass has three times the available surface area for reaction. In the 56-day test, the amount of Pu in solution is larger for the crushed glass than for the disk, but the pH of the crushed-glass experiment is significantly more acidic. The duplicate crushed-glass experiment, for which the Pu in solution was not determined, has a pH nearly the same as that of the disk experiments and has a total Pu release similar to that of the disk experiments. Thus, the Pu solubility data are consistent and may indicate that Pu solubility limits are being approached.

The issue is complicated, as discussed later, in that the largest extent of the water/glass interaction appears to occur in fractures that penetrate into the glass surface. In these fractures, the pH would be more basic and the Pu solubility would be much lower. The amount of Pu in solution may be influenced by the rate of exchange between these fractures and the main solution.

The colloidal fraction of Pu in solution can be obtained from the difference between Pu levels as measured in the filtered and nonfiltered solutions. In the 7-day tests, for which 1000-Å filters were used, there is little indication in any test series that a measurable colloidal fraction exists. The 28- and 56-day fractions were filtered through 50-Å filters. The 28-day test values may show a slight decrease in the measured Pu level for the filtered solutions, but the decrease is comparable to the precision level of the measurements. The 56-day test values show no indication of colloids being filtered from solution. Very little, if any, Pu exists in colloidal form in these tests.

In each series of experiments, a certain amount of Pu has plated out of solution onto the metal test components. This Pu is dissolved from the metal during the acid dissolution and, for tests where no tuff is present, the amount plated out is always about three times that in solution.

When tuff was present, its effect was to influence the pH and to provide a surface for interaction and ion exchange. The total amount of Pu recovered in the disk-tuff experiments was less than in the disk-only experiments, but the recovery ratio (disk-tuff:disk-only) began at $\sim$0.2 at 7 days and gradually increased to ∿0.8 after 56 days. This narrowing of the difference between total Pu recoveries could reflect a limited sorptive capacity of tuff for Pu. Initially, the tuff may be able to sorb Pu, so the ratio is small. Once the capacity is exceeded, no more Pu can be sorbed and the ratio increases. Alternatively, the amount of Pu released may be subject to subtle pH trends that cannot be observed due to the error in the pH measurements. Because the tuff was not analyzed for radioactivity, the actual amount of sorption has not been measured.

The behavior of Am in these tests is significantly different from that of Pu. Essentially no Am was detected in either the initial nonfiltered or filtered samples. Most of the Am was in the acid rinse solutions and had plated out on the metal test components. The lowest Am concentration measurable, based on Am detection limits, is ∿2 x 10^{-10} mol/L.

The effect of tuff with regard to Am release seems to be minimal. In fact, the Am release in the tuff-containing experiments is greater than in the disk-only experiments and is about the same as in the crushed-glass experiments. It may be that the increased amount of Am in the glass used in the tuff experiments is influencing the total amount of Am detected, but the 14-day disk-tuff experiment contained less Am than its disk-only counterpart, yet the total release was still greater. More likely, the amount of Am released from the glass is a function of an interplay between the degree of glass reaction, the affinity of metal for Am, and the solubility of Am in solution.

Neptunium was detected in the nonfiltered solution in only a few isolated tests. These were the long-term tests in which the Np concentrations in the glass were greatest. Based on past experiments [BATES-1983], it would be expected that the Np solubility limit would not be reached in the present experiments and the glass/water reaction would control the amount of Np released from the glass. The fact that very little Np was detected in the present experiments indicates that the degree of glass reaction was far less than in previous experiments done on SRL 131 glass [BATES-1983]. This is indeed the case, as evidenced by the lower values for weight loss and matrix element release. To obtain a more complete data set for Np, a greater amount of Np needs to be contained in the glass. However, the limited data were used to calculate a solution concentration of 4 x 10^{-8} mol/L after 56 days.

The interpretation of the actinide data is influenced by the difficulties encountered in making the glass, e.g., the inhomogeneity for Pu, Am, and Np, and the low concentration of Np. Thus, final conclusions concerning actinide behavior should be based on interpretation of the PNL glass data and on additional testing of SRL A glass. However, it appears the Pu release is governed by solution chemistry, as opposed to the degree of glass reaction or the sorptive properties of tuff or metal. Release of Am appears to be a function of solution chemistry and the sorptive properties of metal, whereas U and Np releases are a function of glass reaction.

D. Component Analyses

A complete description of the reaction process requires that the mass balance between what has been released into solution and what remains of the reacted components (glass, metal, tuff) be studied. In the present experiments, the major emphasis has been placed on the reaction of the glass.

Weight loss measurements have been done on all glass samples, and representative glass samples have been examined with SEM/EDS and SIMS. The Type 304 L SS stands have been measured for weight loss. No examination of the tuff has been performed.

Glass disks from each test period have been examined. Included for analysis were samples from the disk-only and disk + tuff experiments. However, inasmuch as the degree of reaction for each set of experiments was essentially identical, the following results focus on the disk-only experiments, which are not complicated by tuff particles adhering to the glass surface. Two disks from an individual test were chosen for examination. One disk was sectioned in half and used for SEM/EDS analysis (surface and cross section); the other was used for SIMS analysis.

1. Weight Loss

The simplest, yet perhaps most revealing, measure of the extent of glass reaction is provided by the weight change of the sample. It gives a gross measure of the reaction by combining forward (dissolution) and backward (precipitation) reactions. The weight loss measurements for SRL U and SRL A glass are given in Table 2 and shown for SRL A glass in Fig. 2. The precision of these measurements is ∿±3 x 10^{-5} g; thus, for the first three test periods there is considerable error in the values. However, both glass types show similar trends in that little weight loss is observed through 14 days, with a significant increase in weight loss after both 28 and 56 days.

2. SEM/EDS Analyses

The glass disks were sectioned so that the reaction surface and the cross-sectional profile of the same sample could be examined. The section used for the surface examination was mounted on an aluminum stub and carbon coated prior to examination. The sample used in the cross-sectional analysis was mounted in an epoxy resin, and the cross-sectioned sample was polished to enhance the reacted areas. Samples 5 (7 day), 1 (14 day), 9 (28 day), and 15 (56 day) were used in these analyses.

The surfaces of samples 5, 1, 9, and 15, as well as an unreacted sample, are shown in Fig. 4. The unreacted surface has an abraded appearance where the cut edges are sharp and where stress marks are evident; it is similar to the surface of sample 5. The surface finish between the edges and stress marks has a glazed appearance. The surface of reacted SRL U glass retains much of this appearance through 28 days. The 28-day sample shows some evidence of losing the glazed appearance. After 56 days the surface appearance has changed completely. The cell-like structure, typical of reacted SRL glass, is evident and covers the entire surface. Some areas where the cell structure appears concentrated are evident (the whiter areas in Fig. 4e).

The cross sections of the corresponding glass samples show no evidence of surface reaction. Only in sample 15, and possibly sample 9, is there any evidence of reaction. The cross section of sample 15 is shown in Fig. 5. Here, the typical appearance of a reacted glass cross-sectioned layer is observed in a fracture that has penetrated into the glass, but no such

(a) Unreacted surface of SRL U glass (200, 2000X)

(b) Reacted surface of sample 5, 7 days (1000X)

Fig. 4. Micrographs of the Surfaces of SRL U Glass

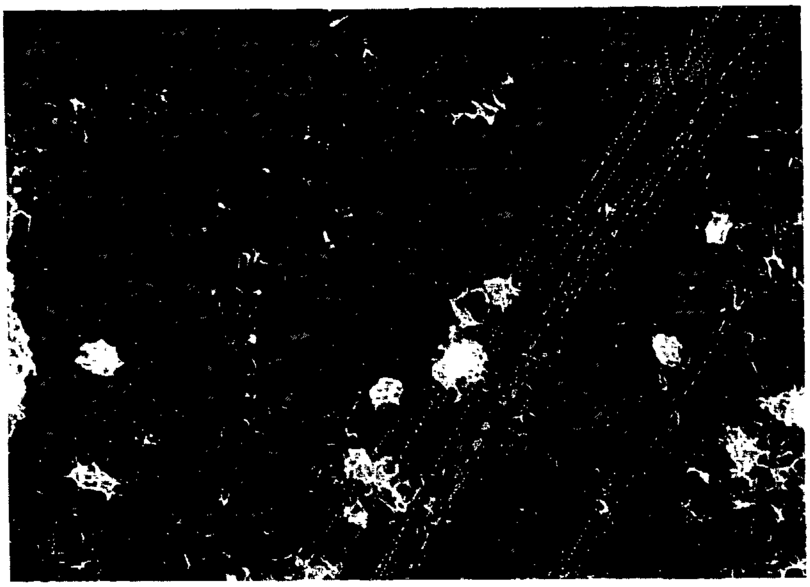
(contd)

(c) Reacted surface of sample 1, 14 days (1000X)

(d) Reacted surface of sample 9, 28 days (500, 5000X)

Fig. 4 (contd). Micrographs of the Surfaces of SRL U Glass

(contd)



(e) Reacted surface of sample 15, 56 days (5000X)

Fig. 4 (contd). Micrographs of the Surfaces of SRL U Glass

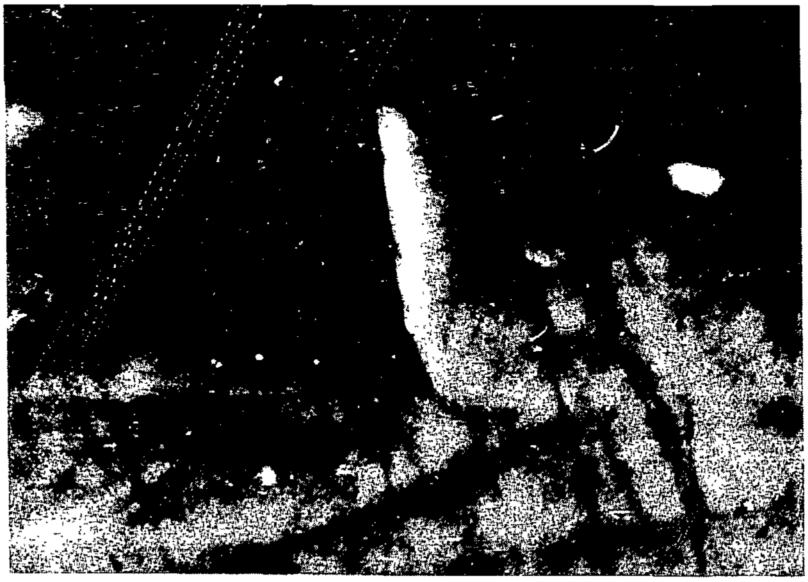


Fig. 5. Micrograph of the Polished Cross Section of Sample 15 (1000X)

layer is observed on the surface. The cell-like surface structure is evident in some areas of the cross section, but its appearance could not be correlated with a reacted layer that penetrates into the glass surface.

An EDS spectrum of each reacted glass surface was taken. Spectra are shown in Fig. 6. The spectra of an unreacted sample and samples 1, 5, and 9 are similar (Fig. 6a), showing no depletion in Na or enrichment of Fe or Mn on the glass surface. The spectrum of sample 15, taken in a region typical of the reacted surface, is shown in Fig. 6b. Some evidence of reaction is evident here, with Na being depleted and Fe enriched. The degree of depletion or enrichment varies for different areas on the surface. A spectrum of the white spots, Fig. 6c, shows less depletion of Na, combined with evidence of Cl and K. These elements are present at low levels in both the glass and the groundwater and have been concentrated in these regions of the reacted surface.

An EDS spectrum of the reacted fracture shown in Fig. 5 was also taken. This spectrum showed a depletion of Na and increase in Fe in the fracture compared with the unreacted glass.

All the EDS spectra shown need to be interpreted based on the spatial resolution limits of the EDS technique. X-rays generated by the impact of the electron beam come from a teardrop-shaped region that is smallest at the surface and becomes larger below the surface. The size of the teardrop depends mainly on the energy of the electron beam, with a lower energy beam resulting in better resolution. Generally, the size of the teardrop region from which the X-rays are generated varied between 0.5 and 1 µm for normal operating conditions. Thus, when the surface layer thickness or fracture diameter is less than 1 µm, the EDS spectrum is representative of both the reacted region and, to some degree, underlying nonreacted glass.

3. SIMS Analyses

This technique allows the extent of surface reaction to be measured by analyzing ions that are sputtered from the glass surface as a function of time. The limitations and difficulties of this technique have been described [PANTANO]. In the present studies, SIMS is used as a method to supply information that may be complementary to the SEM/EDS and solution results. Basically, the present application of SIMS provides a profile of the relative concentration of a particular element as the surface is eroded by the ion beam. The profiles have been obtained by taking the ratios of measured intensities of elements of interest to the intensity of an elemental peak that remains constant throughout the sputtering process. In the present case, Si was used as the base element, although we recognize that Si has been part of the glass/water reaction. Silicon was chosen because its absolute intensity varies little during the sputtering process; however, additional experience is required to completely justify this choice.

Argon was used as the sputtering gas, beam energies of 4.0 to 1.0 keV were used, the beam was rastered over a 150-µm-square area, and the signal was gated to reduce artifacts from the sputtering process. The data are compromised by the surface roughness, but by collecting the signal from a

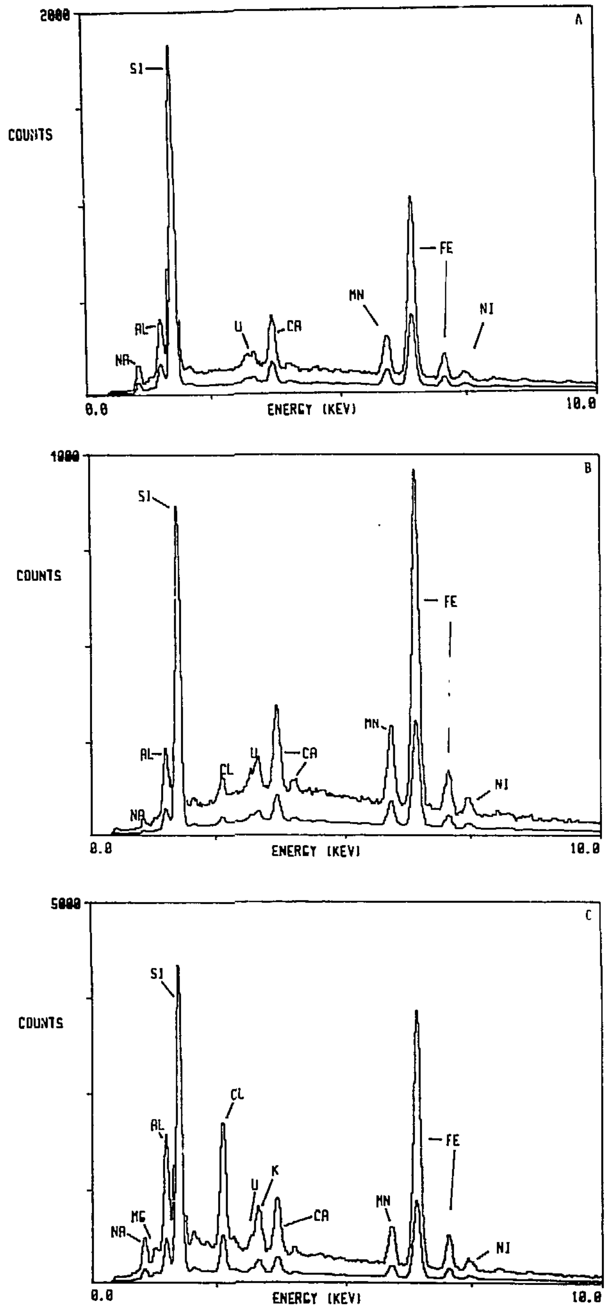


Fig. 6. EDS Spectra of SRL U Glass Surfaces.
(a) Surface of an unreacted sample, and samples 1, 5, and 9,
(b) Surface of sample 15,
(c) Spots on sample 15.

large surface area and assuming that, except for fractures, the extent of reaction is equal over the entire surface, the effect of surface roughness should be minimized.

