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Parametric Effects on Glass Reaction in the Unsaturated Test Method

by Alan B. Woodland, John K. Bates,
and Thomas J. Gerding

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Chemical Technology Division

December 1991

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PARAMETRIC EFFECTS ON GLASS REACTION IN THE UNSATURATED TEST METHOD

by

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ABSTRACT

The Unsaturated Test Method has been applied to study glass reaction under conditions that may be present at the potential Yucca Mountain site, currently under evaluation for storage of reprocessed high-level nuclear waste. The results from five separate sets of parametric experiments are presented wherein test parameters ranging from water contact volume to sensitization of metal in contact with the glass were examined. The most significant effect was observed when the volume of water, as controlled by the water inject volume and interval period, was such to allow exfoliation of reacted glass to occur. The extent of reaction was also influenced to a lesser extent by the degree of sensitization of the 304L stainless steel. For each experiment, the release of cations from the glass and alteration of the glass were examined. The major alteration product is a smectite clay that forms both from precipitation from solution and from in-situ alteration of the glass itself. It is this clay that undergoes exfoliation as water drips from the glass. A comparison is made between the results of the parametric experiments with those of static leach tests. In the static tests the rates of release become progressively reduced through 39 weeks while, in contrast, they remain relatively constant in the parametric experiments for at least 300 weeks. This differing behavior may be attributable to the dripping water environment where fresh water is periodically added and where evaporation can occur.

PARAMETRIC EFFECTS ON GLASS REACTION IN THE UNSATURATED TEST METHOD

I INTRODUCTION

The Unsaturated Test method has been developed^{1,2} as a procedure to monitor the reaction of glass with water under conditions that are relevant to the potential repository at Yucca Mountain, Nevada. The Yucca Mountain site is located in the unsaturated zone and the repository horizon is composed of beds of welded and devitrified tuff. During the waste containment period (300/1000 years), heat generated by the radioactive waste is expected to maintain the temperature of the near-field environment above 100°C.³ In addition, the metal containers which surround the waste are anticipated to retain their integrity during this period. Thus, for the initial 300/1000-year period, the glass waste form is unlikely to contact liquid water. However, once the temperature has cooled to below 96°C, the local boiling point of groundwater at the Yucca Mountain Site, and the container is breached, liquid water will have access to the waste form.

Water contact is likely to occur in several modes: (1) continuous contact between the waste form and water vapor, (2) slow ingress and accumulation of water in the container, and (3) intermittent contact between water and glass as water periodically flows into and passes through the container. The Unsaturated Test method was developed to study glass-water reaction where a number of glass/water contact modes exist so that site-relevant data can be generated to assess the importance of interactive effects between waste package components. The data provide a release rate or glass reaction progress for a specific set of conditions and, if the physical parameters incorporated into the test are chosen judiciously, may be able to provide information to bound releases expected to occur in the repository. The release data can also be used in the validation of geochemical modeling methods that are being developed to project glass reaction.^{4,5}

To facilitate performance of the Unsaturated Test, a rigorous procedure and set of test parameters have been employed. The test is designed to study the three types of interactions that affect the reaction of the glass and that are anticipated to occur under unsaturated conditions. These include (1) contact between the glass and moist air, followed by periodic rinsing of the glass surface with flowing water; (2) contact between the glass and standing water; and (3) contact between the glass and standing water in close contact with partially sensitized 304L stainless steel. The Unsaturated Test provides for the possibility that these interactions will occur and specifies analyses to be performed that are designed to judge the importance of each one.

The apparatus used in the Unsaturated Test has been described previously^{1,2} and a schematic diagram of the system is shown in Fig. 1. The components of the test apparatus are the test vessel, which provides for collection and containment of liquid and support of the waste package; the waste package assemblage (WPA), which consists of the waste form and presensitized metallic components representing the canister (Fig. 1b); and a solution feed system to inject water.

Fig. 1. (a) Schematic Drawing of Unsaturated Test Apparatus. (b) Schematic Drawing of the Side and Top Views of the Waste Package Assemblage

The WPA is contacted every 3.5 days by 0.075 mL (drops) of water from the J-13 well that was preequilibrated with Topopah Spring tuff at 90°C. The tests are conducted at 90°C and the fluid injection system is configured so that the water attains a temperature of ~90°C before contacting the glass. Elemental release is determined by chemical analysis of the water that contacted the WPA and by surface analysis of the assemblage components. Solution samples are collected immediately upon termination of the experiment and after the vessel has been acid stripped to remove any material that may have precipitated or adsorbed onto the vessel walls. Although the solution is sampled at ambient temperature, it dripped from the WPA and collected in the vessel bottom at 90°C. Material interactions are noted and secondary phases, which may influence elemental release, are identified.

The test procedure incorporates batch and continuous tests (Table 1). In the batch mode, tests are terminated at 13-week intervals through 52 weeks. In the batch mode, the apparatus is disassembled, and analyses of both the solution and components are performed. In the continuous mode, the WPA (including liquid associated with the WPA) is transferred to a new vessel, and the test is continued. For the first 52 weeks the continuous tests are sampled at 6.5-week intervals. After 52 weeks, 13- or 26-week intervals are used. Analyses are done on the solution in the old vessel. In addition, visual investigation of the components is possible at the termination points, and yet the test can continue for an unspecified period or until information most useful to repository evaluation is obtained.

One key to the applicability of the data generated by the Unsaturated Test is the relationship between the set conditions used in the test, e.g., temperature, water contact interval, water composition, drop volume, condition of the stainless steel in contact with the glass, and surface area of the glass, and the eventual conditions encountered in the repository. Since it is likely that many of the conditions listed above may vary between individual waste packages, and will certainly vary with time, the conditions were set using reasonable values at the time the test procedure was developed (1984). At that time, it was recognized that the set conditions chosen may not have been the best possible, based on refinement of the description of the waste package environment and on parametric effects not yet identified. Thus, a series of parametric experiments were initiated to determine to what degree each parameter affected the glass reaction.

The parameters chosen to study were:

- (1) exclusion of stainless steel contact with the glass;
- (2) the surface area of the glass;
- (3) the volume of water contacting the glass;
- (4) the interval of water injection; and
- (5) the effect of stainless steel composition and extent of sensitization.

Table 1. Test Matrix for Unsaturated Tests

Test No.	Components	Test Duration, weeks									
		0	6.5	13	19.5	26	32.5	39	45.5	52	65 ^a
#1 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#2 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#3 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#4 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#5 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#6 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#7 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#8 Batch	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#9,10,12 Continuous	glass, 304L ss holder	—	—	—	—	—	—	—	—	—	—
#11 Continuous	blank	—	—	—	—	—	—	—	—	—	—
ANALYSES REQUIRED ^b											
Total radionuclide (solution and metal)		✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓
Total matrix element (solution Li, B)		✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓	✓✓✓✓
Wt loss and surface analyses			✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓
Interaction of stainless steel			✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓

^aThe continuous tests are sampled every 13 weeks after the 52-week interval.

^bA check means this analysis is required; the number of checks indicate replicate analyses possible. The wt loss and surface analyses for the continuous test will be done when the tests are terminated.

These parametric experiments have now been in progress for up to four years. In this report the details of each experiment are described, the results are presented, and a comparison is made between the results from the various parametric experiments and the N2 Unsaturated Test series⁶ to determine the relative importance of each parameter in affecting glass reaction.

II. EXPERIMENTAL PROCEDURE

A. Overview

The apparatus used in the parametric experiments is the same as used in the Unsaturated Test except for the containment vessel and gasket (items 1, 2, 3, and 6 in Fig. 1). In the parametric experiments a 22 mL Parr vessel #4703 modified by reducing the wall thickness 1/32" to a depth 1" from the top of the vessel is used as the vessel body (item 1). This modification creates a ledge on which the retainer bottom (item 5, Fig. 1) is positioned. The cap for the vessel (item 3) was machined to provide the umbrella effect shown in Fig. 1 which directs condensation on the vessel lid to the walls of the vessel body instead of to the glass. All the material used in construction of the vessel is 304L stainless steel. The gasket material used in the parametric experiments is TeflonTM. The above changes were made to reduce the cost of the apparatus and to aid in ease of performing the experiments. None of the changes should appreciably affect the extent of glass reaction except that the vessel used in the parametric experiments is ten times less massive than the one used in the Unsaturated Tests. This reduced mass may increase the effect of the small temperature fluctuations caused by the ovens. As temperature gradients between the vessel and WPA will cause vapor transport, this is an important process that must be considered when comparing results from different experiments.

The conditions used in each parametric experiment plus the rationale for performing the experiment are given in Table 2. The experimental matrix used for each series is detailed in Section III, but in most cases both batch and continuous experiments were run. All of the batch experiments have been terminated, while the continuous experiments are still in progress.

The solutions from the vessel bottom are analyzed for Al, B, Ca, Fe, K, Li, Mg, Mn, Na, Ni, Si, and S using Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES). The analytical uncertainty is 3-10% depending on the element and its concentration. Uranium is determined by the Sintrex method which is based on laser-induced fluorescence ($\pm 10\%$ uncertainty). When enough solution is available, the pH (glass electrode, Orion model 501 Digital Ionanalyzer), total and organic carbon (Dohrmann Total Organic Carbon Analyzer Model DC-80), and the anions F^- , Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , HPO_4^{2-} , CHO_2^- , and $C_2O_4^{2-}$ (ion chromatography) are measured with uncertainties all in the range of 5-10%.

Table 2. Description, Purpose, and Status of Parametric Experiments and N2 Unsaturated Test

Experiment #	Description	Purpose	Status
P-II	Regular-sized glass waste form, no ss holder, 0.075 mL J-13/3.5 days, continuous and batch experiments	To study the release from glass only	Initiated 2/20/84. Batch experiments completed 2/18/85. Continuous experiments in progress.
P-III	Half-sized glass waste form, ss holder, 0.075 mL and EJ-13/3.5 days, continuous and batch experiments	To study the effect of changing the waste form surface area by reducing the as-cast surface area by half	Initiated 12/6/84. Batch experiments completed 12/5/85. Continuous experiments in progress.
P-IV	Half-sized glass waste form, ss holder, 0.0375 mL and EJ-13/3.5 days, continuous and batch experiments	To study the effect of drop volume by reducing the amount of water added and the as-cast surface area by half	Initiated 2/18/85. Batch experiments completed through one year. Continuous experiments in progress.
P-V	Regular-sized glass waste form ss holder, 0.075 mL and EJ-13/14 days, continuous and batch experiments	To study the effect of lengthening the time interval between water additions	Initiated 6/10/85. Batch experiments completed through one year. Continuous experiments in progress.
P-VIII	Regular-sized glass waste forms in presensitized ss holders (heat #22841), 0.075 mL EJ-13/3.5 days, continuous and batch experiments	To study the effect of presensitized the ss waste form holder	Initiated 2/27/86. Batch experiments completed through six months. Continuous experiments in progress.
Test #			
N2	Regular-sized glass waste forms in presensitized ss holders (heat #699960), 0.075 mL and EJ-13/3.5 days, continuous and batch experiments	QA I execution of Unsaturated Test on glass doped with Np, Pu, and Am	Initiated 2/3/86. Batch tests completed. Continuous tests in progress.