Data were collected on samples 6 (7 day), 2 (14 day), 10 (28 day), and 14 (56 day). The 7-day sample showed very little evidence that reaction occurred. Only the intensity ratios of Li and Na had increased, and only by a factor of two, compared with increases of 10-100 observed in the longer-term tests.

The profiles of the 14-, 28-, and 56-day samples, shown in Fig. 7, indicate that the depth of the reacted layer increased with reaction time. In the present results, no attempt has been made to assess the sputtering rate through the reacted layer; so, no estimate of the thickness of the layer is given, based on the SIMS results.

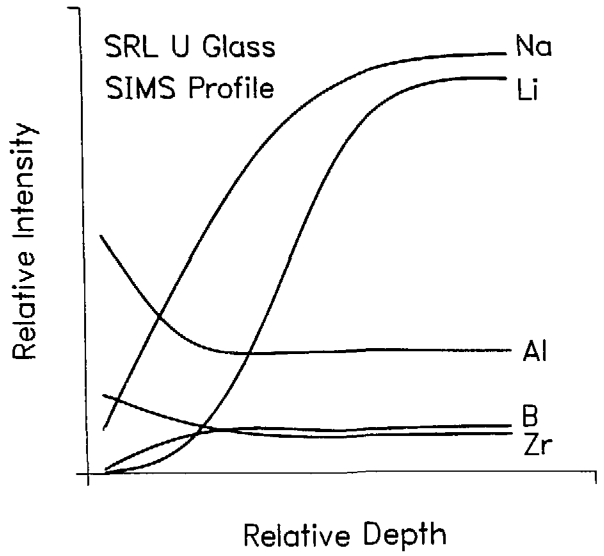


Fig. 7.

SIMS Profiles for Selected Elements in Reacted SRL U Glass

Basically, Li and Na showed depletion to the greatest degree and depth. For samples from the 14- and 28-day tests, the Na concentration began to increase almost immediately on sputtering, and there was a region where the Li was almost completely depleted from the layer. In the sample from the 56-day test, both Na and Li showed total depletion from the near-surface portion of the layer. In all samples the Na concentration increased sooner and more gradually than Li, but both elements attained a constant ratio at nearly the same depth.

Boron was depleted at the near surface; but, in all samples, it reached constant concentration significantly before Na and Li. Also depleted from the near-surface region were Sr, Cs, and Mg. However, Zr, Fe, and Al had higher ratios near the surface than in the bulk glass. The Fe ratio was largest in the first spectrum taken and dropped to the bulk level rapidly. The ratios for Zr and Al were also largest in the first spectrum, but dropped to the bulk level more gradually than Fe did.

The results of the SIMS analyses were reproducible when spectra were taken at different positions on the same sample, and were altered as expected when the beam energy was changed; trends were reproducible for samples of different reaction duration. When combined with the results from the SEM/EDS and solution analyses, a consistent description of the reaction process is obtained.

IV. DISCUSSION

In this section, to provide a concerted description of the reaction process, the results of solution and component analyses are compared. Based on this description, implications of the data are discussed in relationship to events that may occur in the repository. Additionally, the data are compared with the results of MCC-1 and saturated rock cup tests done with similar glasses.

A. Description of the Reaction Process

In the present experiments, the extent of the reaction of SRL 165 glass can be measured by weight loss, solution analysis, and SEM/EDS and SIMS analyses. After seven days of testing, there is little evidence of reaction. The weight loss values are near the precision of the method; the normalized releases for B and Li, elements that are generally used to judge the degree of borosilicate glass reaction, are small, and project a depletion depth between 0.04 μm for B and 0.18 μm for Li; the surface appears unreacted in the SEM; and only minimal depletion of Na and Li is observed with SIMS.

After 14 days there is still little evidence of reaction. The weight loss has increased slightly, but is still not much greater than the measurement error. The normalized elemental mass losses, $(NL)_i$, for Na and Li have increased, but the values for the other elements show little change. The surface appears unreacted with the SEM. The SIMS analysis shows definite profiles for Na and Li extending into the glass, but profiles of other elements (B, Al, Sr, and Zr) change only near the surface. The release of the radionuclides is also very low through 14 days.

After 28 days there is evidence of greater reaction. The weight loss has increased. The $(NL)_i$ values for Na and Li have continued to increase, though in a gradual fashion, while the $(NL)_i$ values for most other elements (B, Al, Ca, Mg, U) have not changed much. The value of $(NL)_i$ for Si, $(NL)_{Si}$, is obscured by the error in the Si measurement and cannot be determined. The SEM shows some evidence of surface reaction, whereas the SIMS profiles indicate a continual depletion of Na, Li, and perhaps Cs, but little depletion of other elements, including B. The actinide (Pu and Am) release has increased dramatically.

With all methods of analyses, the 56-day tests show obvious reaction. The weight loss has doubled from 28 days. The $(NL)_i$ values for Li and Na are still gradually increasing, and for most other elements the values have increased about five times. Actinide release has also increased.

The normalized weight loss, $(NL)_{wt}$, is about 50% of the $(NL)_i$ values for Li and Na, but is nearly 90% of the values for B, Al, Ca, Mg, and U. The $(NL)_{Si}$ is now measurable, and is greater than $(NL)_{wt}$ by 90%. If $(NL)_{wt}$ is equal to $(NL)_i$, then the waste form is dissolving by congruent dissolution. If $(NL)_{wt}$ is smaller than $(NL)_i$, then either diffusion is a dominant factor affecting release or there is reprecipitation on the glass. If $(NL)_{wt}$ is greater than $(NL)_i$, element i preferentially remains in the glass.

The extent of the surface reaction is easily observed with the SEM; however, aside from the fractures, there is no evidence of a reaction layer penetrating into the glass. The thickness of such a layer can be calculated from the amount of an element detected in solution using the relationship

$$(ND)_i = \frac{(NL)_i}{\rho_s}$$

where $(ND)_i$ is the normalized depletion depth in μm and represents the thickness of glass from which element i would have to be completely removed to give the measured concentration of i in solution, and ρ_s is the density of the specimen. The thickness of a reaction layer would be predicted by $(ND)_i$ if there were no dissolution of the glass or precipitation back on the surface of the glass, and if i were completely removed from the layer. These conditions are often met in the leaching of Defense Waste Processing Facility (DWPF) glass [MENDEL] and, so, $(ND)_i$ can accurately be used to predict the thickness of the reaction layer.

In the 56-day tests, such a layer, based on B release, would be ~0.5 μm thick; based on Li or Na release, it would be ~0.8 μm thick. The appearance of such a layer is often marked by an obvious demarcation line between the layer and the unreacted glass. This sharp demarcation is likely caused by an abrupt density change between the layer and the glass and allows the layer to be differentiated from the glass when using the SEM or an optical microscope. In the present experiment, however, SIMS measurements indicate that complete depletion of Na and Li occurs only in a narrow region near the surface, and a gradual increase in Na and Li concentration is then observed until the bulk glass levels are reached. Boron is also greatly depleted in the narrow region near the surface, but then shows a sharp increase in concentration to the bulk glass level.

These data suggest that no advanced reaction layer of the type that is normally observed in DWPF glasses [MENDEL] has formed, other than in the fractured region of the glass; thus, such a layer cannot be observed with the SEM. Further evidence for this conclusion is provided by the relationship between $(NL)_{Na,Li}$ and time. A plot of $(NL)_{Li}$ as a function of $t^{1/2}$ is shown in Fig. 8. A linear relationship is observed through 56 days. A similar relationship is observed for Na, although, due to scatter in the data, the relationship may be interpreted differently. A linear $t^{1/2}$ functionality may be an indication that a diffusion-controlled process is occurring.

The combined solution and surface analysis data result in a fairly consistent description of the reaction process. Initially, Li and Na are removed from the glass by a process that likely involves interdiffusion with

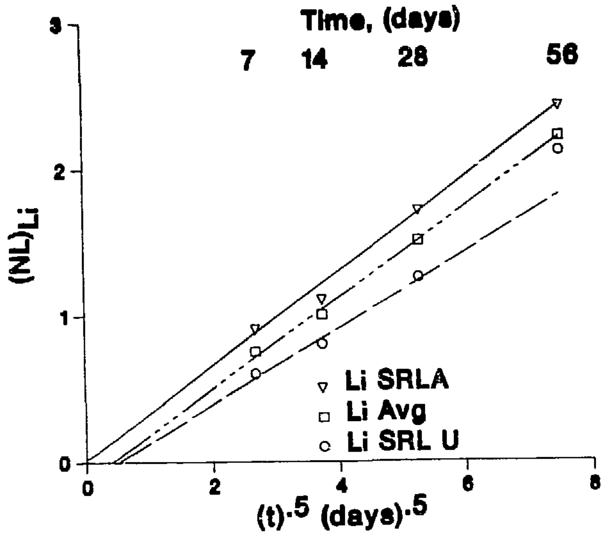


Fig. 8.

$(NL)_{Li}$ as a Function of $Time^{1/2}$

a water species. The glass matrix, however, remains resistant to dissolution until sometime between 28 and 56 days, as evidenced by the low weight loss measurements and by low $(NL)_i$ values for the glass matrix elements, Si and B. By 56 days, breakdown of the glass matrix begins, and a sharp increase in the solution concentration of most elements is observed. The penetration of matrix breakdown into the glass is observed with SIMS, as evidenced by the total depletion of Na, Li, and B, but is not extensive enough to be observed with the SEM.

The breakdown of the glass likely affects the release of the radionuclides U and Np into solution, but the release of Pu and Am seems to be controlled more by the solution pH and the interaction of the radionuclide with the test components. Neptunium and uranium, which have considerable solubilities in the water, are released into solution as the matrix becomes totally hydrated. Plutonium release is limited by solution control and is related to changes in pH more than to breakdown of the matrix. Americium, which has the lowest solubility in the water of the four radionuclides, seems to be affected by both solution pH and interaction with the metal components.

B. Comparison with Other Data

Several other tests have been conducted by SRL and NNWSI, using SRL 165 glass and saturated conditions [BAZAN, BIBLER-1984, SRL]. These tests have used both simulated and actual DWPF waste and have included J-13 water, a tuff cup or crushed tuff, and Type 304 L SS. Some comparison with the present results is possible; however, the comparisons are difficult to make and are not direct for several reasons: slightly different glass compositions were tested, different processing conditions were used to make the glass, the actual testing parameters varied, or the data are incomplete.

The results of all the experiments were influenced by the presence of tuff and repository-type water. Aside from affecting the role of the reaction medium as the primary influence on the degree of reaction, these components contribute Na and Si to the solution in amounts far in excess of that added by the reacting glass. Therefore, $(NL)_i$ values for these elements contain large errors and generally cannot be used to measure the overall degree of glass reaction. Weight loss measurements precise enough to detect trends in the glass reaction and surface analyses are reported only in the present experiments. Thus, a comparison of the overall glass reaction between the different experiments cannot be done.

However, a comparison of B and/or Li release is possible. Bazan and Rego [BAZAN] observed B and Li releases of about 50% of the amount observed in gamma irradiation testing, although the trends over time are similar. They observed that Li has a much greater $(NL)_i$ than B, as is observed in the gamma irradiation testing. Also, $(NL)_{Li}$ as a function of $t^{1/2}$ results in a linear relationship, although there is considerable scatter in the plot.

Comparison with Bibler et al. [BIBLER-1984] is more difficult because their specimens were polished to 600 grit, which may affect the rate of reaction, and because the tuff apparently influenced the reaction to a greater degree than in the other tests.* However, the glass reaction rate, as measured by $(NL)_{Li}$, was nearly the same as in the gamma radiation field. However, B release was also similar to that of Li, in contrast to what was observed in the gamma irradiation tests. The Pu release seemed to be controlled by solubility constraints, and although there was considerable scatter in the disk-only experiment reported by Bibler et al. [BIBLER-1984], the $(NL)_{Pu}$ value is $\sim$10 times less than that observed in the gamma irradiation tests. A lower Pu level would be expected because of the higher pH, as reported by Bibler et al. However, in the disk + tuff experiment, the Pu level and the pH were reduced considerably. Although the Pu solubility should have been increased as a result of the more acidic pH, the amount of Pu in solution actually decreased, presumably because of interaction with the tuff. In the gamma irradiation experiments, interaction with tuff was observed after seven days, but the effect of the tuff decreased with time. The Bibler experiments contained considerably more tuff than did the present experiments ($\sim$100x), and this may explain the difference in the Pu concentration in solution.

The Savannah River Laboratory collected data based on the testing of a glass identical to SRL U glass [SRL]. Unfortunately, the reported data are not complete, and the experimenters used a 600-grit polished surface and an SA/V of 0.1 cm^{-1}. However, projections of (SA/V x t) should be valid in those experiments, and the other factors probably have only a slight influence on the reaction; thus, a more direct comparison is possible. A release in J-13 water of 11.2 g/m^2 of B after an equivalent time of 30.3 days is reported. This value compares with a B release of 0.3 g/m^2 (28 days) or 1.3 g/m^2 (56 days) in the present experiment. It appears as though the extent of the reaction has been reduced in the gamma radiation field. Additional evidence is provided by SRL to support this observation in experiments done with the solution buffered at pH 7 [SRL]. In these experiments, the $(NL)_B$ was 1.12 g/m^2 after 28 days, a decrease of about 12 times compared with the unbuffered solution.

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*The Bibler results are being revised, and further comparisons may be possible when the final version of the work is published.