Raw and "corrected" solution analyses are presented in the appendices. The "corrected" data account for the elemental contribution from the injected water. This is done by subtracting from the total solution analysis the amount of each element contained in the water that was injected during the experiment period and added at the beginning of an experiment period. Such a correction assumes that all the water injected actually goes into the vessel. This concern exists because after several years, the injection lines may become partially plugged which makes complete water injection uncertain. The correction also assumes that any leakage from the vessel is only water (presumably as vapor) and that all cations are retained in the vessel. It should be noted that, when analyzed concentrations were reported to be below the detection limit, the detection limit value was used. Thus, the results for elements frequently at very low concentration represent maximum values. These elements include Al, Mg, Ni, and Sr.

Interpretation of the solution data requires consideration of processes that may occur intermittently during the experiment. For example, if during a certain period there has been considerable evaporation from the WPA surface, it is possible that none of the water that contacts the top surface actually drips off of the glass to be collected in the test solution. If this happens, then all elements will show a negative deviation. However, if during the next period effective water transfer from the glass to the test vessel occurs, then a sharp positive deviation in elemental release may be observed. Consequently, elemental release should be viewed as a trend over the entire experiment duration with little weight given to individual deviations from this trend.

In the batch experiments analysis is also performed on the metal and glass components of the systems. The components are observed first using a low-power optical microscope where color photographs are taken and the surfaces mapped for scanning electron microscopy (SEM) and secondary ion mass spectroscopy (SIMS) analysis. If appropriate, samples are taken for x-ray diffraction (XRD) analysis. The samples are then examined by SEM with associated energy dispersive spectroscopy (EDS) and wavelength dispersive spectroscopy (WDS) to characterize the alteration products that formed during the reaction.

B. Starting Components

The procedures used in setting up, performing, and analyzing the experiments are essentially the same as used in the Unsaturated Test.^{1,2,6} Throughout the entire series of experiments a consistency in methods was maintained.

1. Glass Composition and Homogeneity

The basis for the glass composition is SRL 165 black frit doped with Cs, Sr, and U.⁷ In this report this glass is referred to as SRL U glass. This composition was chosen because of the data available as part of the SRL testing program⁷ and because at the time the experiments were initiated, 165 type black frit was the reference glass composition for processing in the

Defense Waste Processing Facility (DWPF). Subsequently, the glass processing procedure has been altered and glasses based on frit 200 with both sludge and precipitate hydrolysis components added have been designated as DWPF candidate glasses.⁸ Based on hydration theory,⁹ SRL 165 black frit type glasses should have the best durability of glasses that fit into the potential range of glasses to be produced by the DWPF.

A single quantity of SRL black frit has formed the basis of all the parametric experimentation described in this report. The glass composition is given in Table 3 together with analyses of the starting material as obtained by different laboratories. EDS spectra of the glass at 10 and 20 keV are presented in Figs. 2a and 2b for reference.

2. Water

A 5-gal batch of J-13 water from the J-13 well located near the potential repository horizon was used as the source of water for these experiments. In some experiments the water was used as received and in other experiments the J-13 water was equilibrated with tuff at 90°C following established procedures¹ to produce EJ-13 water, which is taken to be more representative of water that will be present in the waste package environment. Several equilibrations have been done over the course of these experiments and the water compositions used in the parametric experiments are given in Table 4.

3. 304L Stainless Steel Waste Form Holders

The waste form holders that enclose the glass during the experiments consist of perforated pieces of 304L stainless steel. The perforations are present to permit direct contact between the dripping water and the glass. Steel from two different heats was used during the course of the experiments (Table 5). In addition, different heat treatments were imposed on the steel to simulate heating that may occur during glass processing and long-term storage in the repository at elevated temperatures. Such heat treatment may cause the steel to lose its resistance to corrosion and become sensitized. In some of the experiments the starting metal was purposely sensitized to measure its influence on glass reaction. Details of the sensitization treatments are presented in the sections describing each individual series of experiments. For reference, an EDS spectrum of 304L stainless steel is presented in Fig. 2c.

III. RESULTS AND DISCUSSION

The results from each series of parametric experiments are presented below as individual subsections. Thereafter a comparison is made between the different series to assess the importance of each physical parameter on glass reaction.

Table 3. Composition of Glasses Used in the Parametric Experiments

Formula	SRL U Glass		Black Frit Oxide wt %	
	Oxide wt %	Element wt %	Ferro ^a	MCC ^b
Al ₂ O ₃	4.08	2.16	4.1	4.3
B ₂ O ₃	6.76	2.09	6.8	6.8
BaO	0.06	0.05		<0.1
CaO	1.62	1.16	1.5	1.6
CeO ₂	<0.05	<0.04		
Cr ₂ O ₃	<0.01	<0.007		
Cs ₂ O	0.072	0.07		
Fe ₂ O ₃	11.74	8.20	12.3	11.7
K	NA ^c			
La ₂ O ₃	<0.05	<0.004		0.2
Li ₂ O	4.18	1.94	4.7	4.8
MgO	0.70	0.42	0.8	0.6
MnO ₂	2.79	1.76	2.9	2.8
MoO ₃	<0.01	<0.007		
Na ₂ O	10.85	8.05	10.3	10.8
Nd ₂ O ₃	<0.05	<0.005		
NiO	0.85	0.67	0.9	0.8
P ₂ O ₅	0.29	0.13		0.3
SiO ₂	52.86	24.71	54.1	51.6
SrO ₂	0.11	0.10		0.2
TiO ₂	0.14	0.08		<0.1
UO ₂	0.92	0.81		
ZnO	0.04	0.03		
ZrO ₂	0.66	0.48	1.2	0.7
F			0.06	
Cl			0.05	
Pb			0.05	

^aBlack frit supplied to ANL by SRL, composition as determined by Ferro Corp.

^bBlack frit supplied by SRL to the Materials Characterization Center (MCC), composition as determined by MCC.

^cNA = not analyzed.

Fig. 2. EDS Spectra of (a) Unreacted Glass at 10 keV, (b) Unreacted Glass at 20 keV, and (c) 304L Stainless Steel at 20 keV

A. P-II Experiments

This set of experiments is being performed following the Unsaturated Test protocol,² except that there is no metal retainer and all vessel components are made of TeflonTM. All measured release should be solely due to glass/water interaction. This provides a baseline for comparison with the results of other experiments where metal components are present. In addition, the results are directly applicable to those areas of the glass where there is no direct metal contact (i.e., the top portions of the glass in the pour canisters).

The detailed experimental matrix and weight change measurements are presented in Table 6.

The experiments were initiated 2/20/84 and have been completed through 301 weeks. For the first year, batch experiments were terminated at the 6.5-, 13-, 26-, 39-, and 52-week periods, while the continuous experiments were sampled every 6.5 weeks. For the second year, the continuous experiments were sampled every 6.5 weeks and thereafter at irregular intervals of approximately 13 weeks.

Table 4. Composition of J-13 and EJ-13 Water Used in the Parametric Experiments

Water Type	Water Composition (ppb)												
	Al	B	Ca	Fe	K	Li	Mg	Mn	Na	Ni	Si	Sr	U
J-J-13	<100	130	11,800	<10	4500	40	1940	<5	44,700	<20	29,100	37	<1
EJ-13 4/30/84	780	180	4500	18		64	390	<5	46,600	<20	36,300	30	4
	720	200	4550	ND		75	415	ND	47,800	92	37,900	39	4.7
	680	190	4560	ND		70	420	ND	49,900	57	38,000	44	4.6
	660	170	4390	<10		79	400	<5	48,200	ND	37,800	47	4.3
	720	180	4370	<10		71	400	<5	46,500	ND	36,900	41	3.9
	750	180	4150	17		66	390	<5	47,800	ND	36,200	41	ND
	710	170	4100	<10		71	390	<5	46,800	ND	36,900	37	3.7
	700	180	4100	<10		79	400	<5	48,700	ND	36,200	37	2.8
EJ-13 5/28/86	250	150	7120	<10		54	270		48,400	<20	35,300	35	<1
	240	163	7160	<10		49	260	<5	50,300	ND	33,600	35	<1
	230	170	7170	<10		ND	260	<5	49,000	<20	33,800	35	
	240	160	7570	<10	6930	45	270	<5	54,400	42	38,500	32	<1
	230	180	7230	15	660	42	260	<5	50,400	<49	33,100	28	<1

Table 5. Composition of 304L Stainless Steel Used in the Parametric Experiments and N2 Unsaturated Test

Composition	Heat #	Element %											
		C	Mn	P	S	Si	Cr	Ni	Cu	Co	N	Mo	V
Retainer N2 and P-IV, -V, and -XII	699960	0.022	1.49	0.025	0.003	0.40	18.22	10.02	0.12	NA	0.036	0.24	NA
Posts (all tests)	70815	0.027	1.61	0.028	0.021	0.26	18.50	10.62	NA	NA	NA	NA	NA
Retainer P-VIII	22841	0.016	1.33	0.029	0.003	0.51	18.15	9.22	0.36	0.11	0.082	0.28	NA

NA = not reported in certificate of analysis.

Table 6. Experimental Matrix and Weight Change Results from the P-II Series

Test #	Test Period (weeks)	Date Started	Date Stopped	Initial Glass Mass (gm)	Final Glass Mass (gm)	Δ Mass ($\text{gm} \times 10^{-5}$)	SA Ends (cm^2)	SA Sides (cm^2)	SA Total (cm^2)	J-13 ^a Added Drops (gm)
P-II-1a	6.5/13	2/20/84	in progress	9.9678			3.82	9.70	13.52	0.98/6.5 weeks
P-II-2a	6.5/13	2/20/84		10.0990			3.82	9.56	13.38	0.98/6.5 weeks
P-II-3	6	2/20/84	4/02/84	9.9378	9.9379	10	3.82	9.56	13.38	0.98
P-II-4	13	2/20/84	5/21/84	10.0620	10.0627	70	3.82	9.65	13.47	1.95
P-II-5	26	2/20/84	8/20/84	9.6495	9.6507	80	3.73	9.39	13.12	3.9
P-II-6	39	2/20/84	11/19/84	9.5870	9.5885	150	3.66	9.34	13.00	5.85
P-II-7	52	2/20/84	2/25/85	9.6366	9.6368	20	3.71	9.36	13.07	7.80

^aThe J-13 water was not pretreated.

The experiments have been conducted using J-13 water of composition given in Table 4. The water was received from Lawrence Livermore National Laboratory (LLNL) and has been stored in its original shipping container. The source water has been analyzed periodically and its composition remains relatively stable (Table 4).

The results of these experiments will be discussed by describing the general appearance of the glass as observed throughout the test period, by examining the glass surfaces from the batch experiments, and by correlating the solution results with these observations.

1. General Observations

(a) The waste form steadily gained weight during successive sampling periods through 39 weeks. This is the result of precipitation on the glass surface. The precipitates were clearly visible after 6.5 weeks. They initially formed on the top surface and coverage began to extend onto the sides after 224.5 weeks in the continuous experiments. The accumulation of precipitates does not occur on the bottom surface. Based upon detailed investigation of the batch experiments, the precipitates are primarily aluminosilicates (see below).

(b) On the top surface, no accumulation of standing water appears to have occurred. Upon opening the vessels (after cooling), the top surface dries within 10-20 seconds and the surface changes from a dark gray to a dirty white color when drying.

(c) The bottom surface of the glass was usually in contact with standing water throughout the sampling interval and remained wet during sampling.

(d) There was some water loss during the sampling intervals due to vapor escaping from the vessels. However, some fluid was always present in the bottom of the vessels upon sampling or experiment termination, indicating that vapor-saturated conditions were maintained throughout the experiment. A new vessel design was introduced at the 210-week sampling in an attempt to reduce vapor loss and to provide a more secure positioning of the glass in the center of the vessel.

2. Component Analyses

Selected samples from the batch experiments were examined by SEM/EDS/WDS. To do this, the top and bottom faces were carefully cut from the waste form and mounted on aluminum stubs. The reaction products observed on all samples are generally similar with greater coverage evident on the longer duration samples. The following is a description of the 26- and 52-week samples.

a. P-II-5, 26-Week Sample

A Si-rich surface layer is well developed on the glass with two types of reacted areas present. In some areas, the surface is covered by a smooth deposit which is similar in composition to that of the unreacted glass, except that it is somewhat depleted in Na and enriched in Mg, S, and K (Figs. 3a and 3b/EDS, compare with Fig. 2a/EDS). This deposit covers ~25% of the surface and appears to have formed by precipitation. The remainder of the surface has a rougher textured appearance, which at high magnification reveals many small platelets (Fig. 3d). This material is similar in composition to the smooth regions (compare Figs. 3e/EDS and 3b/EDS). There are many small areas which are somewhat enriched in S and Ca relative to the typical surface layer suggesting the presence of gypsum or anhydrite.

Many small grains are distributed over the surface (Fig. 3f). The two most common have been identified by XRD as calcite and gypsum. Calcite takes the form of vertical protrusions from the surface. Gypsum grains are typically very irregular in form (Fig. 3a) and have easily distinguishable EDS spectra (Fig. 3c/EDS). Both phases occur up to 100 μm across. Since gypsum is not stable above 42°C, at 1 atm, it must have formed either by low-temperature hydration of preexisting anhydrite or by direct precipitation during cooling of the WPA when the experiment was terminated.¹⁰ There are a number of other phases present; however, they were too fine grained to permit identification by XRD. These other grains are rich in Na, K, or Mg.

The bottom surface has far fewer grains on it compared to the top surface. The points of contact between the TeflonTM grid and the glass are evident to the eye and in the SEM (Fig. 4a). The contours of the as-cut surface are still visible but some places appear to be highly eroded. Some of the surface is covered by a smooth deposit; however, the majority has a rougher textured appearance (Fig. 4b). The roughness is more pronounced in the area of the TeflonTM contact. This reacted surface layer has a similar composition in the contact and noncontact areas (Fig. 4c/EDS). A reaction product, not observed on the top surface, occurs as dark splotches (Fig. 4d) and smooth rounded grains (Fig. 4e) on the SEM and is composed predominantly of Na (Fig. 4f/EDS). While it has not been possible to collect a sample for XRD analysis, the EDS spectra and the fact that the grains are beam sensitive suggests it is Na_2CO_3 . The possibility of this being a borate may be excluded based upon WDS analysis of similar grains on the top surface which revealed no boron. The Si and Al in the EDS spectra probably result from excitation of the surface layer as the beam penetrated the grains.

b. P-II-7, 52-Week Sample

A reacted layer is well developed on the top surface. It has a rough textured appearance and is composed of stacked irregular shaped platelets (Fig. 5a). There is heavier coverage of precipitated grains compared with P-II-5 (Fig. 5b). These grains are predominantly calcite and gypsum. However, there are also many very irregular shaped grains rich in Na and Cl and are presumably NaCl (Fig. 5c).

Fig. 3. SEM Micrographs and EDS Spectra of Reaction Products Formed on the Top Surface of Experiment P-II-5 (26-Week Sample) (a) 2000X, (d) 15,000X, and (f) 100X

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 4. SEM Micrographs and EDS Spectra of Reaction Products Formed on the Bottom Surface of Experiment P-II-5 (26-Week Sample) (a) 13X, (b) 2000X, (d) 1930X, and (e) 4200X/8400X

Fig. 5. SEM Micrographs of Reaction Products Formed on the Top Surface of Experiment P-II-7 (52-Week Sample) (a) 5000X, (b) 100X, and (c) 1750X

The bottom surface has a coarse texture similar to that observed on the top surface. A fine-grained precipitated deposit covers much of the coarse reacted layer (Figs. 6a and 6b/EDS). It is not a continuous deposit and it has a porous structure visible at high magnification. Its composition is essentially the same as the coarse reacted layer (compare Figs. 6b/EDS and 6c/EDS). In places, both the precipitated deposit and the reacted layer have exfoliated, exposing etched glass from below (Fig. 6d). The presence of precipitates on the exposed glass indicates that exfoliation occurred during the experiment rather than after termination. Many small grains of NaCl are present (Figs. 6e and 6f/EDS).

3. Solution Analyses

The elemental releases from the two continuous experiments are presented in Fig. 7. Selected element releases normalized for glass composition and sample surface area are given in Table 7. All raw and corrected solution data are presented in Appendix I for both the continuous and batch experiments.

The release of Li, B, and U can be used to monitor glass reaction because they occur in low concentration in the J-13 water. In addition, they are not generally observed to be incorporated in secondary phases.¹¹ However, some caution must be exercised since tincalconite (hydrated Na-borate) has been detected on the surface of steam-reacted West Valley glass.¹¹ The Li release in both continuous experiments is similar being released at a slowly declining rate over the course of the experiments, reaching a cumulative value of $\sim 67 \mu\text{g}$ after 301 weeks. The release observed in the batch experiments, which includes a final rinse component not present in the continuous experiments, is only slightly greater than observed in the continuous experiments. The release of Li normalized to the total surface area of the sample and its concentration in the glass is $.25 \text{ g/m}^2$ after the 301-week sampling. Boron release is distinctly different from that of Li. Up through the 210-week period in the two

Fig. 6. SEM Micrographs and EDS Spectra of Reaction Products Formed on the Bottom Surface of Experiment P-II-7 (52-Week Sample)
 (a) 1000X/10,000X, (d) 500X/5000X, and (e) 1500X

Fig. 7.

Cumulative Release for Selected Elements from the P-II-1 and P-II-2 Continuous Experiments. (a) Boron, (b) lithium, (c) uranium, (d) sodium, (e) calcium, (f) magnesium, and (g) silicon

Table 7. Normalized Release in the P-II Series

Test #	Period (weeks)	Normalized Release (g/m ²)		
		B	Li	U
P-II-3	6	0.3	0.4	0.07
P-II-4	13	0.9	0.9	0.16
P-II-5	26	0.4	0.8	0.14
P-II-6	39	0.8	1.1	0.27
P-II-7	52	0.9	1.6	0.77
P-II-1	52	2.4	1.0	0.32
	104	3.0	1.8	0.53
	155	3.0	2.0	0.68
	210	3.2	2.5	1.10
	262	10.8	2.7	1.14
	301	11.0	2.7	1.14
P-II-2	52	1.0	1.2	0.26
	104	1.2	1.8	0.31
	155	1.3	1.9	0.57
	210	1.5	2.1	0.61
	262	3.8	2.4	0.65
	301	7.6	2.4	0.66

continuous experiments, B release leveled off. This was followed by a sharp increase in release. This increase coincides with the time when the vessels were modified to reduce fluid loss. After 301 weeks, release in the P-II-1 experiment is about 50% greater than in P-II-2. There are two possible explanations for this behavior. The first is that little or no reaction took place between 80 and 200 weeks due to vapor loss. Reaction then resumed once the vessel design was modified to retain more water. This is unlikely since the release of Li indicates that reaction continued throughout the entire duration of experiments. An alternative is that a B-bearing phase precipitated and then dissolved once more water was retained. As the continuous experiments are still ongoing, it is not yet possible to verify this contention.

There is a slow, steady release of U throughout the 301-week duration of the experiments. Like B, the release of U is about 50% greater in the P-II-1 experiment. It is not clear why this difference exists, although it is probably attributable to differing degrees of water retention in the two experiments.

There is a distinct and regular net negative release of Ca, Mg, and Si. This indicates that these elements were removed from solution during the experiment. This is consistent with the observed occurrence of calcite and gypsum on a Si-rich surface layer on samples from the batch experiments. This behavior suggests that some of the surface layer has formed by precipitation rather than transformation of the glass. Sodium also has a net negative release but its behavior is erratic. This may be the result of periodic precipitation and subsequent redissolution of NaCl and Na₂CO₃. The behavior of these elements demonstrates that the J-13 water plays a role in the formation of the secondary phases.

B. P-III Experiments

The glass surface area is the modified parameter in these experiments. The surface area is reduced by ~50% by shortening the glass cylinders. The area ratio of the "as cut" top and bottom surfaces to the side is reduced from ~2.6 to 0.8. The stainless steel components are from heat #22841. The metal was not heat treated except for the two TIG welds that join the supporting pins to the bottom part of the holder.

This set of experiments was initiated on 12/6/84 and the continuous experiments are still in progress, having completed the 260-week sampling. The experiments were performed at 90°C with an injection volume of 0.075 mL of EJ-13 water every 3.5 days. The batch experiments were terminated in duplicate after 13, 26, 39, and 52 weeks. The continuous experiments were sampled every 6.5 weeks through the 78th week and then about every 13 weeks thereafter. Two different batches of EJ-13 water were used, the compositions of which are given in Table 4. The change in EJ-13 water was on 10/1/86. The experimental matrix, along with selected weight change data, are presented in Table 8.

1. General Observations

(a) The WPA generally lost weight during the experiments. In most cases, the metal components gained a small amount of weight, presumably from precipitating phases; however, this gain was much less than the amount lost from the glass (Table 8). The one exception to this behavior is P-III-9 which showed a small net increase in weight.

(b) The top glass was always damp during sampling of the continuous experiments and termination of the batch experiments. The amount of water varied from being only at the rims of the metal perforations in the metal to almost filling the noncontact areas.

(c) Standing water was present on the bottom surface of the WPA. In some cases, water bridged the gap between the metal support posts and the side of the glass.

(d) Both the top and bottom metal components showed no local discoloration after the experiments. This suggests that reaction of the metal was minimal.