A comparison with the complete SRL data set would be valuable, because a decreased reaction rate in the presence of gamma radiation would be a significant observation. Such a suggestion has been made [YOKAYAMA], based on a series of experiments to study the effect of gamma irradiation on the glass/water reaction. Although the glass type used by Yokayama et al., ABS-118, is different from SRL 165, it is still a borosilicate glass. The test conditions, in selected tests, were quite similar to those the present tests, and a comparison of behavior in and out of the gamma field is possible. Yokayama et al. used an R of 3.41 at 90°C and, after 14 days, found that the pH in the gamma tests was ~6.5, compared with 8.7 in the nonirradiated tests, and that the $(NL)_i$ for all elements was about four times larger in the nonirradiated tests. However, when a similar experiment was done at room temperature, the pH of the gamma irradiated test dropped to 3.2 after 28 days, but was 6.5 in the nonirradiated tests. The degree of glass reaction was four times greater under irradiation. Because it has been generally observed that the degree of glass/water reaction as a function of pH shows a minimum near pH 7, interactions that keep the pH buffered near 7 should minimize the degree of reaction.

This argument should also apply to the present experiments, but the necessary comparisons cannot be made. The degree of lithium reaction may be the same or slightly less in the nonirradiated experiment (SRL reported no Li results). If Li release is a diffusion-controlled process in each set of experiments, this would make sense, because the diffusion rate should not be measurably affected by moderate pH changes. A distinction between the total degree of glass reaction under irradiation and nonirradiation conditions cannot be made because of a lack of data. However, no large increase in the extent of reaction as a result of gamma irradiation is observed.

V. ADDITIONAL ITEMS

A. SA/V Correlations

The ratio of the surface area of the glass to the volume of liquid (SA/V) is a factor that can be used to project (accelerate) the rate at which glass constituents accumulate in solution; i.e., the greater the surface area of glass available to react with a constant volume of water, the faster glass constituents will accumulate in solution. It has often been observed that, if (SA/V x t) is equivalent between tests, then the $(NL)_i$ values will be equivalent. Therefore, this factor may offer a method to project the results of leach tests done at a low SA/V to longer periods by using a higher SA/V. The present experiments were conducted at an SA/V of 0.3 and 0.9 cm^{-1}. If the normal projection were valid, the 56-day test done at 0.9 cm^{-1} would be equivalent to 168 days of testing at 0.3 cm^{-1}, or 16 days of testing at 0.9 cm^{-1} would be equivalent to 56 days of testing at 0.3 cm^{-1}.

However, this is not what is observed. Although the solution concentration of most elements in the crushed-glass experiments is measurably greater than in the disk experiments, the $(NL)_i$ values for the crushed glass experiments are less than those in the disk experiments for the same time period. Additionally, the pH of the crushed-glass experiments is nearly identical to that of the disk experiments. These results suggest that the (SA/V x t) projection is not valid under the current conditions. This is explained because, in order for the (SA/V x t) projection to be valid, the solution chemistry must be controlled by the glass reaction. In the present experiments, the solution chemistry is an interplay between groundwater components, radiolysis components, and glass reaction components, and the projection does not work.

B. Gas-to-Liquid Ratio (R)

Previously, experimenters studying the effects of gamma irradiation on solution/glass interactions paid little attention to the ratio of the volume of air present in closed experiments to the volume of liquid. Exceptions are Burns et al. [BURNS-1982A], who treated the radiolysis processes theoretically and applied their equations to other work, and Yokayama et al. [YOKAYAMA], who recognized the factor but, aside from some experiments done in saturated vapor, did not vary R.

The effect of altering R is to vary directly the concentration of nitric acid in solution. This was studied briefly in two additional experiments, G-113 and G-114. These were done in Type 304 L SS vessels, as used in the other experiments in the set, and included a SS waste-form holder plus the minimum amount of deionized water (DIW) to cover completely the metal holders. Instead of using an R of ~0.35, as was done in the other experiments, values up to 3.57 were used. Thus, the amount of nitric acid produced in these two extra experiments should be about ten times that produced in the regular experiments, and the concentration of nitrate in solution should be ~40 times greater. The results of these experiments are given in Table 9.

At the end of the experiments, the liquid contained a flocculant rust-colored precipitate, and the vessels and SS waste-form holders were visibly corroded. Both solutions were quite acidic and, aside from containing large amounts of SS components (Cr, Cu, Fe, Mn, and Ni), contained silicon and chloride. Silicon could come from either the SS or the gasket; the source of the chloride has not been identified. It is unlikely to have come from the gasket. An SEM/EDS analysis of a clean gasket indicated no chlorine present, and tests done where a clean gasket was soaked in DIW at 150°C for seven days also produced no evidence of chloride.

Table 9. Results of Gamma Irradiation Experiments Done with R > 3[a]

Test No.	pH	Concentration (ppm, µg/mL)										
		Ca	Cr	Cu	Fe	Mn	Ni	Si	F^-	Cl^-	SO_4^{2-}	NO_2^-	NO_3^-
G-113	1.82	0.4	5.0	0.7	31	3.4	15	36	<0.1	589	<1.0	<1.0	27.2
G-114	2.58	0.3	2.0	1.0	17	4.2	16	45	<0.1	103	<1.0	<1.0	25.6

[a] Duration was 28 days at 90°C, using DIW. Test G-113 had 4.60 mL of DIW and R = 3.57; test G-114 had 5.16 mL of DIW and R = 3.07.

The concentration of NO_3^- in solution was ∿26 ppm, whereas no NO_2^- was detected. This is because NO_2^- is not stable in the acidic conditions that existed in these tests. The additional amounts of NO_3^- formed using the large R conditions are less than were projected by Burns et al. [BURNS-1982A], but the acidity of the solution and the extent of the metal reaction were much greater than were noted in the tests with a smaller R. It is not certain that all the observations made in these two tests can be related to the change in R, but the potential of R to influence significantly the extent of reaction in tests done under gamma irradiation is clear, and further testing is necessary to define its role.

VI. CONCLUSIONS

The reaction of SRL 165 glass with water while subjected to a gamma irradiation dose rate of 2×10^5 rad/h has been studied. The results of the reaction were studied using surface and solution analyses, and a consistent description of observed reaction has been obtained.

The extent of glass reaction results from a complicated interplay between the breakdown of the glass matrix, changes in the pH of the solution, and interactions that occur with metal and rock components of the test. The current tests were not run long enough to allow long-term reaction trends to be established or to result in deduction of a mechanism for the glass/water interaction; however, no large increase in the extent of glass reaction was observed during the irradiation. Several ramifications of the data are relevant to repository conditions:

(1) The parameters that control the reaction of glass with water are dependent on the dynamically occurring processes of glass dissolution and nitric acid generation. Anything that artifically upsets this balance will unnaturally affect the degree of reaction. Thus, if a gamma field larger than expected in the repository is used to "accelerate" the reaction in a laboratory experiment, the actual effect may be to alter the mechanisms by which the glass reacts. Nitric acid generation would be accelerated by the larger dose rate, and this may overcome the "buffering" action of the glass and cause dissolution of selected glass constituents that might not occur at lower dose rates. Alternatively, gamma irradiation tests done using deionized water as the starting solution begin with an initial pH of ∿5.8 and quickly become more acidic. This may introduce pH conditions that would not be attained using actual repository dose rates and repository waters, thereby artificially influencing glass leaching. In the present experiments, a dose rate of 2×10^5 rad/h was used. This is the rate expected for freshly generated commercial waste, but is ∿5 to 10 times larger than expected for SRL glass. The actual dose rate at the point of glass/water/air reaction would depend on when the waste package was prematurely breached, and the extent of the glass/water/air interaction would depend on that dose rate. The present experiments indicate that a generic prediction of the effect of gamma radiation on repository behavior would be difficult to formulate. Perhaps, under expected NNWSI

conditions, the effect of gamma irradiation would be to moderate the reaction between glass and water by exerting an influence toward keeping the solution at a neutral pH, thereby retarding the rate of reaction.

(2) The use of (SA/V x t) as a method of projecting the behavior of the glass/water/tuff system to longer time periods could not be validated. This is quite likely because the solutions were affected by the competing effects of acid generation and glass dissolution to an extent that resulted in different reaction rates. Thus; the difficulty in interpreting accelerated reactions in a radiation field is reinforced.

(3) The duration of the present experiments was not long enough to establish the reaction trends that will control the glass reaction over longer time periods. Bazan and Rego [BAZAN] noted a leveling of the reaction rate between 56 and 181 days of testing. Whether the present experiments will also display a slowing of the reaction process, possibly as a result of some type of protective-layer formation, or will show an increase in the reaction rate caused by the acid dissolution of the layer cannot be projected.

An additional description of the effect of gamma irradiation on glass/water reaction will be presented in a subsequent report, which will describe the reactions observed for PNL 76-68 glass under similar irradiation conditions. Some of the observations made in those tests will be used to further support and explain the conclusions made in this report.

Additional studies examining the effect of gamma irradiation on the behavior of the waste form in potential repository conditions are in progress. These tests are being done mainly to examine the effect of dose rate on the glass/water/tuff system, but tests are also included to investigate the effect of varying R to more closely represent conditions that may exist in the repository.

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APPENDIX A

PREPARATION OF TUFF AND PREREACTED J-13 WATER

(D. Fischer)

The test procedure requires the use of caliche-free tuff and J-13 water that has been equilibrated at 90°C with tuff rock. These were prepared using samples of Topopah Spring tuff supplied by NNWSI (UE-25 h #1, 173.0-173.6) that had been obtained so as to avoid caliche-containing outcrop material.* The J-13 water had previously been supplied by NNWSI.

The procedure was as follows:

1. Solid preparation (10 g of tuff, <100 mesh, per liter of J-13 water)
    a. Place chunks of rock into plastic bag and hit with 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. Put the dried pieces of rock into a Tekmark analytical mill. Turn on the mill for numerous bursts of a few seconds. (Do not grind excessively, to prevent contamination from the grinder.)
    d. Sieve an adequate amount of material through a 100-mesh sieve. (If necessary, a mortar and pestle can be used to regrind the fraction of rock material to >100 mesh.)
2. Equilibration
    a. Weigh out 10 g of <100-mesh crushed rock into a clean 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 to near the top with J-13 water (allow some space for expansion), cap tightly, shake for one minute, and place into a 90°C oven.

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*Subsequent use of this tuff by ANL and LLNL suggests that the levels of Si obtained during equilibration are ∿5 ppm lower than normally obtained in tuff equilibration experiments.

e. Twice daily for five days, remove the bottle and shake for one minute. Leave the bottle stationary in the oven for an additional nine days.

3. Filtering

   a. After two weeks in the 90°C oven, remove the bottle and air cool it for one hour.

   b. Filter the water through high-quality filter paper.

   c. Refilter the water using a 0.1-µm 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. Remove the tuff from the Teflon vessel and rinse it with deionized water.

   b. Dry the tuff to constant weight at 90°C.

   c. Store the tuff in a marked container for use in the experiments that require crushed tuff.

APPENDIX B

GLASS PREPARATION AND TEST PROCEDURES

The procedures used to make the SRL glass and set up and perform the experiments are documented here. Certain people had assigned tasks during these experiments and were the only persons who performed those tasks. The procedures have been written by those people performing the tasks and include the detail each person feels is required to duplicate the procedures.

1. Glass Preparation
(T. Gerding and D. Bowers)

Glass for test samples was prepared using SRL 165 borosilicate frit that was doped with uranium, cesium, and strontium. The glass was prepared as an admixture of SRL 165 black frit to which 0.15 wt % SrO_2, 0.17 wt % Cs_2O, and 1.2 wt % U_3O_8 was added. The black frit was received from John Plodnic of SRL, and had the nominal composition given in Table 2 in the main text. The mixture was melted at 1150°C in a Pt dish, and held at temperature for four hours. The molten glass was poured into water to form a highly fractured product; it was further crushed and sieved to give a final product that was used for subsequent melting-casting procedures.

a. Casting of SRL 165 + U (SRL U)

Eighty grams of frit produced as described above was air melted in a Pt dish at 1150°C for 0.5 hour. The molten glass was poured into a rectangular Pt-5% Au mold with tapered sides and immediately transferred to an oven at 500°C and held at temperature for two hours. The power to the oven was then shut off, and the glass allowed to cool at the same rate the oven cooled. Glass at room temperature was easily separated from the mold.

b. Preparation and Casting of SRL 165 + U + Selected Actinides (SRL A)

The actindides, ^{237}Np, ^{239}Pu, and ^{241}Am, were added to the SRL 165 + U frit to provide samples for testing. The actinide mixture was prepared using ^{237}Np in HNO_3 solution (^{237}Np content >99.2% by alpha spectrometric analysis), ^{239}Pu in HCl solution (NBS 949e standard), and ^{241}Am in HNO_3 solution (Amersham). The nominal Pu and Am compositions of the glass were based on the amount of each actinide present in actual Savannah River Plant (SRP) waste; the amount of Np was increased over that in SRP waste to produce measurable amounts of Np in the test solutions. The actinide mix was dried and dissolved in 9N HCl and redried. This process was repeated three times to remove the NO_3^-. The SRL frit will foam if NO_3^- is present during melting. Water was added to the dried actinides, and this solution was added to 40 g of frit in three additions; i.e., 1/3 of the frit placed in a Pt-5% Au crucible and 1/3 of the actinide solution added, the procedure repeated until a layered mixture had been prepared. The sample was heated at low temperature (<100°C) to dry the frit. After drying, the frit was melted at 1050°C in a Brew furnace containing argon at a pressure of 400 mm of Hg. The sample remained molten for 30 minutes and then cooled to room temperature (∿2 h). The sample was removed from the crucible and placed in a Pt dish. The dish was placed in an oven set to 1050°C and the glass immediately fractured into ~100 smaller pieces. Then, 60 g of black frit was added and mixed with the fractured pieces, and the sample was heated to 1050°C in air and held at temperature for four hours. About 40 g of molten glass was poured into a rectangular Pt-5% Au mold with tapered sides and immediately transferred to an oven at 500°C and held at temperature for two hours. The power to the oven was shut off, and the glass was allowed to cool to room temperature at the same rate at which the oven cooled. After cooling to room temperature, the glass was easily separated from the mold. Two cores were then taken from the glass, following the procedure described below. The remainder of the casting was placed back into the Pt dish, which still contained ~60 g of the original melt. The glass was heated to 1050°C for 30 min, and a new rectangular casting was made. This was necessary to produce the required number of samples. The ramifications of these procedures are discussed in the characterization section.

Details of the glass preparation procedures are contained in ANL notebook 000111.