Table 8. Experimental Matrix and Weight Change Results for the P-III Series

Test No.	Test Period (weeks)	Date Started	Date Stopped	Initial Glass Mass (gm)	Final Glass Mass (gm)	Δ Mass ($\text{gm} \times 10^{-5}$)	SA Glass (cm^2)	Initial Top Canister Mass (gm)	Final Top Canister Mass (gm)	Δ Mass ($\text{gm} \times 10^{-5}$)
P-III-1a	6.5	12/06/84	in progress	3.16816			6.95	2.34690		
P-III-2a	6.5	12/06/84	in progress	2.70018			6.64	2.35423		
P-III-3	13	12/06/84	3/07/85	3.10109	3.10105	(4)	6.95	2.34086	2.34081	(5)
P-III-4	13	12/06/84	3/07/85	3.02165	3.02153	(12)	7.04	2.34245	2.34249	4
P-III-5	28	12/06/84	6/20/85	3.02670	3.02625	(45)	6.93	2.34668	2.34680	8
P-III-6	28	12/06/84	6/20/85	3.09710	3.09528	(182)	7.04	2.33905	2.33922	17
P-III-7	39	12/06/84	9/05/85	3.15518	3.15361	(157)	7.06	2.34517	2.34517	0
P-III-8	39	12/06/84	9/05/85	3.09808	3.09707	(101)	6.87	2.48966	2.48971	5
P-III-9	52	12/06/84	12/05/85	3.13821	3.13785	(36)	6.85	2.36099	2.36133	34
P-III-10	52	12/06/84	12/05/85	3.00496	3.00395	(101)	6.99	2.35664	2.35685	21

Cont'd

Table 8 (Cont'd)

Initial Bottom Canister Mass (gm)	Final Bottom Canister Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Initial Total Vessel Mass (gm)	Final Total Vessel Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Water Added During Testing
3.34069			318.94	319.74	0.80	0.975
3.34735			312.07	312.99	0.92	0.975
3.34158	3.34152	(6)	316.93	318.64	1.71	1.95
3.34538	3.35432	(6)	313.36	314.96	1.60	1.95
3.32778	3.32782	4	318.62	322.23	3.61	4.20
3.33474	3.33526	52	318.12	321.63	3.51	4.20
3.35074	3.35113	39	318.48	323.32	4.84	6.15
3.32720	3.32739	19	318.49	323.29	4.80	6.15
3.33064	3.33098	34	319.14	325.31	6.17	7.80
3.34616	3.34637	21	321.49	327.07	5.58	7.80

2. Component Analyses

The glass and metal components were first examined optically up to a magnification of 140X. At this time, surface features were mapped and areas for further investigation were identified. Some samples were examined by SEM/EDS/WDS and/or SIMS. At least one sample from each experiment was examined.

a. P-III-3 and P-III-4, 13-Week Samples

The metal components of the P-III-3 and P-III-4 samples are very similar in appearance. The parts of the components not in direct contact with the glass have no evidence of accelerated reaction. In the areas where glass contact occurred, there is a thin Si-rich mat developed (Fig. 8a, 8b/EDS). Its texture is essentially the same as that observed on the glass (see below). In a few places this mat forms thicker clumps (Figs. 8c, 8d/EDS, 8e, and 8f/EDS). Overall, precipitate coverage is heavier on the bottom component. Aside from the Si-rich deposit, other precipitated phases include chloride (NaCl?) and sulfates ($\text{CaSO}_4?$) as shown in Figs. 8e, 8f/EDS, 8g, and 8h/EDS. Note the small Ca and S peaks in the EDS spectrum in Fig. 8f/EDS. This suggests the intermingling of phases at a very fine scale. There are also some small irregular-shaped masses rich in Na (Figs. 8i and 8j/EDS). These are electron beam sensitive and are similar to that observed on the P-II samples which were tentatively identified as Na_2CO_3 (compare Fig. 8i with Figs. 4d and 4e).

The bottom glass surface has partially defined regions of metal and nonmetal contact. This duality in appearance suggests that there was not close metal-glass contact over the entire surface. The contact and noncontact regions have the same appearance where the "as-cut" contours of the glass are still clearly defined but the surface appearance has been transformed from a smooth fractured surface to one covered with an interwoven phase with a "cardhouse" texture (Fig. 9a). Its texture and composition are consistent with a smectite clay (Figs. 9b/EDS and 9c/EDS). Small precipitates are present in crevices and fractures on the glass surface (Fig. 9d). From EDS analysis, these range in composition from only containing Si to having Si and Al to having Si, Al, Cr, and Mn (Figs. 9e/EDS, 9f/EDS, and 9g/EDS). This apparent compositional range may be attributable to the presence of multiple phases at a fine scale.

On the top glass surface, the noncontact areas are clearly defined as light gray to tan circular regions set on a dark brown-black background. The contact areas (with the metal component) have the same textured appearance as observed on the bottom glass (Fig. 9a), but the noncontact areas either retain an unreacted appearance or show incipient development of a textured layer (Fig. 9d). EDS spectra taken from all regions of the top surface are similar to unreacted glass.

(a)

1000X

10,000X

(b)

(c)

1000X

(d)

Fig. 8. SEM Micrograph and EDS Spectrum of (a and b) the Metal Surface in Contact with Glass from the Top Section of the Waste Form Holder in Experiment P-III-4; (c and d) Clumps of the Mat Materials that Formed on the Top and Bottom Metal Sections from Experiment P-III-4; (e-j) Reaction Products Observed on the Bottom Metal Section from Experiment P-III-4.

(e)

1000X

(f)

(g)

800X

(h)

(i)

1010X

(j)

Fig. 8. Cont'd

(a)

(b)

(c)

(d)

Fig. 9. SEM Micrographs and EDS Spectra of Reaction Products on the Bottom Surface of the Glass from Experiment P-III-4. This is typical of both metal contact and noncontact regions. (a) 1000X/10,000X. EDS spectra of the contact and noncontact regions are shown in (b) and (c), respectively, (d) 1000X/10,000X (see text)

Fig. 9. Cont'd
SEM Micrograph and EDS Spectra of Reaction Products on the Bottom Surface of the Glass from Experiment P-III-4. (h) 1000X/10,000X view of noncontact area

SIMS depth profiling was performed on the P-III-3 glass. The profiles are normalized to ^{28}Si intensity. The normalization is a standard technique used to account for variations in the sputtering conditions. As a result, the profiles only show preferential depletion or enrichment relative to Si which is the most abundant component in the glass. Depth profiles of Li, B, and Mg from the contact and noncontact areas of the bottom glass and from the side glass are presented in Fig. 10. In all cases, Li is depleted to a depth of at least 1 μm . The depletion is not sharp, but instead is of a gradual nature. Boron is also depleted on the bottom surface but it appears to be restricted to the outer 0.3 μm (see mark on Fig. 3b profile). No B depletion is apparent on the side glass surface, however. Relative to Si, the distribution of Mg is constant.

In summary, the extent of reaction is greatest on the bottom surface and least on the sides. Depletion of Li appears to occur to a greater depth than B. Precipitation of Si-rich "clay" and other phases occurs on both the metal and glass components. This masks the original concoidally fractured appearance of the glass surfaces.

b. P-III-5 and P-III-6, 26-Week Samples

The metal components have the same general appearance as that described for sample P-III-4. The noncontact-contact boundaries are well defined. A Si-rich deposit covers the metal especially where it was in contact with the glass and is much thicker on the P-III-6 components. Development of this deposit is greatest on the bottom component in the contact areas and in the noncontact areas where standing water was present during the experiment (Fig. 11a). This Si-rich material also occurs in clumps. Some of these clumps contain a mixture of phases which may be rich in Ti, Cl, and/or S (Figs. 11b, 11c/EDS, 11d, and 11e/EDS). The presence of anhydrite or gypsum is suggested by the Ca and S peaks in the EDS spectrum shown in Fig. 11e/EDS. A U-bearing phase occurs on the noncontact area (Figs. 11f and 11g/EDS). It contains Si and Ca and has an acicular form, suggestive of uranophane. There was not enough material available for XRD analysis.

The top glass surface has no clearly marked circular noncontact regions and the original surface contours are still apparent. The surface is covered by a Si-rich layer similar in composition to that observed on other samples. Clumps of this same material are also present.

The bottom glass surface is megascopically different in appearance from the outer samples. It has a uniform gold-colored haze and the contact and noncontact areas are only partially visible. At higher magnification, the surface has a thick textured surface layer which is somewhat coarser than observed elsewhere (Fig. 12a). Its composition is consistent with a Ca-smectite (Fig. 12b/EDS). The original surface contours are only barely visible and are considerably rounded. In one region, the surface layer is discontinuous, exposing the glass from below (Fig. 12c). Here, it appears that the thick surface layer exfoliated during the experiment and the glass is now partially overgrown by precipitation of Si-rich "clay." A small cluster of yellow grains is also present on the exfoliated surface (Figs. 12d and 12e/EDS). These grains contain Na, Ca, S, and Cl but have not been positively identified.

Fig. 10. SIMS Spectra Showing the Profiles of Li, Mg, and B Relative to Si for Sample P-III-3 (a) Bottom Section Non-Metal Contact, (b) Bottom Section Metal Contact, and (c) Side Surface. Note the different depth scale in (c)

Fig. 11.
SEM Micrographs and EDS Spectra of
Reaction Products on the Metal
Components of P-III-6. (a) 150X, contact
area, (b and c) SEM micrograph (3500X)
and EDS spectrum of a Ti-rich alteration
product. Note the thick matted
appearance of the metal surface. (d) SEM
micrograph 1250X of Si-rich alteration
product. (e) EDS spectrum of Deposit
shown in (d), (f) SEM micrograph of
U-rich phase at 4500X, and (g) EDS
spectrum of phase shown in (f).

Fig. 12.
SEM Micrographs and Associated EDS Spectra from the Bottom Glass Section from Experiment P-III-6. (a) Reacted contact area (1000X/10,000X); (b) EDS spectrum of surface in (a); (c) exfoliated, precipitated area (990X); (d) yellow crystals (100X/1000X) from near the exfoliated region; and (e) EDS spectrum of yellow crystals. Note the high Na and Cl content

c. P-III-7 and P-III-8, 39-Week Samples

Sample P-III-8 visually appears to be somewhat more altered so it was investigated further by SEM/EDS. A Si-rich deposit, probably smectite, occurs on both the contact and noncontact regions of the top metal component. The noncontact-contact boundary is well marked (Fig. 13a). The Si-rich deposit also occurs in clumps, some of which contain Mn, Cr, or Fe (Figs. 13b and 13c/EDS). Based upon numerous EDS spectra, the Al content appears to be somewhat variable. A Ti-rich phase occurs rarely and seems to be intimately associated with clumps of Si-rich "clay" (Fig. 13d/EDS). It may be anatase (TiO_2), but XRD analysis was not possible to confirm this.