2. Core Drilling Radioacitve Glasses

(D. Fischer)

a. Suggested Materials

(1) Blickman hood

(2) Drill press (table-top size)

(3) Core drill

(4) Glass loaf (4 x 3 x 1.3 cm)

(5) Metal water pan (~16 x 5 x 4 cm deep)

(6) Glass plate (~10 x 3.5 x 0.6 cm thick)

(7) C-clamps (2, large)

(8) Plastic bag (large and transparent)

(9) Water

(10) Eye dropper with large bulb

(11) Beakers

(12) Metal plate (~8 x 3 x 1 cm thick)

(13) Small scrap pieces of Lucite (to be used with C-clamping)

(14) Coarse grinding paper

(15) Tissues

(16) Plastic sheeting

(17) Apiezon (black adhesive)

b. Preparation

Depending upon the type of glass to be cored, consideration must be given to the type of hood area, level of contamination in the hood, and amount of contamination that will be introduced during the core drilling. A Blickman hood was used in this work.

For the easiest cleanup, a sheet of plastic was placed on the floor of the hood where the coring and related work were performed. If the drill press is to be removed after coring glasses containing actinide materials, all surface areas of the drill press should be covered with plastic and/or surgical tape before placing the drill press inside the hood. If wide surgical tape is used, make little tabs on the tape for easy removal of tape.

Special precautions and preparations should be used whenever working with samples containing actinide materials. First, a lab coat should be worn with the sleeves folded and taped around the wrist. Two pairs of surgical gloves should be worn. The first pair should be taped securely onto the lab coat sleeve around the wrist. The second pair of gloves is worn over the first pair and should be removed whenever the experimenter feels that they have become contaminated. Whenever this top pair of gloves is removed, it should be done inside the hood. and the gloves should be peeled off in such a manner that the outside portion of the glove is folded to become the inside. The gloves should be disposed of in the dry active waste (DAW) receptable. The experimenter can then remove his arms from the hood to put on another clean pair of gloves, or a second person can hand the experimenter a clean pair, one at a time, through the hood opening.

Another safety precaution is to tape a sheet of plastic on the floor in front of the hood for the experimenter to stand on. In this way, whenever the coring operation and related work are completed, the plastic can be folded up and disposed of in the DAW. This helps to prevent the spread of contamination, should any occur during any of the processes. Be aware that the plastic sheeting may be slippery to walk on.

For the safety of the experimenter and fellow workers, it is strongly recommended to have a "backup" person present, such as a radiation safety person, to monitor and assist whenever needed.

c. Procedure

At this point, the materials required for core drilling should be in the hood or easily accessible.

The glass loaf must have one large relatively flat face. If none is available, place the coarse grinding paper on a flat surface, add a little water to the paper surface, and grind one surface flat.

There are two methods for positioning and holding the glass loaf on the glass plate, which will be located inside the water pan. One method is to melt Apiezon adhesive onto the glass plate in a 130°-150°C oven, place the flat face of the glass loaf on the adhesive, reheat the glass plate and glass loaf in the oven for better adhesion, remove them from the oven, press the glass loaf and plate together, and cool to room temperature. Place this plate and loaf assembly on the metal plate inside the metal water pan. Place the water pan inside a large, transparent plastic bag and position it on the table of the drill press with the installed core drill inside the bag opening. Insert the two pieces of Lucite scrap on either end of the glass plate inside the water pan, which extend above the lip of the water pan. Fold the plastic bag on top of the Lucite and position the stationary portions of the C-clamps over this portion of the bag and Lucite and have the movable portion of the C-clamps under the drill press table. Tighten the C-clamps carefully until the contents in the bag are snug. The thick metal plate inside and on the bottom the water pan maintains a flat surface under the glass plate during the tightening of the C-clamps to prevent the glass plate from breaking. By adjusting the drill press table and/or C-clamps, align the glass loaf under the core drill.

The second loaf-holding method is to eliminate the use of the Apiezon adhesive by placing a thin scrap piece of Lucite onto the glass loaf and clamping it carefully with a C-clamp to stabilize the loaf. The advantage of this second method is that the core-drilled sample will not be contaminated by Apiezon adhesive. The purpose of the glass plate immediately under the glass loaf is to protect the core drill when drilling through the glass loaf. (Drilling into metal with a core drill dulls the core drill!)

After the glass loaf is positioned for the first drilling, water should be added to the water pan to completely cover the glass loaf. The plastic bag should be positioned up and around the drill in such a manner as to confine the water spatter to the inside of the plastic bag. A workable drill speed should be about 1000 rpm. Drill pressure should be moderate to light for a four- or five-second period, with complete raising of the core drill after each period. This method will flush the sample and core drill and prevent the glass loaf from breaking or shattering. If drilling is done with too much pressure and/or for too long a time period, the glass loaf will shatter.

After each coring, the water level must be reduced with the eye dropper to permit repositioning of the glass loaf for the next core drilling. When the loaf is repositioned, refill the water level in the pan so that the glass loaf is again submerged with water.

d. Cleanup

At the completion of the core drilling, the contaminated waste water can be poured into a beaker and left in the hood for the water to evaporate before disposal. The other materials can be removed from the plastic bag, cleaned, and wiped down to remove loose contamination before proper storage for future use or disposal into the DAW. After loose contamination has been cleaned up, the drill press may be unwrapped. With care, the adhesive tape and plastic can be removed with minimum contamination to the drill press.

The drill press should be wiped and monitored to detect if there is any contamination. The drill press can be removed from the hood when the radiation survey results are acceptable. As a precautionary measure, one should always consider this drill press to be suspect with respect to contamination.

3. Sectioning of Radioactive Glass Core Drillings

(D. Fischer)

a. Suggested Materials

(1) Blickman hood

(2) Buehler Isomet low-speed saw with diamond saw blade and a rectangular block mount

(3) Water

(4) Tweezers

(5) Apiezon adhesive

(6) Oven (130° to 150°C) or hot plate

(7) Beakers

(8) Ultrasonic cleaner

b. Preparation

The experimenter should use the same precautionary measures as stated in Section C.2.b.

c. Procedure

Heat the Buehler rectangular block mount to about 150°C, coat with the Apiezon adhesive, and reheat in oven. Remove the block from the oven and position several glass cores perpendicular to the mount with at least 3/8 inch between cores. Return the mount with the glass cores to the oven until temperature equilibrium is obtained. Remove the block of cores from the oven, press the cores into the block, and make any last-minute adjustments in positioning of cores before the block cools and the adhesive hardens. Mount the block of cores onto the arm of the Buehler cut-off saw, make adjustments, and position for the first cut to square off the core. Water is used in the pan provided with the Buehler saw as the blade coolant and lubricant. A 75-g load on the saw arm is adequate, as is a saw-speed setting of 6 to 8. As the cut nears completion, the weight of the arm could be lessened to obtain a cleaner cut of the slice. As a precautionary measure, place a piece of cardboard upright in front of the saw to prevent the sample disks from flying out of the hood at the completion of the slicing. It should be noted that the slower the saw-blade speed, the more likely the sample will drop into the pan of water and not fly away from the saw. If the disk has a rough edge at the point of separation, sometimes one can hold the disk to the saw blade to remove that edge. (Extreme care must be taken to do this particular maneuver.)

After the cores have all been sliced, the liquid in the water pan can be poured into a beaker or some other waste container and be left to evaporate to dryness before further disposal. The water pan, saw blade, and saw housing should be wiped down with wet and then dry tissues or paper towels to remove any loose contamination.

The sliced disks are rinsed and then cleaned ultrasonically for five minutes in a beaker of high-purity water (HPW), followed by three separate ultrasonic cleanings in fresh ethanol for five-minute periods. No residual film should remain after drying. These cleaning liquids can also be poured into a liquid-waste container for liquid evaporation before further disposal.

Place the cleaned disks into a clean beaker and heat in a 100°C oven for at least four hours. Then carefully place each disk into a cleaned glass vial, marked for identification, for removal from the hood. This is easily accomplished by having another person hold that cleaned vial at the hood opening and then gently placing the specimen on the bottom of the vial. The vial is then capped and removed from the hood area.

4. Physical Measurements of Radioactive Glass Disks
(D. Fischer)

a. Suggested Materials

(1) Tweezers, Teflon-coated

(2) Calibrated balance (Mettler)

(3) Caliper (Starret)

b. Preparation

On a clean bench top put down a clean lint-free piece of paper on which the disk will be placed for measurement.

c. Procedure

With clean Teflon-coated tweezers, carefully remove the disk from its vial and place it on the clean lint-free paper. Measure the diameter and thickness of the disk using the NNWSI Starret caliper. Several measurements should be taken to ensure the accuracy and reproducibility of the readings. After all the disks have been measured, fold up the paper on the bench top and dispose of it into the DAW.

Weight measurements may be made on any balance, depending upon the accuracy and precision desired. In these experiments, the five-place NNWSI Mettler balance was used.

In summary, care should be taken when handling the radioactive glass disks. There is little chance of contamination to surrounding areas, because there should be no loose contamination on the disks. As a precautionary measure, always survey areas where the radioactive glasses have been handled or worked with.

5. Preparation of Crushed Radioactive Glasses

(D. Fischer and T. Gerding)

a. Suggested Materials

(1) Mortar and pestle

(2) -40 +80 sieves

(3) Clean vials

(4) Beakers (2)

(5) A 90°C oven

(6) Ultrasonic cleaner

(7) Ethanol

(8) High-purity water (HPW)

(9) Glovebox and/or Blickman hood

b. Preparation

If the glasses to be crushed contain only depleted uranium as the radioactive tracer, these glasses can be prepared and crushed on the bench top. However, a hood would still be advised. The glasses containing actinides must be prepared in a glovebox and/or hood.

Use thin glass samples for crushing. The glass samples are to be cleaned ultrasonically in HPW, cleaned three times ultrasonically in fresh ethanol, and then dried. The mortar must be adapted with a cover during crushing to contain particulates. This cover can be as simple as a piece of paper large enough to cover the mortar, with a hole in its center for the pestle handle to protrude. Another aid in controlling loose particulates is to place the mortar in a large clean porcelain-type pan. In this way, the particulates can be contained easily and cleaned up.

c. Procedure

Place about twice the desired weight of cleaned sample material into the mortar, cover and crush the glass until enough -40 +80 sieve-sized material is obtained. To clean this crushed glass, place it into a clean beaker, cover it with HPW, and ultrasonically clean it for five minutes. Repeat this same ultrasonic cleaning process three times using ethanol, then pour the waste liquids into an open container for evaporation. Decant the ethanol and place the beaker containing the crushed glass into a 90°C oven until constant weight is attained. Then place the crushed glass into a clean vial for storage for future use. The actinide-containing crushed glass can be separated and weighed into individual vials as required for each experiment. In this way, the entire contents of each vial can be transferred into its assigned, tared, test vessel and be reweighed for an accurate test sample weight. Alternatively, the sample weight can be determined by weighing the sample vial before and after transferring the sample into the vessel and observing the weight difference. Either of these two methods minimizes the handling and possibility of contaminating surrounding work areas.

6. Cleaning Procedures

(D. Fischer)

a. Stainless Steel Parr Vessels and Caps

If new stainless steel Parr vessels and caps are to be used, the first procedure is to stamp an identification number or letter on each cap and vessel.

Clean the vessels and caps ultrasonically in acetone, rinse them three times in HPW, submerge them in a 1% HNO_3 bath and heat to 90°C for one hour, rinse three times with HPW, and either dry the components in a 90°C oven or allow them to air dry.

b. Silicon Gaskets

The fabricated silicon gaskets for the Parr vessels were placed individually into a clean beaker of HPW. (This individual placement of the gaskets into the water helped to prevent the gaskets from sticking together.) The beaker was heated to 90°C for two hours, after which the gaskets were rinsed in five full-volume rinses with HPW. The gaskets were then blown dry with N_2 gas and placed into clean glass storage containers for future use.

c. Stainless Steel Disk Supports

Newly fabricated stainless steel disk supports are to be cleaned for five minutes each in acetone, Freon, and two times in ethanol. Then they are placed into a clean Teflon jar filled with HPW, capped, shaken vigorously for one to two minutes, and rinsed several times with HPW. The jar is refilled with HPW and placed in a 90°C oven for two hours. The supports are removed from the water, dried to a constant weight, and placed into clean containers that are marked for identification.

d. Glass Disks

The glass-disk samples were ultrasonically cleaned one or two times in HPW and three or four times in fresh ethanol. Each disk was individually moved from one beaker to another for each cleaning. After the final ethanol cleaning, the disks were placed into a clean beaker and put into a 90°C oven for about two to four hours until dry. The disks were then placed into clean and identified vials.

e. Crushed-Glass Sample Material

Place the crushed-glass sample material into a clean beaker, cover with HPW, and clean ultrasonically for five minutes. Repeat this same procedure three more times using fresh ethanol. Decant the ethanol after the final cleaning and place the beaker into a 90°C oven until the material is dry.

f. Teflon Bottle for Preequilibrated J-13 Water

Rinse the bottle and cap several times with HPW. Then fill the bottle with HPW, cap, and place it in a 90°C oven overnight. Remove it from the oven and rinse it thoroughly three to five times with HPW.

g. Tuff Material for Specified Tests

Some of the experiments require that additional tuff be added to the test vessel. This tuff can be obtained from the bulk of the residual solid material remaining in the Teflon bottle at the completion of the procedure described in Appendix A.

Pour this residue into a clean beaker and place it in a 90°C oven to drive off the water. After three to four hours, remove the beaker from the oven and mix the material, then return it to the oven for one to two hours. After this drying period, put this material into a capped vial until it is needed.

h. LPE Containers

The new LPE container caps were removed, placed onto a tray along with the containers, and heated for four hours in an 80°C oven. The containers were removed, cooled to room temperature, and then completely filled with HPW. The caps were screwed on and the containers were shaken. The water was allowed to stand in the container for one to two days, after which it was poured out, and the container and cap were rinsed three times with HPW. The container and cap were placed into an 80°C oven for three hours to dry. Finally, the containers were capped for future use.

7. Loading of Test Vessels

(D. Fischer and J. Bates)

An important consideration is to have a checklist prepared prior to the loading operation, to identify such things as:

(1) test numbers,

(2) vessel numbers,

(3) types of samples (whether highly radioactive or not),

(4) sample numbers, and

(5) sample support numbers.

The following items are to be weighed and/or numbered before the actual loading process begins:

(1) test numbers,

(2) vessel numbers,

(3) sample numbers and weights, and

(4) sample support numbers and weights.

Depending upon the number of vessels to be loaded and assembled, two persons can do the functions efficiently. The following describes a typical loading sequence:

(1) Individually, tare the empty vessels that will contain dried tuff material, add the desired amount of tuff, and record the tuff weight.

(2) Place the preweighed sample supports into their designated vessels.

(3) Add the preweighed and measured glass disks to the sample supports in the appropriate vessels.

(4) Tare the empty vessels that will contain the crushed-glass samples. Add the appropriate amount of crushed glass, reweigh, and record these sample weights. (As discussed in Sec. A.5.c, the radioactive crushed glasses could be preweighed in individual vials. Therefore, one needs only to tare the appropriate vessel and cap, go to an open-faced hood, carefully pour in the vial contents, cap the vessel, reweigh, and record the weight change as that of the crushed-glass sample.)

(5) Tare each vessel, add the predetermined amount of preequilibrated J-13 water from a wash bottle, and record the vessel water weight. (Special attention must be given when adding the water to vessels containing tuff. The water stream going into the vessel should be such as to minimize water and tuff turbulence to prevent the sample surface from being covered with tuff material upon settling.)

(6) Zero the empty balance, place the vessel cap on the vessel, and record the "in" weight for the loaded vessel.

(7) Install the fittings to these vessels and tighten according to the type of gasket material used in the caps. If Teflon gaskets are used, tighten as hard as possible and then tighten again 10 to 15 minutes later. (Teflon has a tendency to flow under these conditions.) If silicon gaskets are used, tightening once is sufficient; do not overtighten. When using new Parr bomb fittings, one or two coats of Teflon spray will prevent galling and aid in easy assembling and disassembling of these fittings.

(8) The assembled vessels are now ready for the oven. Keep the assembled vessels upright at all times.

8. Opening of Test Vessels

(D. Fischer, J. Bates, T. Gerding, and D. Bowers)

The exact procedure to be used to open the vessels after a test period will vary and be predicated on considerations such as the type of test, test conditions, and information desired.

To illustrate one procedure, the following steps were taken at the termination of the 56-day gamma-irradiation tests.

A checklist is required for the opening of the vessels. In addition, have all analytical containers, vials, storage containers and beakers, etc., premarked and on display for easy access.

(1) The test vessel assemblies were removed from the oven at the gamma-irradiation facility and placed on a bench top to cool. The vessels were sorted into two groups. One group consisted of the highly radioactive samples, and the other consisted of the blank vessels and vessels with less-radioactive materials. The highly radioactive sample vessels were opened last because they require special handling and precautionary measures.

(2) All vessel assemblies were removed, and the capped vessels were weighed to determine the "out" weight.

(3) A vise and pipe wrench had to be used to remove the caps from the vessels.

(4) Observations were made of the contents and conditions inside the opened vessels, and notes were taken when warranted.

(5) Any silicon gasket particulate that may have fallen into the vessel and/or liquid was carefully removed. Any loose gasket material on the cover was removed because the vessel would be reassembled at a later step in these procedures (14).

(6) A 2-mL aliquot was taken from each vessel for anion analyses.

(7) A 100-λ aliquot was taken from all vessels containing actinides and placed onto a premarked stainless steel planchet for actinide counting. An additional 200-λ aliquot was taken from preselected vessels and placed into a 0.003-μm filter tube containing 500 λ (0.5 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.

(8) The pH measurements were made in the vessels. (Problems arose in trying to obtain pH readings from a 1- to 2-mL aliquot with the stirring method. Apparently, dissolved gases interfered with the pH readings and produced inconsistent results.)

(9) The glass-disk samples were carefully removed from the vessels with tweezers, rinsed with HPW, and placed into their respective sample vials, maintaining the same sample orientation as the samples were in the vessels. After the disks dried, weights were taken and recorded.

(10) The stainless steel supports were removed, rinsed with HPW, dried, and weighed, and the weights were recorded.

(11) Vessels which contained crushed glass or tuff went through a special step. The liquid in such a vessel was drawn into a clean syringe. The solid contents in the vessel were washed into a prelabeled 30-mL beaker. Any tuff or crushed glass that adhered to the vessel was wiped out with lint-free tissues before the liquid was filtered through a 0.45-μm filter back into the vessel. The filter from each syringe was saved along with the corresponding solid contents in the 30-mL beaker.

(12) The stainless steel supports were placed back into their respective vessels.

(13) Six drops of concentrated nitric acid (Ultrex) were added to each vessel.

(14) The vessels were capped, reassembled with their fittings, swirled to mix the liquid, and placed in a 90°C oven overnight.

(15) The next morning, vessel assemblies were removed and cooled to room temperature.

(16) Vessel assemblies were disassembled, and the vessel caps were once again removed.

(17) A 100-λ aliquot was taken from each vessel that had contained actinide glass samples and was placed onto stainless steel planchets for additional actinide counting.

(18) The stainless steel supports were once again removed, rinsed, placed into prelabeled containers, dried, and eventually reweighed.

(19) The liquids from each vessel were poured into tared LPE containers, weighed, and sent for analyses.

9. Calculation of Nitric Acid Production

The following equation can be used to calculate the amount of nitric acid produced during irradiation (Burns et al., Radiation Effects and the Leach Rates of Vitrified Radioactive Waste, J. Nucl. Mater. 107, 245, 1982):

$$N = 2\,C_0R\,[1 - \exp(-1.45 \times 10^{-5} \times G \times D \times t)]$$

where N = the number of moles of nitric acid produced per system volume;

APPENDIX C

GLASS CHARACTERIZATION
(J. Bates and D. Bowers)

Disks of SRL U glass were analyzed for compositional homogeneity, surface appearance, and phase separation using SEM/EDS and optical microscopy. Archive samples from each core were taken and analyzed.

Compositional homogeneity between samples was measured by taking low-magnification EDS spectra from each archive sample, using the same instrument settings for each spectrum. The peak intensities for Na, Mg, Al, Si, Zr, Ca, Mn, Fe, and Ni were compared and, for each element, were found to vary by less than 15% between samples. The compositional homogeneity of each sample was determined by taking a multielement line profile across each sample. Because the sample was not polished, some fluctuation existed in individual profiles, but the variation was less than 15% and is attributed to the variation in take-off angle caused by the surface roughness. Overall, for the elements analyzed, there was no evidence of large-scale compositional homogeneity.

The surface appearance of the cut-and-cored surfaces was examined for several, but not all, samples. The cut-and-cored surfaces had similar appearances and contained a small number of bubbles (∿10-μm dia).

Phase separation was measured by examining a polished thin section using an optical microscope and the SEM with backscattered electron detection. Some iron-rich phases were observed that had the appearance of spinel, a commonly observed phase in this type of glass. We estimated that this phase constituted less than 1% of the total amount of glass.

The crushed glass was examined by SEM, after cleaning, to determine whether the cleaning procedure was successful in removing fines. Only minimal amounts of fines were observed adhering to the larger particles, and we felt that the crushed glass had been adequately prepared.

The SRL A glass was examined only for actinide homogeneity. This was done by dissolving disks and crushed glass and doing α spectroscopy. Also done were total α counting on opposite surfaces of selected disks and γ spectroscopy on all samples.

The total dissolution provided the actual composition of ^{239}Pu and ^{241}Am in the glass, but the amount of ^{237}Np was too little to be analyzed. It also provided an indication as to the homogeneity of actinide distribution in the glass. The actinide concentrations are given in Table 2 in the main text, and are based on the analysis of two crushed glass samples. These analyses were identical within experimental error (±15%). The analyses of the glass disks, however, indicated that substantially more inhomogeneity existed in the disk samples, and this was further investigated using γ spectroscopy.

Gamma spectroscopy was done using identical counting procedures for each disk. Each disk was placed in a standard position and counted for a predetermined period of time. For selected samples, counts were done with each flat surface of the sample facing the detector. Also, a series of ten counts was done on the same sample to obtain an indication of the instrumental precision. The standard deviation of the counting procedures was less than 10%.

Peaks attributable to ^{241}Am (60 keV), ^{237}Np (85 keV), and ^{232}Pa (311 keV), which is a decay product of ^{237}Np, were analyzed. The results are shown in Table C-1. The degree of Np and Am homogeneity between samples, except for the crushed glass, would normally be unacceptable. The degree of Pu homogenenity could not be measured using γ spectroscopy. The inhomogeneity was a result of inadequate mixing of the glass prior to preparing the samples. The inhomogeneity was recognized before the radiation tests began, but we felt that judicious selection of samples would minimize any adverse effects, and the samples were not remade.

We felt that cores taken from the second casting were more homogeneous than those made from the first casting. Although the history of all cores was not recorded, some cores from each casting set could be identified and were subjected to a total α count of each surface. Sample #60, which was from the second casting, gave identical results for each surface, whereas sample #70, which was from the first casting, gave results that differed by 50% between surfaces.

Some indication as to which casting a sample came from was provided by the γ-spectroscopy results, and samples were matched for testing according to activity. The samples known to have come from the second casting, or with activity levels that indicated they may be relatively more homogeneous, were used in the disk-only experiment. Samples that were relatively more inhomogeneous were used in the disk + tuff experiments, where it was felt the tuff might control the solution concentration of each actinide. In addition, samples for each test period in the disk + tuff experiment were matched according to Am activity.

C_o = the initial nitrogen concentration;

R = vol_{gas}/vol_{liq};

G = irradiation efficiency of nitrate production;

D = dose rate; and

t = time of irradiation.

In the present system, which has a total volume of ∿22 mL, the values for these factors are

C_o = 0.032 mol/L;

R = 0.35;

G = 1.9; and

D = 0.2 mrad/h.

The amount nitrate formed after 56 days (1344 h) is

$$N = 2 \times 0.032 \text{ mol/L} \times 0.35 \; [1 - \exp(-1.45 \times 10^{-5} \times 1.9 \times 0.2 \times 1344)]$$

$$N = 1.65 \times 10^{-4} \text{ mol/L}.$$

In the present system, the volume is 22 mL, so the amount of HNO_3 produced is 3.64×10^{-6} mol.

The equation can be simplified to give the maximum amount of nitrate that can be produced in a closed system:

$$N_{max} = 2 \; C_o R$$

$$N_{max} = 2 \times 0.032 \text{ mol/L} \times 0.35 = 2.24 \times 10^{-2} \text{ mol/L}$$

or for 22 mL, $N_{max} = 4.93 \times 10^{-4}$ mol. Comparison of N_{max} with $N_{56\ days}$ indicates that, after 56 days, only ∿0.75% of the available nitrogen in the system has been converted to nitric acid.

Table C-1. Actinide Content of SRL A Glass[a]

Test Type	Test No.	Duration (days)	Sample No.	Activity[a] (cps/g)		
				^{241}Am	^{237}Np	^{232}Pa
SRL A + J-13	G 27	7	42	430	2.24	2.31
			64	473	2.23	2.21
	G 28	7	41	482	2.00	1.96
			53	514	2.42	2.48
	G 25	14	47	304	2.55	2.62
			48	302	2.22	2.26
	G 26	14	52	360	1.68	1.66
			67	345	1.60	1.59
	G 29	28	55	371	2.79	2.77
			44	379	2.83	2.88
	G 30	28	43	386	2.35	2.45
			46	384	2.73	2.88
	G 31	56	49	404	1.52	1.57
			68	385	1.73	1.73
	G 32	56	60	429	1.77	1.76
			65	414	1.87	1.94
SRL A + J-13 + Tuff	G 35	7	58	636	3.68	3.73
			72	807	3.75	3.87
	G 36	7	57	829	3.44	3.53
			71	921	3.88	4.00
	G 33	14	45	248	1.77	1.85
			51	213	1.34	1.36
	G 34	14	54	253	1.47	1.48
			61	266	1.58	1.60
	G 37	28	50	547	3.26	3.40
			69	546	2.45	2.38
	G 38	28	59	673	3.40	3.53
			63	662	3.36	3.38
	G 39	56	56	625	2.69	2.72
			66	652	3.01	2.94
	G 40	56	62	653	2.92	2.97
			70	682	2.80	2.93
Crushed SRL A + J-13	G 43	7	75	397	1.70	1.74
	G 44	7	76	395	1.82	1.62
	G 41	14	73	377	1.78	1.68
	G 42	14	74	394	1.83	1.73
	G 45	28	77	390	1.71	1.64
	G 46	28	78	395	1.89	1.69
	G 47	56	79	392	1.79	1.79
	G 48	56	80	370	1.93	1.67

[a] Not corrected for detector efficiency.

APPENDIX D

TEST CONDITIONS AND WEIGHT CHANGE DATA FOR SRL GLASS TESTING

This appendix is a Digi-Calc spreadsheet, and it contains all the test matrix data and weight change data recorded for the present tests. The LPE net weight is the weight of liquid submitted for analysis.

THE GAMMA IRRADDIATION LEACH TESTS___NNWS

Test Type	Test no.	Length Days	Sample no.	Vessel No.	Date In	Date Out	Length mm
SRL U + J-13	G 3	7	5	29	7/02/84	7/09/84	3.20
			6				3.08
	G 4	7	7	30	7/02/84	7/09/84	3.04
			8				3.09
	G 1	14	1	29	7/11/84	7/25/84	3.10
			2				3.04
	G 2	14	3	30	7/11/84	7/25/84	3.05
			4				3.44
	G 5	28	9	29	7/27/84	8/24/84	3.02
			10				3.12
	G 6	28	11	30	7/27/84	8/24/84	3.06
			12				3.05
	G 7	56	13	1	7/02/84	8/27/84	3.05
			14				3.09
	G 8	56	15	2	7/02/84	8/27/84	3.08
			16				3.06
SRL U + J-13 + TUFF	G 11	7	21	31	7/02/84	7/09/84	2.88
			22				2.99
	G 12	7	23	32	7/02/84	7/09/84	3.02
			24				3.07
	G 9	14	17	31	7/11/84	7/25/84	3.02
			18				3.13
	G 10	14	19	32	7/11/84	7/25/84	3.24
			20				3.05
	G 13	28	25	31	7/27/84	8/24/84	3.12
			26				3.12
	G 14	28	27	32	7/27/84	8/24/84	3.11
			28				2.83
	G 15	56	29	3	7/02/84	8/27/84	2.96
			30				3.26
	G 16	56	31	4	7/02/84	8/27/84	3.09
			32				3.04
Crush SRL U + J-13	G 19	7	35	33	7/02/84	7/09/84	–
	G 20	7	36	34	7/02/84	7/09/84	–
	G 17	14	33	33	7/11/84	7/25/84	–
	G 18	14	34	34	7/11/84	7/25/84	–
	G 21	28	37	33	7/27/84	8/24/84	–
	G 22	28	38	34	7/27/84	8/24/84	–
	G 23	56	39	5	7/02/84	8/27/84	–
	G 24	56	40	6	7/02/84	8/27/84	–

(contd)