The bottom metal component is discolored in areas around the support pin welds, but there is no indication of glass-metal reaction. The noncontact-contact boundary is well defined. Like the top component, a Si-rich deposit also covers the bottom metal piece. Clumps of precipitates are extensively developed, many of which have the same composition as the deposit (Fig. 13e). Some thin disc-shaped masses are present which are rich in Ca and S suggesting they are either gypsum or anhydrite (Figs. 13f and 13g/EDS). Other, thicker disc-shaped grains occur which appear to be pieces of the surface layer that stuck to the metal when the sample was disassembled after termination of the experiment (Fig. 13h).

The circular noncontact areas are well marked on the top glass surface. However, there is no significant difference in composition between the noncontact and contact areas. The "as-cut" contours are partially obscured by growth of the reacted layer. Exfoliation of this layer has occurred in places, exposing the glass from below. In these areas, precipitates now partially cover the glass surface. These precipitates, like numerous clumps elsewhere, have a similar composition and appearance to that of the surface layer.

The bottom glass surface also appears highly reacted with the identity of the "as-cut" contours being almost obscured by the presence of a surface layer. The layer, as well as many clumps on the surface, have the same texture and composition as found on the top glass. However, in one area, a smooth overgrowth is present that is somewhat enriched in Ca. The surface layer has exfoliated in some places and a discontinuous cover of precipitates is present on the newly exposed surface.

The side glass near the bottom surface was also investigated by SEM/EDS. The surface has a textured appearance with a "cardhouse" type structure and composition consistent with smectite. There are two layers closest to the bottom surface with a precipitation front visible several millimeters up the side (Fig. 14a). Many chloride-bearing grains are present at this front (Fig. 14c/EDS). Some mottled regions of the upper layer are rich in Fe and Mn suggesting the presence of Fe-Mn oxides or hydroxides intermingled with smectite (Figs. 14d and 14b/EDS). The lower layer has a similar morphology and composition to the upper layer. In places where the lower layer has broken away during sample preparation, a view in the third dimension is possible (Fig. 14d). The layer appears to only be a coating on an otherwise smooth glass surface which suggests the layer developed solely by precipitation rather than by direct glass reaction. This is supported by the presence of small regions

(a)

(b)

(c)

(d)

Fig. 13. SEM Micrographs and EDS Spectra of Features from the Top Metal Component of Experiment P-III-8. (a) Glass contact/noncontact interface (6000X); (b) Mn-enriched cluster of alteration products (1000X/10,000X); (c) EDS spectrum of material shown in (b); (d) EDS spectrum of Ti-rich grain

(e)

(f)

(g)

(h)

Fig. 13. Cont'd
 SEM Micrographs and EDS Spectra of Features from the Top Metal Component of Experiment P-III-8. (e) micrograph (300X) showing general view of precipitate coverage; (f) micrograph (1000X/5000X) of dark splotches. (g) EDS spectrum of splotches shown in (f); and (h) micrograph (600X) of a piece of the altered layer from the glass that stuck to the metal component on separation

Fig. 14. SEM Micrographs and EDS Spectra of the Side Glass of P-III-8.
 (a) View (700X) of the precipitation front (see text); (b) EDS spectrum of precipitated surface layer; (c) EDS spectrum from the precipitation front where chlorides are intergrown with the Si-rich "clay"

where the lower layer is incomplete. Here, loosely connected precipitates encroach on small open areas where apparently etched glass is exposed (Fig. 14f). However, investigation of the layer formed on the side surface using analytical electron microscopy provides a more detailed description of the structure of the reacted glass, and should help identify the process by which the glass reacts (see addendum).

d. P-III-9 and P-III-10, 52-Week Samples

The glass surfaces of both samples were analyzed by SEM/EDS and SIMS, but the metal components were not examined.

(1) P-III-9

This sample appears to be more reacted than P-III-10. The top glass surface looks highly reacted and cracked and is covered with precipitates (Fig. 15a). However, the noncontact areas are not distinct from the contact areas. The light-colored streaks in Fig. 15a are due to charging along cracks in the surface layer. The layer is Si-rich and is essentially the same composition as observed for other samples (Fig. 15b/EDS). Exfoliation of portions of the surface layer is common (Fig. 15a). Other areas are in the processes of exfoliating as shown in Fig. 15c. The newly exposed glass has the appearance of having been etched (Figs. 15a and 15c). There are numerous precipitates on the surface, often associated with the exfoliated areas. Many are Ca- and S-rich and are probably gypsum or anhydrite (Figs. 15d and 15e/EDS). Round grains and thin threads of NaCl occur over the entire surface (Fig. 15f). Other chlorides, possibly CaCl_2 , are also indicated from the EDS spectrum shown in Fig. 15g/EDS. Small grains of Fe-Mn oxide or hydroxide are often intimately associated with the Si-rich "clay" surface layer.

The bottom glass surface has distinctly lighter color noncontact areas (Fig. 16a). Like the top surface, a thick surface layer has developed which is extensively cracked and is exfoliating, especially in the noncontact areas (Figs. 16a, 16b, and 16c). The "as-cut" appearance is completely masked and there are numerous precipitates on the surface. Most of the precipitates, like those in Fig. 16c, are probably either gypsum or anhydrite.

SIMS profiles were obtained from the top and bottom surfaces. Silicon normalized profiles for several elements from the bottom surface are presented in Fig. 17. Lithium is depleted relative to Si to a depth of 2.5 μm , while Mg, Mn, and K (not shown) are relatively enriched close to the surface. Boron shows some depletion in the near-surface region.

(2) P-III-10

Only the bottom surface of P-III-10 was investigated. The noncontact areas are partially visible and the "as cut" contours are obscured by the growth of a Si-rich surface layer. This layer is generally coarser grained than observed on P-III-9 (Fig. 18a). Exfoliation of the surface layer has occurred in places, although to a lesser extent than on P-III-9. The newly exposed glass is etched and appears to be somewhat altered (Fig. 18b). Small round precipitates dot the surface which contain Ca and S and are probably either gypsum or anhydrite.

Fig. 15. SEM Micrographs and EDS Spectrum from the Top Glass Surface of P-III-9. (a) General surface with Ca/S-rich precipitates and exfoliated region (500X), (b) EDS spectrum of surface layer, (c) initial phase of exfoliation (400X), and (d) Ca-S precipitates on surface (5000X)

Fig. 16. Optical Photographs of the Bottom Glass Surface of P-III-9. (a) 6X; (b) ~12X, the spot with the dark halo is the result of a SIMS analysis. SEM micrographs of features from the bottom glass surface of P-III-9. (c) General surface appearance (1000X) and (d) higher magnification of surface (10,000X) showing a cracked region plus small Ca/S-rich grains

Fig. 17. SIMS Profiles of the Bottom Glass Section from Experiment P-III-9 in a Region of Glass-Metal Contact

Fig. 18. (a) SEM Micrograph (5000X) Showing the Coarse-Grained Appearance of the Surface Layer; (b) Micrograph (10,000X) Showing Exposed Etched Glass; and (c) SEM Micrograph of a Cross Section of the Bottom Glass Surface from P-III-10

A polished cross section of the bottom glass was also prepared and studied by SEM (Fig. 18c). A band $\sim 1.5 \mu\text{m}$ thick is visible at the edge of the glass. The band is comprised of regions of varying electron density contrast with the bright streaks due to charging at the sample-epoxy interface. A survey of the unreacted glass was performed to check for inhomogeneities in the glass. Overall, the composition is quite uniform except that traces of S and Cl are intermittently detectable.

SIMS profiles were obtained from the bottom surface and the side of the glass (Figs. 19a and 19b). The profiles, normalized to Si, are broadly similar to those from P-III-9. Lithium is depleted to a depth of $\sim 1.5 \mu\text{m}$ on the bottom surface, which is consistent with the thickness of the altered layer observed by the SEM (Fig. 18c). Boron is also depleted in the near surface. The depletion is more gradual on the bottom than it is on the side.

3. Solution Analyses

Elemental releases from the continuous experiments are shown in Fig. 20, and normalized releases for selected elements are given in Table 9. The raw data and the background subtracted cumulative releases are included in Appendix I for both the continuous and batch experiments.

Partial blockage of the inlet lines occurred in P-III-2 after the second year of the experiment and has continued intermittently to date despite efforts to clear the line without disassembly of the system. However, at no time was the line completely blocked. As a result, less water was injected during these periods than was required.

Fig. 19. SIMS Profiles of the Reacted Bottom and Side Surfaces of the Glass from Experiment P-III-10. (a) Bottom surface metal contact and (b) side surface

There is good agreement in the element release trends between the P-III-1 and P-III-2 experiments. There is some divergence apparent in the most recent analysis, which correlates with the smaller amount of fluid recovered from the P-III-2 vessel. Normalized release of Li is the greatest of all elements, reaching a value of $\sim 6.5 \text{ g/m}^2$ after 260 weeks. The rate of Li release in both experiments decreased steadily for the first two years after which the rate became relatively constant. However, since about 170 weeks, the rate has increased fairly sharply, especially in the P-III-1 experiment (Fig. 20). The normalized release of B at 260 weeks is $\sim 3.1 \text{ g/m}^2$ or about half that of Li. The trend of release closely follows that of Li over the entire duration of the experiments. The rate of U release has been fairly constant, although a slight increase seems to have occurred after about 170 weeks. The normalized release reached $\sim 3.3 \text{ g/m}^2$ after 260 weeks which is about the same as for B.

Fig. 20. Cumulative Release of Selected Elements from the P-III-1 and P-III-2 Continuous Experiments

Table 9. Normalized Release in P-III Series

Test #	Period (weeks)	Normalized Release (g/m ²)		
		B	Li	U
P-III-3	13	0.2	1.0	0.1
-4	13	0.3	1.1	0.2
-5	28	0.7	1.8	0.6
-6	28	3.2	4.3	2.3
-7	39	3.1	4.2	2.1
-8	39	2.0	3.3	1.5
-9	52	3.7	5.6	2.6
-10	52	2.3	4.0	1.7
P-III-1	52	0.7	2.1	0.6
	104	1.1	3.2	0.8
	156	1.5	4.1	1.2
	208	2.2	5.4	2.3
	234	2.8	6.3	2.8
	260	3.6	7.3	3.4
P-III-2	52	0.5	1.9	0.4
	104	0.9	2.8	0.8
	156	1.4	3.8	1.1
	208	1.9	4.7	2.2
	234	2.3	5.3	2.7
	260	2.6	5.8	3.3

There is a consistent net negative release of Ca and Mg, indicating that these elements have been removed from the injected EJ-13 water and incorporated into the secondary phases. This is consistent with the ubiquitous occurrence of gypsum or anhydrite on the batch samples. The Mg may be accommodated in the Si-rich "clay" layer.