	G 27	7	42	53	7/02/84	7/09/84	3.10
			64				3.00
	G 28	7	41	36	7/02/84	7/09/84	3.06
			53				3.00
	G 25	14	47	35	7/11/84	7/25/84	3.01
			48				3.02
SRL A	G 26	14	52	36	7/11/84	7/25/84	3.04
+			67				3.00
J-13	G 29	28	55	53	7/27/84	8/24/84	3.20
			44				3.22
	G 30	28	43	36	7/27/84	8/24/84	2.97
			46				3.03
	G 31	56	49	7	7/02/84	8/27/84	3.01
			68				3.04
	G 32	56	60	8	7/02/84	8/27/84	3.00
			65				2.97
	G 35	7	58	37	7/02/84	7/09/84	3.00
			72				3.00
	G 36	7	57	38	7/02/84	7/09/84	3.05
			71				2.98
	G 33	14	45	37	7/11/84	7/25/84	2.98
SRL A			51				3.00
+	G 34	14	54	38	7/11/84	7/25/84	2.98
J-13			61				3.06
+	G 37	28	50	37	7/27/84	8/24/84	3.03
TUFF			69				3.01
	G 38	28	59	38	7/27/84	8/24/84	3.02
			63				3.01
	G 39	56	56	9	7/02/84	8/27/84	2.96
			66				3.01
	G 40	56	62	10	7/02/84	8/27/84	2.99
			70				2.93
	G 43	7	75	39	7/02/84	7/09/84	—
	G 44	7	76	40	7/02/84	7/09/84	—
Crush	G 41	14	73	39	7/11/84	7/25/84	—
SRL A	G 42	14	74	40	7/11/84	7/25/84	—
+	G 45	28	77	39	7/27/84	8/24/84	—
J-13	G 46	28	78	40	7/27/84	8/24/84	—
	G 47	56	79	11	7/02/84	8/27/84	—
	G 48	56	80	12	7/02/84	8/27/84	—

(contd)

I (SRL Glass)

Dia. mm	SA sq.mm	Glass Mass In	Glass Mass Out	Weight Change (xE+5)	pH Out	Tuff Mass g	Support Mass In	Support Mass Out
9.84	251.0	0.64548	0.64544	- 4	6.97	_	4.78168	4.78158
9.82	246.5	0.62520	0.62523	+ 3				
9.83	245.7	0.61776	0.61776	0	6.72	_	4.90954	4.90938
9.83	247.2	0.63027	0.63034	+ 7				
9.82	247.1	0.63076	0.63066	-10	6.98	_	4.81382	4.81339
9.83	245.7	0.61810	0.61806	- 4				
9.82	245.6	0.61923	0.61919	- 4	6.40	_	4.72568	4.72525
9.82	257.6	0.70442	0.70439	- 3				
9.84	245.5	0.61791	0.61797	+ 6	6.84	_	4.80280	4.80276
9.82	247.7	0.63648	0.63640	- 8				
9.84	246.7	0.62523	0.62515	- 8	6.74	_	4.79536	4.79532
9.84	246.4	0.62350	0.62333	-17				
9.83	246.0	0.62184	0.62166	-18	6.31	_	4.83674	4.83653
9.82	246.8	0.62879	0.62853	-26				
9.84	247.3	0.62822	0.62789	-33	6.38	_	4.91300	4.91281
9.82	245.9	0.62470	0.62437	-33				
9.81	239.9	0.58443	0.58448	+ 5	7.15	0.2097	4.83249	4.83243
9.84	244.5	0.61014	0.61014	0				
9.85	245.9	0.61863	0.61864	+ 1	7.23	0.2045	4.92264	4.92261
9.83	246.6	0.62730	0.62733	+ 3				
9.82	244.6	0.61380	0.61376	- 4	7.12	0.2016	4.82985	4.82952
9.80	247.2	0.63638	0.63638	0				
9.80	250.6	0.65648	0.65641	- 7	7.00	0.2015	4.92891	4.92862
9.84	246.4	0.62108	0.62107	+ 1				
9.82	247.7	0.63533	0.63522	-11	7.12	0.2030	4.81338	4.81339
9.84	248.5	0.63944	0.63935	- 9				
9.82	247.4	0.63368	0.63362	- 6	7.15	0.2060	4.92862	4.92864
9.84	239.6	0.57842	0.57834	- 8				
9.82	242.8	0.60346	0.60556	+210	6.58	0.2020	4.82753	4.82736
9.81	251.6	0.65396	0.65649	+253				
9.83	247.2	0.63010	0.63270	+260	6.70	0.2021	4.84562	4.84551
9.83	245.7	0.61949	0.62240	+291				
_	1390.0	0.1936			7.02	_	_	
_	1414.5	0.1970			7.01	_	_	
_	1372.1	0.1911			6.63	_	_	
_	1362.7	0.1898			6.71	_	_	
_	1426.6	0.1987			6.68	_	_	
_	1400.5	0.1959			6.56	_	_	
_	1416.6	0.1973			6.58	_	_	
_	1411.6	0.1966			6.47	_	_	

(contd)

9.82	247.1	0.63663	0.63658	- 5	6.83	_	4.80816	4.80795
9.84	244.8	0.61771	0.61773	+ 2				
9.83	246.3	0.62824	0.62820	- 4	6.96	_	4.84990	4.84972
9.86	245.6	0.61785	0.61783	- 2				
9.85	245.5	0.62034	0.62028	- 6	6.96	_	3.91980	3.91975
9.82	244.6	0.61937	0.61941	+ 4				
9.80	244.5	0.61956	0.61955	- 1	6.71	_	4.78436	4.78431
9.81	243.6	0.61519	0.61516	- 3				
9.82	250.2	0.65518	0.65501	-17	6.57	_	3.91975	3.91974
9.85	252.0	0.66413	0.66394	-19				
9.85	244.3	0.61359	0.61346	-13	6.64	_	4.83835	4.83827
9.85	246.2	0.62284	0.62265	-19				
9.84	245.1	0.61842	0.61816	-26	6.64	_	4.90010	4.89975
9.85	246.5	0.62626	0.62602	-24				
9.79	242.8	0.60908	0.60873	-35	6.61	_	5.00481	5.00461
9.86	244.7	0.61378	0.61359	-19				
9.86	245.6	0.62046	0.62051	+ 5	7.01	0.2016	4.75994	4.75973
9.82	244.0	0.61686	0.61693	+ 7				
9.82	245.6	0.62467	0.62474	+ 7	6.91	0.2066	4.85031	4.85022
9.83	243.8	0.61112	0.61118	+ 6				
9.82	243.4	0.61298	0.61309	+11	7.02	0.2045	4.87168	4.87138
9.80	243.2	0.61065	0.61068	+ 3				
9.86	245.0	0.61356	0.61379	+12	6.89	0.2021	4.88490	4.88460
9.82	245.9	0.62376	0.62392	+16				
9.86	246.6	0.62530	0.62536	+ 6	6.88	0.2012	4.84390	4.84387
9.86	246.0	0.62160	0.62157	- 3				
9.84	245.5	0.62160	0.62182	+22	6.84	0.2004	4.78434	4.78430
9.84	245.1	0.61857	0.61875	+18				
9.82	242.8	0.60636	0.60737	+101	6.70	0.2015	4.93727	4.93705
9.82	244.3	0.61632	0.61748	+116				
9.87	245.7	0.61715	0.61818	+103	6.73	0.2018	4.96052	4.96024
9.83	242.3	0.60140	0.60268	+128				
_	1342.7	0.1870	-		7.02	_	_	
_	1339.8	0.1866	-		7.01	_	_	
_	1401.6	0.1952	-		6.77	_	_	
_	1227.1	0.1709	-		6.77	_	_	
_	1401.6	0.1952	-		6.69	_	_	
_	1377.9	0.1919	-		6.65	_	_	
_	1291.0	0.1798	-		6.35	_	_	
_	1334.8	0.1859	-		6.68	_	_	

(contd)

A IRRADIION LEACH TESTS---NNSWI (SRL GLASS)

Weight Change (xE+5)	Volume J-13 g	Complete Assembly In	Complete Assembly Out	Weight Change (x100)	LPE Net wt
-10	16.05	135.09	135.08	-1	11.61
-16	15.90	135.18	135.17	-1	11.58
-43	15.88	134.84	134.82	-2	11.56
-43	16.23	135.39	135.38	-1	12.02
-4	15.91	134.94	134.90	-4	11.91
-4	15.98	135.08	135.05	-3	14.07
-21	15.90	135.30	135.29	-1	13.03
-19	15.93	134.74	134.70	-4	13.36
-6	15.64	134.67	134.67	0	10.77
-3	15.91	134.73	134.73	0	11.15
-33	15.86	134.97	134.96	-1	10.61
-29	16.06	135.00	134.98	-2	10.80
+1	16.01	134.98	134.92	-6	12.72
+2	15.70	134.49	134.42	-7	12.68
-17	15.94	133.64	133.58	-6	12.71
-11	15.92	135.82	135.77	-5	9.87
	16.49	129.59	129.59	0	11.57
	16.75	129.33	129.34	+1	11.48
	(16.54)	129.73	129.71	-2	11.72
	16.44	129.08	129.06	-2	12.00
	16.87	129.91	129.88	-3	13.87
	16.94	129.47	129.42	-5	13.80
	16.82	130.07	130.03	-4	14.03
	16.90	129.69	129.67	-2	13.98

(contd)

-21	15.88	136.30	136.30	0	11.15
-18	15.88	135.24	135.23	-1	11.28
-5	15.90	133.71	133.69	-2	11.39
-5	15.74	135.08	135.07	-1	11.29
-1	16.20	135.89	135.84	-5	13.31
-8	15.91	135.29	135.26	-3	13.17
-35	15.86	133.70	133.67	-3	12.92
-20	15.77	134.34	134.33	-1	12.86
-21	16.03	134.44	134.44	0	10.53
-9	15.78	133.76	133.75	-1	10.07
-30	15.74	134.24	134.22	-2	11.21
-30	15.87	133.91	133.89	-2	11.02
-3	15.88	134.41	134.36	-5	12.40
-4	15.81	133.64	133.61	-[illegible]	12.42
-22	15.73	135.58	135.56	-2	12.10
-28	15.89	135.71	135.67	-4	12.50
	15.93	129.28	129.28	0	10.40
	15.90	129.51	129.51	0	10.74
	16.63	130.00	129.96	-4	11.88
	14.80	128.48	128.46	-2	10.70
	16.63	130.00	129.95	-5	13.34
	16.47	130.25	130.19	-6	13.12
	15.30	128.31	128.27	-4	12.10
	15.83	129.42	129.37	-5	12.70

(contd)

BLANKS	G 99	7	-	35	7/02/84	1207	7/09/84	915	-	-
	G 100	7	-	54	7/02/84	1207	7/09/84	915	-	-
	G 97	14	-	53	7/11/84	1130	7/25/84	910	-	-
VESSEL	G 98	14	-	54	7/11/84	1130	7/25/84	910	-	-
+	G 101	28	-	35	7/27/84	1110	8/24/84	845	-	-

Test Type	Test no.	Length Days	Sample no.	Vessel No.	Date In	Time	Date Out	Time	Length mm	Dia. mm
J-13	G 102	28	-	54	7/27/84	1110	8/24/84	845	-	-
	G 103	56	-	25	7/02/84	1207	8/27/84	845	-	-
	G 104	56	-	26	7/02/84	1207	8/27/84	845	-	-
BLANKS	G 107	7	-	51	7/02/84	1207	7/09/84	915	-	-
	G 108	7	-	56	7/02/84	1207	7/09/84	915	-	-
VESSEL	G 105	14	-	55	7/11/84	1130	7/25/84	910	-	-
+	G 106	14	-	56	7/11/84	1130	7/25/84	910	-	-
J-13	G 109	28	-	51	7/27/84	1110	8/24/84	845	-	-
+	G 110	28	-	56	7/27/84	1110	8/24/84	845	-	-
TUFF	G 111	56	-	27	7/02/84	1207	8/27/84	845	-	-
	G 112	56		28	7/02/84	1207	8/27/84	845	-	-
J-13	G 113	28	-	57	7/27/84	1110	8/24/84	845	-	-
+	G 114	28	-	58	7/27/84	1110	8/24/84	845	-	-
SS										

-	-	6.76	-	-	16.02
-	-	6.66	-	-	16.04
-	-	6.31	-	-	16.03
-	-	6.48	-	-	16.04
-	-	7.05	-	-	15.94

(contd)

GLASS)

SA sq.mm	Glass Mass In	Glass Mass Out	Glass Wt.Diff. (xE+5)	pH Out	Tuff Mass g	Support Mass In	Support Mass Out	Support Wt.Diff. (x100)	Volume J-13 g
–	–			7.15	–	–			15.98
–	–			6.56	–	–			16.04
–	–			6.81	–	–			16.05
–	–			6.88	0.2014	–			16.06
–	–			6.94	0.2058	–			16.01
–	–			6.94	0.2020	–			16.05
–	–			6.84	0.2012	–			16.01
–	–			7.27	0.2001	–			16.09
–	–			7.45	0.2043	–			13.62
–	–			6.71	0.2015	–			16.00
–	–			6.61	0.2031	–			16.02
-	-			9.09		4.76375	4.76366	- 9	4.60
-	-			7.03		4.81636	4.81509	-127	5.16

128.65	128.65	0	11.74
129.47	129.46	-1	11.78
130.50	130.51	+1	11.94
129.57	129.55	-2	11.96
128.57	128.56	-1	10.70

(contd)

THE GAMMA IRRADIATION TESTS---(PNL)

Complete Assembly In	Complete Assembly Out	Assembly Wt.Diff. (x100)	LPE Liquid wt
129.44	129.40	-4	12.16
128.39	128.34	-5	13.72
129.46	129.38	-8	13.75
130.92	130.92	0	10.70
130.29	130.29	0	11.74
130.62	130.60	-2	11.35
130.29	130.27	-2	11.48
131.02	131.00	-2	11.87
127.90	127.89	-1	8.86
128.48	128.45	-3	12.84
129.12	129.08	-4	12.62
122.20	122.18	-2	9.09
122.04	122.02	-2	7.03

APPENDIX E

COMPLETE ANALYTICAL RESULTS FOR GAMMA IRRADIATION TESTS

This appendix is a Digi-Calc spreadsheet. It contains the analytical data for cation analyses. The solutions as submitted (LPE net weight, Appendix D) were diluted with 20 mL of DIW and the ACL value reported in Appendix E is the reported concentration (ppb) of this diluted solution. The ppm values in Appendix E are the calculated concentrations (ppm) for each element in the nondiluted test solutions.

				Al			B			Ba		Ca			
Test Type	Test no.	Length Days	pH Out	ACL	ppm	(NL)i	ACL	ppm	(NL)i	ACL	ppm	ACL	ppm	(NL)i	ACL
SRL U + J-13	G 3	7	6.97	390	0.33	0.49	85	0.05	0.08	<30		3330	0.21	0.63	710
	G 4	7	6.72	390	0.33	0.50	79	0.04	0.06	<30		3220	-0.08	-0.23	730
	G 1	14	6.98	430	0.48	0.71	130	0.18	0.28	<30		3260	0.33	1.00	900
	G 2	14	6.40	420	0.42	0.63	130	0.18	0.27	<30		3280	0.17	0.51	970
	G 5	28	6.84	320	0.10	0.15	160	0.14	0.21	<30		3280	0.13	0.40	310
	G 6	28	6.74	360	0.12	0.17	180	0.15	0.22	<30		3610	0.09	0.26	300
	G 7	56	6.31	610	0.75	1.11	430	0.85	1.30	<30		3690	0.41	1.25	610
	G 8	56	6.38	630	0.78	1.15	440	0.86	1.31	<30		3780	0.50	1.50	690
SRL U + J-13 + TUFF	G 11	7	7.15	1050	2.44	3.64	85	0.06	0.09	<30		6890	0.35	1.07	540
	G 12	7	7.23	850	1.82	2.71	79	0.04	0.06	<30		6620	-0.84	-2.52	700
	G 9	14	7.12	640	0.69	1.02	110	0.12	0.18	<30		7870	-1.32	-3.99	790
	G 10	14	7.00	640	0.67	0.99	120	0.14	0.22	<30		7900	-1.50	-4.53	780
	G 13	28	7.12	330	0.00	0.01	170	0.16	0.24	<30		9520	-5.68	-17.05	220
	G 14	28	7.15	670	0.88	1.31	200	0.24	0.36	<30		11000	-1.81	-5.44	270
	G 15	56	6.58	1620	3.71	5.49	470	0.93	1.41	<30		18000	11.08	33.26	490
	G 16	56	6.70	1560	4.26	6.32	370	0.84	1.28	<30		15200	10.76	32.37	680
Crush SRL U + J-13	G 19	7	7.02	230	-0.10	-0.05	86	0.06	0.03	<30		3090	-0.43	-0.40	250
	G 20	7	7.01	240	-0.07	-0.03	94	0.08	0.04	<30		3090	-0.38	-0.36	250
	G 17	14	6.63	280	0.06	0.03	120	0.15	0.07	<30		3140	-0.07	-0.07	280
	G 18	14	6.71	260	0.00	0.00	120	0.15	0.07	<30		3160	-0.14	-0.14	210
	G 21	28	6.68	260	-0.12	-0.06	320	0.49	0.23	<30		3560	0.04	0.04	170
	G 22	28	6.56	300	-0.02	-0.01	280	0.40	0.19	<30		3570	0.09	0.08	130
	G 23	56	6.58	300	-0.07	-0.03	700	1.46	0.69	<30		3780	0.23	0.21	210
	G 24	56	6.47	300	-0.07	-0.03	610	1.24	0.59	<30		3810	0.32	0.30	270
	G 27	7	6.83	380	0.33	0.49	110	0.13	0.20	<30		3180	0.03	0.08	890

(contd)

	G 28	7	6.96	370	0.30	0.44	110	0.13	0.19	<30	3270	0.21	0.63	940
	G 25	14	6.96	300	0.13	0.20	110	0.13	0.20	<30	3150	0.11	0.34	330
SRL A	G 26	14	6.71	360	0.14	0.20	130	0.19	0.29	<30	3130	0.11	0.32	420
+ J-13	G 29	28	6.57	280	-0.06	-0.08	200	0.21	1.32	<30	3430	-0.07	-0.21	200
	G 30	28	6.64	350	0.13	0.19	260	0.35	0.56	<30	3420	-0.04	-0.13	300
	G 31	56	6.64	680	0.93	1.39	510	1.06	1.62	<20	3870	0.92	2.78	780
	G 32	56	6.61	650	0.86	1.29	530	1.11	1.71	<20	3660	0.41	1.24	510
	G 35	7	7.01	650	1.33	2.00	97	0.10	0.15	<30	6220	-1.30	-3.97	850
	G 36	7	6.91	990	2.40	3.56	94	0.10	0.15	<30	6550	0.23	0.69	940
SRL A	G 33	14	7.02	760	0.96	1.43	120	0.14	0.21	<30	7890	-2.06	-6.23	670
+	G 34	14	6.89	650	0.67	1.00	140	0.20	0.30	<30	8600	0.18	0.54	710
J-13 +	G 37	28	6.88	650	0.85	1.27	210	0.27	0.41	<30	10500	-2.73	-8.20	250
TUFF	G 38	28	6.84	860	1.40	2.08	230	0.32	0.49	<30	11500	-0.15	-0.44	180
	G 39	56	6.70	940	2.03	3.02	470	0.96	1.47	<20	16000	7.20	21.71	660
	G 40	56	6.73	1060	2.29	3.43	460	0.91	1.41	<20	15400	4.80	14.56	790
	G 43	7	7.02	230	-0.06	-0.03	97	0.11	0.05	<30	2980	-0.15	-0.14	280
	G 44	7	7.01	240	-0.04	-0.02	100	0.11	0.05	<30	3050	-0.13	-0.12	260
Crush	G 41	14	6.77	210	-0.13	-0.06	120	0.15	0.07	<30	3170	-0.06	-0.06	270
SRL A	G 42	14	6.77	220	-0.06	-0.03	140	0.23	0.11	<30	2960	-0.08	-0.07	210
+	G 45	28	6.69	220	-0.21	-0.09	250	0.33	0.16	<30	3300	-0.41	-0.38	170
J-13	G 46	28	6.65	220	-0.20	-0.09	260	0.37	0.17	<30	3350	-0.20	-0.19	140
	G 47	56	6.35	210	-0.24	-0.11	660	1.51	0.71	<30	3480	0.29	0.27	230
	G 48	56	6.68	290	-0.05	-0.02	770	1.74	0.82	<30	3530	0.15	0.14	220

(contd)

Cr	Cu		Fe		Li			Ce		Nd		La		Mg	
ppm	ACL	ppm	ACL	ppm	ACL	ppm	(NL)i	ACL	ppm	ACL	ppm	ACL	ppm	ACL	ppm
1.16	50	0.08	5990	12.96	175	0.40	0.58	<150		<100		<20		480	0.31
1.22	69	0.13	6340	13.94	151	0.33	0.49	<150		<100		<20		460	0.26
1.71	87	0.19	7470	17.48	250	0.60	0.89	<150		<100		<20		410	0.14
1.83	110	0.25	7360	16.69	250	0.59	0.87	<150		<100		<20		410	0.12
0.34	27	0.01	1680	2.27	380	0.94	1.38	<150		<100		<20		400	0.09
0.23	34	0.02	1630	1.71	390	0.86	1.28	<150		<100		<20		430	0.06
0.96	51	0.06	5420	10.52	550	1.32	1.95	<150		<100		<20		570	0.65
1.13	56	0.07	5710	11.04	570	1.35	1.99	<150		<100		<20		600	0.70
0.77	32	0.04	4450	9.54	167	0.39	0.58	<150		<100		<20		560	0.25
1.18	49	0.09	6000	13.58	164	0.37	0.55	<150		<100		<20		560	0.21
1.45	52	0.10	6640	16.08	190	0.47	0.69	<150		<100		<20		560	0.10
1.40	66	0.14	6140	14.43	210	0.52	0.76	<150		<100		<20		550	0.05
0.00	60	0.11	1180	0.98	300	0.68	1.00	<150		<100		<20		570	-0.14
0.13	19	0.00	1450	1.69	380	0.89	1.31	<150		<100		<20		650	0.07
0.67	27	0.02	4000	7.88	590	1.44	2.12	<150		<100		<20		920	0.58
1.47	33	0.05	5120	13.08	470	1.34	1.98	<150		<100		<20		840	0.75
-0.09	15	-0.02	1340	0.31	236	0.56	0.26	<150		<100		<20		360	-0.02
-0.08	15	-0.02	1310	0.24	233	0.56	0.26	<150		<100		<20		360	-0.01
0.01	42	0.07	1590	1.39	370	0.92	0.04	<150		<100		<20		380	0.05
-0.19	30	0.03	1060	-0.09	370	0.91	0.42	<150		<100		<20		370	0.01
-0.08	200	0.43	950	0.09	710	1.65	0.75	<150		<100		<20		440	0.10
-0.18	13	-0.03	760	-0.37	570	1.31	0.61	<150		<100		<20		440	0.10
-0.08	16	-0.03	1230	-0.23	970	2.28	1.04	<150		<100		<20		510	0.44
0.07	16	-0.03	1400	0.19	870	2.04	0.94	<150		<100		<20		510	0.44
1.72	71	0.14	7210	16.79	240	0.59	0.87	<150		<100		<20		400	0.12

(contd)

1.84	170	0.41	7210	16.64	240	0.58	0.86	<150	<100	<20	410	0.14
0.16	170	0.42	1680	1.72	300	0.75	1.11	<150	<100	<20	370	0.04
0.42	100	0.23	1800	2.07	300	0.75	1.11	<150	<100	<20	370	0.05
0.01	26	0.01	940	0.12	540	1.27	1.87	<150	<100	<20	410	0.05
0.26	67	0.11	1590	1.77	520	1.23	1.82	<150	<100	20	420	0.08
1.40	95	0.17	6620	13.65	690	1.68	2.49	<150	<100	<20	540	0.58
0.71	310	0.72	4600	8.54	690	1.69	2.51	<150	<100	<20	590	0.71
1.69	63	0.14	7710	19.18	232	0.59	0.88	<150	<100	<20	480	0.04
2.03	70	0.16	8020	20.77	210	0.54	0.80	<150	<100	<20	500	0.14
1.04	55	0.11	5190	11.37	260	0.64	0.95	<150	<100	<20	620	0.21
1.17	53	0.10	5530	12.49	300	0.76	1.13	<150	<100	<20	630	0.26
0.09	30	0.03	1400	1.61	420	1.01	1.48	<150	<100	<20	620	0.02
-0.10	410	1.03	970	0.48	450	1.08	1.60	<150	<100	<20	650	0.09
1.16	42	0.07	5540	12.28	620	1.57	2.32	<150	<100	<20	870	0.52
1.46	52	0.09	5950	13.05	630	1.56	2.32	<150	<100	<20	880	0.50
0.05	43	0.07	1330	0.54	225	0.58	0.26	<150	<100	<20	340	-0.01
-0.03	33	0.04	1250	0.23	222	0.55	0.25	<150	<100	<20	350	0.00
-0.02	13	-0.01	1280	0.52	340	0.83	0.38	<150	<100	<20	370	0.02
-0.15	12	-0.01	1110	0.27	340	0.90	0.42	<150	<100	<20	350	0.03
-0.07	14	-0.02	880	-0.03	600	1.42	0.65	<150	<100	<20	400	0.02
-0.14	69	0.12	790	-0.24	610	1.46	0.67	<150	<100	<20	410	0.06
0.02	21	-0.02	1180	-0.09	920	2.37	1.08	<150	<100	<20	480	0.47
-0.02	22	-0.02	1420	0.44	1030	2.58	1.18	<150	<100	<20	490	0.46

(contd)

	Mn		Mo		Na			Ni		Si			Sr		
(NL)i	ACL	ppm	ACL	ppm	ACL	ppm	(NL)i	ACL	ppm	ACL	ppm	(NL)i	ACL	ppm	ACL
2.07	390	0.21	<20		17700	0.89	0.38	330	0.60	18200	5.94	0.76	23	0.00	6
1.72	370	0.16	<20		17500	0.42	0.18	270	0.44	18300	6.30	0.80	24	0.00	6
0.96	480	0.95	<20		18100	2.51	1.06	500	1.00	17900	-2.60	-0.33	25	0.02	16
0.78	480	0.92	<20		18300	1.85	0.78	520	1.02	18000	-3.52	-0.45	25	0.02	17
0.63	140	0.24	<30		18600	3.23	1.36	190	0.17	18600	-2.05	-0.26	24	0.00	<5
0.43	140	0.20	<30		20600	3.28	1.39	180	0.10	20300	-2.72	-0.35	31	0.01	<5
4.34	640	1.18	<30		20000	6.00	2.53	380	0.77	24100	14.18	1.81	42	0.04	8
4.70	640	1.16	<30		20300	5.99	2.53	410	0.83	24300	15.27	1.95	42	0.04	10
1.67	400	-0.82	<20		17100	1.95	0.83	210	0.32	18700	9.57	1.22	35	0.00	13
1.44	390	-0.87	<20		17000	0.59	0.25	340	0.67	19100	9.50	1.22	35	0.00	11
0.68	560	1.01	<20		17200	2.12	0.90	390	0.80	17600	3.16	0.40	34	-0.01	22
0.37	550	0.96	<20		17200	1.55	0.66	350	0.67	17600	2.57	0.33	36	0.00	21
-0.92	190	0.03	<30		16800	-3.48	-1.47	91	-0.04	17600	-7.90	-1.00	41	-0.03	7
0.48	210	0.08	<30		19800	4.33	1.82	120	0.04	21000	0.95	0.12	55	0.01	11
3.88	600	0.84	<30		20700	7.67	3.23	210	0.42	28400	19.09	2.43	82	0.05	23
5.06	980	2.26	<30		17500	7.36	3.10	330	0.88	23300	16.51	2.11	70	0.05	22
-0.03	210	-0.28	<20		17200	-0.37	-0.06	77	-0.09	16700	1.96	0.08	23	0.00	<5
-0.02	210	-0.27	<20		17100	-0.41	-0.05	71	-0.10	17300	3.83	0.15	23	0.00	<5
	110	-0.06	<20		18100	2.09	0.28	130	-0.01	16300	-7.35		23	0.01	<5
0.02	90	-0.12	<20		18100	1.37	0.18	74	-0.16	18000	-3.47	-0.14	21	0.01	5
0.20	190	0.33	<30		21200	5.17	0.67	97	-0.10	21500	0.62	0.02	38	0.02	<5
0.21	180	0.30	<30		20800	4.34	0.58	88	-0.12	20800	-0.94	-0.04	34	0.01	<5
0.91	410	0.55	<30		21700	7.93	1.04	92	0.03	26000	16.15	0.64	51	0.06	7
0.93	440	0.63	<30		21400	7.32	0.97	110	0.08	25500	15.07	0.60	53	0.06	7
0.80	1040	2.06	<20		17600	1.87	0.79	450	0.96	21500	16.46	2.10	24	0.00	15

(contd)