Both Na and Si have erratic release patterns which are similar in the P-III-1 and P-III-2 experiments. This variable behavior may be attributable to periodic precipitation and redissolution of NaCl (or Na₂CO₃?) which is observable on the batch samples. There was a net negative release of Si through the first year followed by a sharp positive release. Then, at the 104-week period for P-III-1 and the 91-week period for P-III-2, the Si release rate diminished. The reason for this behavior is unclear; however, it may be caused by secondary phase formation such as smectite. The sharp increase in release may indicate the initiation of surface layer exfoliation. Since the surface layer is composed predominantly of Si, if pieces of the layer were to fall into the solution, the subsequent acidification of the solution during sampling would preferentially enhance the Si concentration relative to the other elements.

Except for the 13-week samples, elemental release is usually much greater in the batch experiments compared to the continuous experiments (Table 9). At the 13-week period, releases are about the same in both types of experiments. While the WPA wash that is incorporated into the termination procedure of the batch experiments adds about 10% to the total release, this cannot account for the up to five-fold difference that is observed for some elements (Appendix I). The extent of element release is markedly different between the duplicate batch experiments terminated after 28 and 52 weeks. The reason for this discrepancy is unknown, although there is a correlation between larger release and a greater volume of solution recovered from the vessel upon termination of the experiments.

4. Discussion

The observation that normalized release of Li is twice that of B suggests these elements behave differently during glass reaction and that nonstoichiometric dissolution has occurred. SIMS profiles are consistent with the solution release trends in that B is retained to greater degree than Li in the residual altered layer (Figs. 10, 17, and 19). Another possibility is that B is incorporated in secondary phases. No B-bearing phases have been detected using the WDS system. While both Li and B are removed from the glass during reaction, Li is depleted to a greater depth than B (Figs. 10, 17, and 19). This suggests that Li is more mobile than B and, therefore, a greater volume of glass is leached of Li per unit time. Correlation of the SIMS data with AEM data will hopefully more clearly define the leaching process.

Depletion of Ca, Mg, and Na in solution is associated with the formation of secondary phases on the WPA. The erratic nature of Na release may be due to periodic precipitation of NaCl or Na₂CO₃? followed by dissolution.

The most abundant secondary phase is the Si-rich layer that is present on both the glass and metal components. Its composition and "cardhouse" type texture suggests it is composed of smectite (e.g., Figs. 12a and 12b/EDS). The deposit on the metal and at least some of the layer on the glass formed by precipitation. Other parts of the layer on the glass may have transformed *in situ* from the altered glass, although this has not been demonstrated definitively. Release of Si into solution does not follow a systematic trend (Figs. 20a and 20b). This may in part be due to exfoliation of the surface layer.

Exfoliation of the surface layer is observed in all samples that reacted for at least 26 weeks (i.e., P-III-6, P-III-8, P-III-9, P-III-10). Precipitation of Si-rich "clay" on the newly exposed glass indicates that exfoliation must have occurred during the experiment. This process has important implications for the rate of glass reaction and for interpretation of solution chemistry data.

C. P-IV Experiments

The purpose of these experiments is to examine the effect of reducing the water volume during each injection period. While maintaining the normal injection interval of 3.5 days, the drop volume is reduced by 50% to 0.038 mL. The surface area of the glass is also reduced by ~50%, which is the same as for the P-III experiments.

The experiments were initiated on 2/18/85 and have been completed through 247 weeks. The batch experiments were terminated in duplicate at 25.5 and 52 weeks. The continuous experiments are ongoing and have been sampled every 13 weeks up to 221 weeks and for longer intervals since. Two batches of EJ-13 water have been used (Table 4). The switch in batches occurred after 91 weeks. The experimental matrix is given in Table 10.

1. General Observations

The appearance of the WPA during the sampling periods and at termination was very similar to that noted for the P-III experiments. The top surface of glass was damp in the areas not in contact with the stainless steel and there was standing water around the circumference of each hole in the metal. There were small droplets of water present on the top surface of the stainless steel. However, there was no evidence of localized reaction between the metal and glass. The bottom surface had standing water around the circumference of the glass and between the glass and the metal rim. The regions of nonmetal contact were also wet. In some experiments water bridged the gap between the glass and the metal support pin(s).

The weight change measurements (Table 10) indicate that the glass lost weight during all experiments. There is good reproducibility between duplicate samples, and the 52-week samples show slightly more than twice the weight loss of the 25.5-week samples. The metal sections gained weight in most cases with the weight gain being greater for the shorter tests than the longer.

2. Component Analyses

The glass from all the terminated batch experiments was examined optically, and the top and bottom surfaces of P-IV-3 and P-IV-5 were investigated by SEM/EDS.

a. P-IV-3 and P-IV-4, 25.5-Week Samples

The general appearance of the two samples is similar. The noncontact areas on the bottom surfaces are clearly visible, appearing as light gray circles on a dark background. There is no such demarkation on the top surface of P-IV-3. However, small irregular whitish patches occur in the central portions of the noncontact areas. Dark circular regions are discernible on the top surface of P-IV-4. The side surfaces are generally shiny brown-black with irregular-shaped areas that correspond to regions of standing water during the experiments. This includes the lower third of the sides where a cracked and peeled bronze-colored scale is present. Near the top surface is an irregularly distributed whitish deposit.

Table 10. Experimental Matrix and Weight Change Results for the P-IV Series

Test No.	Test Period (weeks)	Date Started	Date Stopped	Initial Glass Mass (gm)	Final Glass Mass (gm)	Δ Mass ($\text{gm} \times 10^{-5}$)	SA Glass (cm^2)	Initial Top Canister Mass (gm)	Final Top Canister Mass (gm)	Δ Mass ($\text{gm} \times 10^{-5}$)
P-IV-1a	13	2/18/85	in progress	3.06736			6.90	2.35246		
P-IV-2a	13	2/18/85	in progress	2.92639			6.81	2.36709		
P-IV-3	25.5	2/18/85	8/19/85	3.17915	3.17880	(350)	6.84	2.35355	2.35306	310
P-IV-4	25.5	2/18/85	8/19/85	3.01384	3.01334	(500)	6.81	2.35334	2.35334	100
P-IV-5	52	2/18/85	2/17/86	3.03562	3.03438	(1240)	6.85	2.36914	2.36924	100
P-IV-6	52	2/18/85	2/17/86	2.74079	2.73976	(1030)	6.55	2.36495	2.36500	50

Cont'd

Table 10 (Cont'd)

Initial Bottom Canister Mass (gm)	Final Bottom Canister Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Initial Total Vessel Mass (gm)	Final Total Vessel Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Water Added During Testing
3.34578			319.14	319.65	0.51	0.975
3.33530			317.33	317.99	0.66	0.975
3.37079	3.37114	350	319.39	310.48	1.09	1.988
3.34849	3.34877	280	320.08	321.09	1.01	1.988
3.34193	3.34216	230	313.67	315.89	2.22	3.90
3.34688	3.34685	(030)	318.49	320.84	2.35	3.90

Examination of the bottom glass surface of P-IV-3 by SEM reveals a surface layer has developed similar to that observed on the P-III samples (compare Figs. 21a and Fig. 12a). The layer is Si-rich and is depleted in Na and enriched in Fe and Mn relative to the glass. The development of this layer in the noncontact areas is incomplete (Fig. 21b). Here, glass is still exposed over approximately 10% of the area. It appears that most of the surface layer has formed by precipitation (Figs. 21b and 21c). The glass is quite smooth, even at 10,000X magnification, although there is some fine-scale structure indicating reaction has occurred (Fig. 21c).

The top glass surface has retained most of its original "as cut" appearance; however, clear evidence of reaction is revealed at higher magnification (Figs. 22a, 22b, and 22c). A Si-rich layer has developed across the entire surface.

The contact and noncontact areas are texturally indistinguishable at the scale of the SEM. There are numerous isolated precipitates present which are too small for XRD analysis, but EDS spectra indicate several different compositions. Some have essentially the same composition as the surface layer, while others are composed only of silica and are possibly quartz or opal. Some calcite is present. There are also clusters of precipitates rich in Cr, Fe, and Mn and are probably an oxide or hydroxide phase.

b. P-IV-5 and P-IV-6, 52-Week Samples

The bottom surfaces of these two samples have clearly marked noncontact areas that are light gray in color. These areas are intact on P-IV-6, but on P-IV-5, a surface layer is observable which is cracked and has separated from the glass in many places. This is similar to the appearance of several samples from the P-III experiments.

The top surfaces are very different in appearance. The noncontact areas on P-IV-5 are fairly well marked, being darker than the light blue-green to brown contact areas. Small whitish patches of precipitates are present in the center of a few of the noncontact areas. The noncontact areas on P-IV-6 are barely discernible. An extensive array of saw marks is the most prominent feature which form whitish streaks on a relatively uniform dark background.

The bottom surface of P-IV-5 has a similar appearance to that of P-IV-3 under the SEM, except that there are many small Ca- and S-bearing grains which are probably gypsum or anhydrite (Fig. 23a). A Si-rich layer is present but it is incomplete, exposing glass from below. In some places, the layer is cracked and pieces have exfoliated (Fig. 23a). The process of cracking and exfoliation has begun even before the surface layer has completely developed. The exposed glass surface shows only slight evidence of etching but, otherwise, it looks unreacted (Figs. 23a and 23b). However, the early stages of alteration, where a gel layer forms, may not be readily discernible by SEM.¹² Precipitation of a Si-rich layer appears to be quite rapid in the freshly exposed areas.

Fig. 21. SEM Photomicrographs of the Bottom Glass Surface from Experiment P-IV-3. (a) General surface, ss contact (5000X); (b) general surface, noncontact (1000X); and (c) localized precipitation in the noncontact area (10,000X)

Fig. 22. SEM Photomicrographs of the Top Glass Surface from Experiment P-IV-3. (a) General surface (2000X); (b) general surface texture (10,000X); and (c) general surface (5000X)

Fig. 23. SEM Micrographs of the Bottom Glass Surface from Experiment P-IV-5. (a) Exfoliation of surface layer and numerous Cs-S grains (600X) and (b) glass surface with only partial coverage of precipitates (300X)

The top surface of P-IV-5 is also similar to the top of P-IV-3. Although the "as cut" contours are still readily visible, a uniform continuous fine-grained surface layer has developed (Fig. 24a). Its Si-rich composition is typical of the layers developed on other samples. No exfoliated areas are present. However, there are numerous places where the layer is cracked and small pieces are raised up from the glass (Fig. 24a). This suggests an incipient stage in the exfoliation process. The surface is dusted with small ($\leq 2 \mu\text{m}$) round grains of gypsum or anhydrite (i.e., Ca + S bearing). Other precipitates include clusters of Cr-, Mn-, Fe-, and Ni-bearing grains (Fig. 24b) which are probably oxide or hydroxide phases. Their composition is variable from containing mostly Fe and Ni, to containing Ni only, to containing predominantly Cr and Mn (Figs. 24c/EDS, 24d/EDS, and 24e/EDS). Others have compositions similar to stainless steel (compare Fig. 24f/EDS with Fig. 2c/EDS).

3. Solution Analyses

Elemental releases from the continuous experiments are presented in Fig. 25 and normalized release of Li, B, U, Na, and Si are given in Table 11. The raw data and the background subtracted cumulative releases are included in Appendix I for the batch and continuous experiments.

The trends in element release are similar between experiments P-IV-1 and P-IV-2 (Fig. 25). However, the magnitude of release from P-IV-2 is on the order of two times that of P-IV-1. It is not clear why these two experiments, which show the same release pattern, should have such different overall release. In both experiments Li, B, Na, Si, and U all have positive releases. After 182 weeks, however, a sharp reduction in the rate of release is apparent for all these elements suggesting a slowing of glass reaction and/or release from the WPA.

Lithium has the greatest normalized release, although it is not much greater than B or Na (Table 11). Release of U is only slightly less than B and Na. Silicon release is much less than these elements. This is attributable to the formation of the Si-rich surface layer on the glass and metal which acts as a sink for Si. The only element with a negative release is Ca. This indicates significant precipitation of a Ca-bearing phase or phases which depletes Ca in the EJ-13 water. This correlates with the observation of tiny grains of gypsum or anhydrite distributed over the surfaces of the batch samples.

4. Discussion

The top and bottom surfaces in the P-IV batch experiments have a different appearance visually as well as under the SEM. The surface layer on the bottom surfaces has a textured appearance and coverage is incomplete. In some places, it is evident that pieces of the surface layer have exfoliated, exposing patches of glass from below. Elsewhere, it appears that the surface layer never developed completely across the glass. Based upon the generally unreacted appearance of the exposed glass, and the distribution of new deposits in the partially covered areas, it seems that the surface layer has formed mostly by precipitation. Other precipitated phases are conspicuous by their absence.

Fig. 24. SEM Micrographs and EDS Spectra of Reaction Products on the Top Surface of P-IV-5. (a) Micrograph (2000X/10,000X) of surface layer); (b) micrograph (2000X) of surface layer and Cr-, Mn-, Fe-, and Ni-bearing grains; (c-f) EDS spectra of grains shown in (b)

Fig. 25. Cumulative Release of Selected Elements from the P-IV-1 and P-IV-2 Continuous Experiments

Table 11. Normalized Elemental Release for the P-IV Series

Test #	Period (weeks)	Normalized Release (g/m ²)				
		Na	Si	B	Li	U
P-IV-3	25.5	2.4	0.6	1.4	2.3	1.0
P-IV-4	25.5	2.1	0.6	1.2	2.0	1.0
P-IV-5	52	4.4	1.5	2.9	3.8	2.0
P-IV-6	52	4.5	1.0	1.7	3.1	1.0
P-IV-1	52	4.1	1.4	3.9	5.0	3.9
	104	9.3	3.4	9.8	11.0	7.8
	156	19.8	9.0	20.6	23.2	15.8
	208	24.2	10.9	24.6	28.4	18.8
	247	23.2	10.9	24.9	29.0	19.7
P-IV-2	52	2.9	0.6	2.7	3.8	2.7
	104	4.8	1.2	5.8	7.1	4.8
	156	9.7	3.4	9.7	11.9	8.5
	208	13.5	5.3	13.2	16.4	11.7
	247	12.2	5.1	13.4	16.7	12.0

In contrast, the top surfaces are completely covered with a rather uniform fine-grained material whose morphology is only apparent at very high magnification. The "as-cut" contours of the original glass surface are still easily discernible. Cracking and puckering of the layer are visible but this has not progressed to the point of exfoliation. The uniformity of this deposit, and the preservation of the original surface topography, suggest this layer formed mostly through alteration of the glass rather than by precipitation. A precipitated layer tends to have irregular coverage and masks surface features. However, numerous small precipitated grains rich in Ca and S or Cr, Mn, Fe, and Ni occur on the surface.

The P-IV experiments have the greatest normalized elemental release of any of the parametric experiments. This is a curious result considering that the volume of injected water is less than for the other experiments. It is possible that the smaller fluid volume saturates more rapidly, thereby causing precipitation of secondary phases. This could in turn enhance glass reaction by maintaining solute concentrations significantly below the apparent saturation level for the glass. However, the amount of precipitates on the P-IV samples is certainly no more and probably less than that observed on samples from other experiments. Furthermore, observation of the WPA's during sampling of the continuous experiments indicates that the surfaces were always wet or damp which is not the case for most other experiments. This suggests greater

water-glass contact despite the fact that less water is injected. An explanation for the high release in the P-IV experiments may be that glass reaction is continuous due to the perpetual availability of water. In other experiments, where WPA surfaces are occasionally observed to be damp or dry, glass reaction would only be periodic in nature.

D. P-V Experiments

In this set of experiments, the injection rate is reduced from one drop every 3.5 days to one drop every 14 days. All other parameters follow the standard configuration and procedure. The experimental matrix is given in Table 12. The P-V series was initiated on 6/10/85 and the batch experiments were terminated after 26, 52, 110, and 254 weeks. One continuous experiment has been in progress for 234 weeks while the other was terminated after 39.5 weeks because of problems that arose with the WPA during sampling. At the onset, the experiments were conducted using silicone gaskets in an attempt to minimize water loss. This sort of gasket has been used in MCC-1 type leaching experiments with no observed loss of solution.¹³ However, in the P-V experiments, the silicone rubber extruded inside the vessel during closure, providing the opportunity for Si contamination of the solution that collected at the bottom of the vessel. The gasket material in the continuous experiments was changed to TeflonTM after the 26-week sampling.

1. General Observations

Upon termination of the batch experiments, the bottom of the WPA was always wet with some standing water present. The top of the WPA ranged from wet with standing water rimming the inside of the circular holes in the metal, to damp with no standing water, to completely dry in the exposed surface areas. For the continuous experiment, the bottom was usually wet with standing water, however, sometimes it was damp or dry. The top ranged from wet to dry, with dry being the most common state.

All the metal components have a shiny appearance with no local discoloration occurring in any of the experiments. No particulates were ever observed in the solutions during sampling. The glass gained a small amount of weight in all the experiments (Table 12). Some of the metal components gained a very small amount of weight while others showed a slight weight loss.

2. Component Analyses

The glass from all the terminated batch experiments was examined optically. The top and bottom surfaces of P-V-3, P-V-4, and P-V-7 were studied by SEM/EDS, but only the top of P-V-6 was investigated. None of the metal components were examined in detail.

Table 12. Experimental Matrix and Weight Change Results for the P-V Series

Test No.	Test Period (weeks)	Date Started	Date Stopped	Initial Glass Mass (gm)	Final Glass Mass (gm)	Δ Mass ($\text{gm} \times 10^{-5}$)	SA Glass (cm^2)	Initial Top Canister Mass (gm)	Final Top Canister Mass (gm)	Δ Mass ($\text{gm} \times 10^{-5}$)
P-V-1a		6/10/85	in progress	10.06318			13.6	2.63885		
P-V-2a	39.5	6/10/85	3/13/86	9.98827			13.4	2.61856	2.61860	4
P-V-3	26	6/10/85	12/09/85	10.13239	10.13270	310	13.6	2.62487	2.62490	30
P-V-4	52	6/10/85	6/09/86	9.99708	9.99739	310	13.5	2.62150	2.62150	0
P-V-5	52	6/10/85	6/09/86	10.09275	10.09309	340	13.5	2.62564	2.62552	(120)
P-V-6	110	6/10/85	7/20/87	9.89224	9.89259	350	13.2	2.61303	2.61300	(30)
P-V-7	254	6/10/85	4/23/90	9.91531	9.91535	4	13.4	2.61129	2.61133	4

Cont'd

Table 12 (Cont'd)

Initial Bottom Canister Mass (gm)	Final Bottom Canister Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Initial Total Vessel Mass (gm)	Final Total Vessel Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Water Added During Testing
3.41033			320.60			
3.40645	3.40668	23	325.98			
3.41020	3.41022	20	320.39	320.95	0.36	0.975
3.51410	3.51414	40	323.78	325.29	1.51	1.95
3.39282	3.39268	(140)	319.30	320.44	1.14	1.95
3.40535	3.40534	(10)	318.49	321.13	2.64	4.05
3.39052	3.39062	10	317.91	322.49	4.58	9.73

a. P-V-3, 26-Week Sample

The top surface has clearly marked circular regions corresponding to the noncontact areas. Five of the circular regions are a light gray in contrast to the brown/black background of the glass. The remaining two circular regions have a splotchy light blue-gray appearance, as though the reaction has not progressed to the extent observed in the other noncontact areas. The general appearance of the top surface is not much different than the bottom surfaces from the P-III and P-IV experiments. Several string-like deposits occur at the noncontact-contact boundary. Approximately one half of the contact area has a bluish cast. Superimposed upon this color scheme is a coarser area caused by saw marks. There is a mottled appearance in this region. This appears to be the result of puckering of the surface layer away from the glass. Within some of the saw marks there is a deep blue iridescent appearance, possibly from exposed glass.

For the most part, the top surface preserves the original "as-cut" appearance. A surface layer is developing, although it is not complete and glass is still exposed (Fig. 26a). The distinction between the original glass and the surface layer is not always clear. In general, the sharp edges and ridges become more rounded and stress and chattermarks begin to disappear (Fig. 26a). In some areas, a textured surface is beginning to develop, visible only at high magnification. A Si-rich deposit, essentially the same composition as the surface layer has locally precipitated (Fig. 26b). This is the origin of the string-like marks observed optically at the noncontact-contact boundary. In the rougher regions (caused by saw marks), the surface layer is beginning to pucker and pull away from the glass (Fig. 26c). No complete exfoliation has occurred.

There are a number of phases that have precipitated on the top glass surface. In addition to the Si-rich deposit, small isolated clumps of Si-rich "clay" are present on the surface. These often have CaSO_4 intermingled with the "clay". Small "flowers" of CaSO_4 (whether this is gypsum or anhydrite has not been determined) occur randomly on the surface (see Figs. 26a and 26c). The next most abundant phase is Cr-Mn rich and occurs mostly in small ($<5 \mu\text{m}$) spheres, although some grains are tabular. Some grains have $\text{Mn} > \text{Cr}$ and contain Fe, but the dominant composition is Cr and Mn only with $\text{Cr} > \text{Mn}$ (Fig. 26d/EDS). These are probably oxides or hydroxides. One portion of the surface has colonies of small Cr-Mn grains (Fig. 26e). The abundance of Cr is unusual and this phase has only rarely been observed on the stainless steel components of other experiments (e.g., on P-VIII-7). Several other precipitated phases include silica, Al-rich grains, NaCl, KCl, calcite, and a Ca-P phase, possibly apatite.

The noncontact areas on the bottom surface are poorly defined, being only a little lighter in color than the brown-black contact areas. Like the top, there is a rougher region which has a coarse speckled appearance.

The surface layer is less well developed than the top. The criteria described for the top glass were used to distinguish altered and unaltered surfaces. The layer consists of dispersed altered areas which have an irregular distribution and appear to be a function of the original surface roughness. No puckering of the altered surface was observed. Unlike most other experiments, the top surface appears to be more reacted than the bottom surface.