0.93	820	1.42	<20	17700	1.78	0.75	480	1.03	20800	14.07	1.80	25	0.01	15
0.29	430	0.82	<20	17800	2.16	0.91	130	0.00	19200	1.44	0.19	21	0.01	5
0.33	290	0.44	<20	17700	2.16	0.91	190	0.17	18500	-0.20	-0.03	23	0.01	5
0.33	150	0.24	<30	20300	4.20	1.77	150	0.04	20800	0.17	0.02	30	0.01	<5
0.54	190	0.34	<30	20300	4.53	1.92	230	0.24	21400	2.02	0.26	30	0.01	15
3.88	730	1.42	<30	19700	5.50	2.32	490	1.06	26200	19.85	2.53	49	0.06	13
4.78	[illegible]	1.09	<30	19800	5.89	2.49	330	0.65	24500	15.69	2.01	50	0.06	18
0.28	600	-0.22	<20	17400	3.55	1.52	430	0.96	21200	17.6	2.28	34	0.00	20
0.95	680	0.07	<20	16700	2.97	1.25	440	1.03	23400	26.01	3.32	34	0.00	27
1.43	300	0.23	<20	17300	0.67	0.28	320	0.56	20900	10.57	1.35	40	0.01	15
1.74	310	0.27	<20	17100	0.63	0.27	360	0.68	17000	0.23	0.03	38	0.00	20
0.11	190	0.04	<30	19600	4.51	1.90	120	0.04	22000	4.31	0.55	51	0.00	10
0.62	180	0.01	<30	19600	4.46	1.88	92	-0.03	23000	6.87	0.87	54	0.01	12
3.50	1000	1.95	<30	19300	5.60	2.36	340	0.78	26500	16.30	2.08	76	0.04	14
3.39	650	0.98	<30	19600	5.36	2.28	360	0.81	26000	13.60	1.75	77	0.04	17
-0.01	210	-0.24	<20	16500	0.93	0.12	85	-0.05	17700	8.13	0.32	23	0.02	<5
0.01	210	-0.25	<20	17000	1.36	0.18	110	0.02	18500	9.34	0.37	22	0.00	<5
0.04	110	-0.07	<20	17800	0.87	0.11	100	-0.09	17500	-4.51	-0.18	26	0.02	<5
0.06	96	-0.09	<20	16800	1.30	0.17	89	-0.11	17100	-2.41	-0.10	23	0.01	<5
0.05	130	0.19	<30	20000	3.39	0.44	92	-0.11	20500	-0.65	-0.03	30	0.01	<5
0.12	120	0.17	<30	20300	4.65	0.61	77	-0.14	22400	4.67	0.19	33	0.01	<5
0.99	500	0.88	<30	19300	6.50	0.85	89	0.05	31000	35.33	1.39	51	0.07	7
0.96	350	0.46	<30	20200	7.31	0.95	110	0.09	24900	17.20	0.68	50	0.06	7

(contd)

Ti	Zn		V			Cs			U		
ppm	ACL	ppm	ACL	ppm	(NL)†	ACL	ppm	(NL)†	ACL	ppm	(NL)†
0.00	27	0.02	11	0.00	0.01	0.04			8.4	19.80	0.06
0.00	30	0.03	12	0.01	0.02	<0.02			6.4	14.40	0.10
0.03	38	0.09	17	0.02	0.06				28.4	75.00	0.24
0.03	30	0.06	17	0.02	0.06				27.3	70.20	0.23
	17	0.01	<10			<0.01			46.9	91.20	0.30
	14	-0.01	<10			<0.01			52.0	108.60	0.35
0.01	37	0.05	14	0.00	0.00	0.02	0.00		182	451.00	1.47
0.01	31	0.04	16	0.01	0.02	0.02	0.00		190	471.00	1.53
0.02	28	0.04	11	0.00	0.01	<0.02			9	23.20	0.08
0.02	37	0.06	12	0.00	0.01	<0.02			6.1	14.50	0.05
0.05	32	0.03	17	0.02	0.06				21.6	54.60	0.18
0.04	31	0.03	16	0.01	0.05				23.6	59.60	0.19
0.00	40	0.07	<10			<0.01			54.7	99.70	0.32
0.01	16	0.00	<10			<0.01			60.3	113.70	0.37
0.04	21	0.03	17	0.01	0.02	0.01	0.00		201	495.00	1.61
0.05	23	0.04	17	0.01	0.04	0.01	0.00		147	422.00	1.37
	14	-0.02	10	0.00	0.00	<0.02			11.3	28.70	0.03
	11	-0.02	10	0.00	0.00	<0.02			13.1	32.80	0.03
	31	0.07	11	0.00					31.4	82.50	0.09
0.60	20	0.03	13	0.01	0.01				21.9	55.90	0.06
	130	0.28	10	0.00	0.00	0.01	0.00		125	248.00	0.25
	13	-0.01	<10			0.01	0.00		110	214.00	0.22
0.00	12	-0.01	15	0.00	0.00	0.03	0.00		298	720.00	0.73
0.00	12	-0.01	15	0.00	0.00	0.03	0.00		271	656.00	0.67
0.03	37	0.05	15	0.01	0.05	<0.02			17.5	45.80	0.15

(contd)

0.03	56	0.10	15	0.01	0.05	<0.02		17.3	44.90	0.15
0.00	30	0.06	14	0.01	0.04			15.6	40.50	0.13
0.00	31	0.07	14	0.01	0.04			28.1	75.40	0.25
	15	0.00	11	0.00	0.00	0.01	0.00	45.3	90.30	0.29
0.02	46	0.08	11	0.00	0.00	0.02	0.00	99.4	204.50	0.67
0.02	34	0.05	21	0.02	0.06	0.03	0.00	215	543.00	1.77
0.03	210	0.50	19	0.01	0.05	0.03	0.00	219	557.00	1.82
0.04	34	0.05	15	0.01	0.05	<0.02		10.1	26.80	0.08
0.07	35	0.06	16	0.02	0.06	<0.02		9.5	25.80	0.08
0.03	29	0.02	18	0.02	0.06			20.3	48.80	0.16
0.04	42	0.06	20	0.02	0.08			26.4	66.60	0.22
0.01	22	0.02	10	0.00	-0.02	<0.01		57.0	104.20	0.34
0.01	250	0.62	10	0.00	-0.02	<0.01		68.8	128.90	0.42
0.02	26	0.04	18	0.01	0.03	0.01	0.00	206	524.00	1.71
0.03	28	0.05	18	0.01	0.03	0.01	0.00	198	492.00	1.61
	34	0.04	<10	0.00	0.00	<0.02		15.0	40.70	0.04
	16	-0.02	<10	0.00	0.00	<0.02		14.4	38.10	0.04
	10	0.01	10	0.00	0.00			30.5	79.30	0.08
	20	0.04	10	0.00	0.00			33.8	94.50	0.10
	17	0.00	<10			0.01	0.00	83.9	165.00	0.17
	48	0.08	<10			0.01	0.00	92.2	183.00	0.19
0.00	18	0.01	14	0.00	0.00	0.03	0.00	302	798.00	0.04
0.00	15	0.00	15	0.00	0.00	0.03	0.00	316	810.00	0.37

The Final BLANK Data For PNL & S

Test	Test #	Length	pH	LPE wt	Al Analysis	Al ppm	B Analysis	B ppm	Ba Analysis
BLANKS	G 99	7	6.76	11.74	260	0.703	67	0.181	<30
	G 100	7	6.66	11.78	280	0.755	65	0.175	<30
	G 97	14	6.31	11.94	260	0.696	62	0.166	<30
VESSEL	G 98	14	6.48	11.96	260	0.695	66	0.176	<30
+	G 101	28	7.05	10.70	260	0.746	110	0.316	<30
J-13	G 102	28	7.15	12.16	290	0.767	100	0.264	<30
	G 103	56	6.56	13.72	330	0.811	100	0.246	<20
	G 104	56	6.81	13.75	320	0.785	96	0.236	<20
BLANKS	G 107	7	6.88	10.70	190	0.545	65	0.186	<30
	G 108	7	6.94	11.74	210	0.568	67	0.181	<30
VESSEL	G 105	14	6.94	11.35	530	1.464	72	0.199	<30
+	G 106	14	6.84	11.48	310	0.850	72	0.197	34
J-13	G 109	28	7.27	11.87	180	0.483	110	0.295	<30
+	G 110	28	7.45	8.86	370	1.205	80	0.261	<30
TUFF	G 111	56	6.71	12.84	200	0.512	110	0.281	<20
	G 112	56	6.61	12.62	160	0.414	110	0.284	<20
	G 113	57	1.82	9.09	<100		<30		<30
	G 114	58	2.58	7.03	<100		<30		<30
					no-tuff	tuff	no-tuff	tuff	no-tuff
			7-Day		0.729	0.556	0.178	0.184	0.081
			14-Day		0.695	1.157	0.171	0.198	0.080
			28-Day		0.756	0.844	0.290	0.278	0.083
			56-Day		0.798	0.463	0.241	0.283	0.049

(contd)

Ca		Cr		Cu		Fe		Li	
ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm	Analysis
	3300	8.922	240	0.649	17	0.046	1240	3.352	<30
	3260	8.795	330	0.890	25	0.067	1240	3.345	<30
	3190	8.533	300	0.803	17	0.045	1150	3.076	<30
	3220	8.605	260	0.695	18	0.048	1030	2.752	<30
	3010	8.636	160	0.459	28	0.080	810	2.324	<30
	3280	8.675	200	0.529	13	0.034	810	2.142	<30
	3650	8.971	220	0.541	39	0.096	1300	3.195	<30
	3630	8.910	260	0.638	20	0.049	1320	3.240	<30
	6890	19.769	240	0.689	15	0.043	1000	2.869	<30
	6990	18.898	320	0.865	19	0.051	1290	3.488	<30
	8820	24.362	250	0.691	15	0.041	960	2.652	<30
0.093	8640	23.692	350	0.960	19	0.052	1280	3.510	<30
	11600	31.145	180	0.483	15	0.040	630	1.691	(32)
	8960	29.186	200	0.651	15	0.049	740	2.410	<30
	12300	31.459	220	0.563	16	0.041	940	2.404	(32)
	15100	39.030	240	0.620	20	0.052	940	2.430	<30
	60	0.192	780	2.496	110	0.352	4890	15.649	<30
	44	0.169	3810	14.649	180	0.692	3270	12.573	<30

tuff	no-tuff	tuff	no-tuff	tuff	no-tuff	tuff	no-tuff	tuff	no-tuff
0.084	8.858	19.333	0.770	0.777	0.057	0.047	3.349	3.178	0.081
0.088	8.569	24.030	0.749	0.825	0.047	0.047	2.914	3.081	0.080
0.089	8.655	30.165	0.494	0.567	0.057	0.045	2.233	2.051	0.083
0.051	8.940	35.244	0.589	0.592	0.072	0.046	3.218	2.417	0.074

(contd)

Ce		Nd		La		Mg		Mn	
ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm	Analysis
	150	0.41	<100		<20		370	1.00	210
	150	0.40	<100		<20		370	1.00	420
	150	0.40	<100		<20		360	0.96	120
	150	0.40	<100		<20		370	0.99	150
	150	0.43	<100		<20		340	0.98	22
	150	0.40	<100		<20		370	0.98	80
	150	0.37	<100		<20		330	0.81	180
	150	0.37	<100		<20		320	0.79	180
	150	0.43	<100		<20		480	1.38	630
	150	0.41	<100		<20		490	1.32	780
	150	0.41	<100		<20		550	1.52	210
	150	0.41	<100		<20		550	1.51	230
0.086	150	0.40	<100		<20		600	1.61	160
	150	0.49	<100		<20		490	1.60	150
0.082	150	0.38	<100		<20		670	1.71	270
	150	0.39	<100		<20		720	1.86	280
	150	0.48	<100		<20		<10		530
	150	0.58	<100		<20		<10		790
tuff	no-tuff	tuff	no-tuff	tuff	no-tuff	tuff	no-tuff	tuff	no-tuff
0.084	0.405	0.418	0.270	0.279	0.054	0.056	0.999	1.351	0.850
0.083	0.401	0.413	0.271	0.275	0.053	0.055	0.976	1.514	0.361
0.092	0.414	0.446	0.276	0.297	0.055	0.059	0.977	1.604	0.137
0.080	0.368	0.386	0.246	0.257	0.049	0.051	0.799	1.787	0.442

(contd)

	Mo		Na		Ni		Si		Sr
ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm	Analysis
0.57	20	0.05	17500	47.31	81	0.22	15500	41.91	24
1.13	20	0.05	17500	47.21	140	0.38	16800	45.32	23
0.32	20	0.05	17600	47.08	130	0.35	18800	50.29	19
0.40	20	0.05	17500	46.76	140	0.37	19700	52.64	19
0.06	30	0.09	16200	46.48	88	0.25	19200	55.09	26
0.21	30	0.08	17700	46.81	160	0.42	18400	48.66	24
0.44	30	0.07	18200	44.73	76	0.19	19800	48.66	27
0.44	30	0.07	18200	44.67	78	0.19	18400	45.16	28
1.81	20	0.06	16600	47.63	94	0.27	15600	44.76	33
2.11	20	0.05	17100	46.23	110	0.30	15900	42.99	36
0.58	20	0.06	17200	47.51	100	0.28	17800	49.17	37
0.63	20	0.05	17300	47.44	140	0.38	16800	46.07	39
0.43	30	0.08	17700	47.52	81	0.22	19100	51.28	48
0.49	30	0.10	14100	45.93	99	0.32	16900	55.05	41
0.69	30	0.08	18000	46.04	47	0.12	20500	52.43	57
0.72	30	0.08	17500	45.23	49	0.13	21500	55.57	65
1.70	30	0.10	<100	0.32	2390	7.65	5700	18.24	<10
3.04	30	0.12	<100	0.38	3120	12.00	8500	32.68	<10
tuff	no-tuff	tuff	no-tuff	tuff	no-tuff	tuff	no-tuff	tuff	no-tuff
1.958	0.054	0.056	47.3	46.9	0.298	0.284	43.61	43.86	0.063
0.605	0.053	0.055	46.9	47.5	0.361	0.330	51.47	47.62	0.051
0.459	0.083	0.089	46.7	46.7	0.338	0.270	51.88	53.17	0.069
0.707	0.074	0.077	44.7	45.6	0.189	0.123	46.91	54.00	0.068

(contd)

	Ti		Zn		V		Cs	
ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm	Analysis	ppm
0.06	<5		21	0.06	10	0.03		
0.06	<5		19	0.05	10	0.03		
0.05	<5		8	0.02	<10			
0.05	<5		6	0.02	<10			
0.07	<5		18	0.05	<10			
0.06	<5		<10		<10			
0.07	6	0.01	19	0.05	14	0.03		
0.07	6	0.01	<10		14	0.03		
0.09	<5		11	0.03	10	0.03		
0.10	<5		21	0.06	11	0.03		
0.10	7	0.02	15	0.04	11	0.03		
0.11	<5		27	0.07	12	0.03		
0.13	<5		11	0.03	11	0.03		
0.13	6	0.02	14	0.05	10	0.03		
0.15	7	0.02	<10		15	0.04		
0.17	7	0.02	11	0.03	15	0.04		
0.03	<5		23	0.07	<10			
0.04	<5		37	0.14	19	0.07		
tuff	no-tuff	tuff	no-tuff	tuff	no-tuff	tuff		
0.097	0.014	0.014	0.054	0.044	0.027	0.029		
0.105	0.013	0.017	0.019	0.058	0.027	0.032		
0.131	0.014	0.016	0.039	0.038	0.028	0.031		
0.157	0.015	0.018	0.040	0.027	0.034	0.039		