Fig. 26. SEM Micrographs of the Surface Layer and Reaction Products on the Top Surface of P-V-3. (a) 1200X, (b) 2000X, (c) 750X, and (e) 3000X (see text).

Small patches of precipitates occur on both the altered and unaltered surfaces. The amount of precipitates is small compared to the top glass. The most common phases are Si-rich "clay" and CaSO_4 (gypsum or anhydrite). In addition to occurring as small "flowers," there is a large round mat (~130 mm) of CaSO_4 near the edge of the glass. There are a number of beam sensitive grains distributed on the surface that appear to only contain Na like those observed on the P-II experiments. These may very well be Na_2CO_3 . Other phases include calcite, dolomite, Al-rich grains, mixed grains with Na, K, Ca, Cl, and S, and a Ti-bearing mixed grain.

b. P-V-2, 39.5-Week Sample

Although this sample was intended as a continuous experiment, it was abruptly terminated during the 39.5-week sampling due to problems with the WPA. The top surface has a similar appearance to the top of P-V-3. Most of the surface has a brown-black color. Several areas in the contact and noncontact areas have a light blue cast. The noncontact areas are partially covered by light-colored precipitates. String-shaped deposits occur at the noncontact-contact area boundaries. There is also a small coarse-grained area that has a speckled appearance.

The bottom is generally coarser grained with speckles like that of P-V-3. The noncontact areas are gray with bluish haloes extending into the contact areas. Very few precipitates are observable.

c. P-V-4 and P-V-5, 52-Week Samples

Sample P-V-4 was investigated optically and by SEM/EDS, but P-V-5 was only examined optically. The top glass surfaces are somewhat different in appearance. The contact areas on P-V-4 are either brown-black or have a milky blue hue, similar to the tops of P-V-3 and P-V-2. The majority of the P-V-5 contact area has a shiny honey-brown color. On both samples the noncontact areas have a deposit of precipitates in the middle, surrounded by a grayish region. Discontinuous string-shaped deposits are developed at several of the noncontact area boundaries.

From SEM/EDS observation, the top glass of P-V-4 has reacted much more than the top of the P-V-3 experiment. The surface has a fuzzy appearance at low magnification indicating that an altered layer has developed. At high magnification, the surface has a variable texture. In some places it is quite smooth with only a hint of fine scale structure. Elsewhere, a coarser texture is developed, reminiscent of the "cardhouse" texture observed on the P-VIII samples (Fig. 27a). There is a range in the coarseness which may correspond to progressive recrystallization of an initially amorphous hydrated layer, although this is only a hypothesis. Alternatively, the coarser areas may have formed by precipitation.

In a number of places the surface layer is cracked and exfoliation has begun. This is best developed in the noncontact areas although it also occurs in the contact areas, especially where the "as-cut" surface is rough. A more complex layer structure is revealed in these areas. The altered layer is actually composed of three or four discrete layers (Fig. 27b). The bottom layer has a coarse texture. Above this are one or two smoother layers. The outermost layer is coarse, having an appearance similar to the bottom layer. The outermost layer is discontinuous, suggesting it formed by precipitation. This patchy distribution results in the observed variation in surface texture described above. The compositions of all the layers are similar and are consistent with the coarse layers being Fe-rich smectite. Small clumps of precipitates are present on all exposed surfaces and have the same composition as the altered layer (see Figs. 27a and 27b). In some places the smooth layer has a mottled appearance (Fig. 27c). EDS analysis indicates that this is due to the incorporation of Cr-Mn-Fe oxide or hydroxide grains within this layer (Fig. 27d/EDS).

Fig. 27. SEM Micrographs and SEM Spectrum of Reaction Products on the Top Glass Surface of P-V-4. (a) 7000X, (b) 3200X, (c) 3500X (see text).

Aside from the Si-rich "clay" (smectite?) and the Cr-Mn+Fe oxide/hydroxide grains, CaSO_4 (gypsum or anhydrite) is the predominant secondary mineral. There are also some Al-rich grains present that may be gibbsite.

The bottom surfaces of P-V-4 and P-V-5 are coarser than the tops and are similar to P-V-3. The contact area of P-V-5 is generally brown-black while that of P-V-4 is a lighter shiny tan color. The noncontact areas are grayish on both samples and the circular marks extend into the contact area. There are very few precipitates optically visible.

The bottom surface of P-V-4 has a general fuzzy appearance but this is not as well developed as on the top surface. The altered surface is fairly smooth with only a little fine scale texture. In places the texture is somewhat coarser although this material may have formed by precipitation. This is suggested by the areas where the coarser material is restricted to high points and ridges and appears to spread into surface depressions (Fig. 28a). Etching of the surface is suggested by the presence of cusped depressions on the surface. Preferential etching of stress marks is also apparent and, in some cases, these etched marks provide nucleation sites for Si-rich "clay" precipitates (Fig. 28b). In the rougher areas cracking and exfoliation have begun, but this is much less advanced compared to the top surface. The only other precipitated phase besides the Si-rich "clay" is CaSO_4 (either gypsum or anhydrite).

Fig. 28. SEM Micrographs of the Bottom Surface of P-V-4. (a) 4500X and (b) 4000X (see text)

d. P-V-6, 110-Week Sample

The top and bottom surfaces were examined optically but only the top surface was investigated by SEM/EDS. The bottom surface has an appearance like the other P-V samples (see above). The noncontact areas have complex variations in color, creating bull's eye type features. The central portions are gray and are surrounded by successive rings which are brown-black, then blue, followed by gray at the outer margins.

The top surface of P-V-6 is megascopically smoother than any other sample surface (Fig. 29a). It appears that the "as-cut" surface was ground down somewhat prior to the experiment. There are, however, numerous shallow striations with different orientations distributed across the surface, which occur as white streaks on a brown-black background. The noncontact areas have a variably developed milky white hue. Some light-colored precipitates occur in the noncontact areas.

From observation using the SEM/EDS, there is a fine-scale texture which varies from smooth to coarse, although it is never as coarse as observed on the top of P-V-4. The surface has more of a flaky texture rather than a "cardhouse" texture (Fig. 29b, compare with Fig. 27a). In some areas, mostly in proximity to the contact-noncontact boundaries there is a thicker buildup of the surface layer. This may be due to a thickening of the surface layer or from precipitation. There is no evidence for the presence of a complex layer structure. Some minor cracking and puckering of the surface layer is observable (Fig. 29c). The location of the puckered areas seems to be controlled by the shallow striations and the few remaining saw marks on the surface. Overall, the surface layer appears to be less well developed compared to P-V-4, even though the duration of P-V-6 was twice as long. This suggests that initial surface roughness may play a role in accelerating surface layer development and the initiation of exfoliation.

Fig. 29. SEM Micrographs Showing the General Surface Features on the Top of P-V-6. (a) ~6X, (b) 4000X, (c) 500X, and (d) 4000X (see text)

In contrast with all the other samples in the P-V series, no CaSO_4 is present. Instead, CaCO_3 occurs in fine fluffy masses and as fairly large (up to $20\ \mu$) euhedral grains (Fig. 29d). The large euhedral grains show evidence of having undergone an episode of dissolution. As CaCO_3 has retrograde solubility, this may have occurred when the sample was cooled during termination of the experiment. The only other secondary phase is Cr-Mn-Fe oxide or hydroxide. These occur as fine grains distributed across the surface and sometimes in small colonies similar to P-V-7 (see Fig. 30d). In some places, small clusters of grains occur within the layer which imparts a mottled appearance, similar to that observed on the top of P-V-4.

e. P-V-7, 254-Week Sample

This sample is from the longest duration batch experiment. The top surface is similar to the other P-V experiments except that no saw marks are present. There are two well-defined regions, one which is brown-black and another which has a light blue-gray cast. The noncontact areas are poorly discernible. In two of these areas, there are small masses of milky-blue precipitates. There are a number of string-shaped deposits in the contact area (see below). In two noncontact areas and near the edge of the glass, there are patches of large prismatic grains, which EDS analyses suggest are calcite (see below).

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Fig. 30.
SEM Micrographs of the Surface Layer and
Other Reaction Products on the Top of
P-V-7. (a) 7500X, (b) 4000X, (c) 600X,
and (d) 500X (see text)

A reacted layer has developed on the top surface, giving a fuzzy appearance at low magnification. The "as-cut" surface is generally preserved although the contours are noticeably rounded. At higher magnification the surface has a variably developed flaky texture similar to that observed on P-V-4 (Fig. 30a). The flaky texture is generally coarser in the noncontact areas. A hummocky appearance has developed, indicating local variations in layer thickness. The flaky texture and composition suggest the layer is composed of Fe-smectite.

A complex layer structure has locally developed in both the contact and noncontact areas. A thin, smooth layer is draped over the flaky textured material. This deposit is frequently cracked and split, revealing the coarser material from below (Fig. 30b). The smooth areas are somewhat enriched in Si relative to Al. Discontinuous sheets of precipitates have formed on top of the smooth layer, although to a lesser extent than that observed on P-V-4. It would seem, based on examination of the surfaces only, that the top of P-V-4 has evolved to a greater extent even though it was terminated after only 52 weeks. There is no evidence of large-scale exfoliation; however, there are many places where the layer has cracked and pieces have raised up from the surface. The lack of considerable exfoliation may be attributable to the absence of rough saw-marked regions on the surface.

Calcite is abundant, especially in the noncontact areas. Several colonies of large ($\sim 60 \mu\text{m}$) etched prismatic grains are present (Fig. 30c). Small isolated grains of calcite are also present, often associated with other secondary phases. Fine Cr- and Mn-rich grains, presumably oxide or hydroxide, occur as small clusters and as large colonies (Figs. 30d and 30e/EDS). This phase is responsible for the string-shaped deposits observed under the optical microscope. Both calcite and the Cr-Mn-rich phase were observed on P-V-6. Other colonies on the top glass are composed of Ca- and P-bearing grains (Figs. 30f and 30g/EDS). These may very well be apatite. Rare Ti-rich grains are present which may be anatase (TiO_2).

The bottom glass surface is similar to the other P-V samples. The noncontact areas are well marked and the light gray coloration extends into the adjacent contact area. The contact area is brown-black with some light-colored speckles. The surface layer appears to be pulling away from the glass but no exfoliation is apparent.

The bottom surface has a fuzzy surface at low magnification under the SEM. The "as-cut" contours are partially obscured. In detail, the surface layer is quite different compared to the top. Two distinct layers are apparent, although the upper layer is discontinuous (Fig. 31a). The upper layer has a "cardhouse" texture indicative of precipitated smectite. Its composition is consistent with this interpretation. In some places, it seems as though the upper layer has only partially formed (Fig. 31b), while elsewhere it appears to have formed and exfoliated (Fig. 31a). The lower layer has a bumpy texture with the individual bumps $\sim 0.5 \mu\text{m}$ across (Figs. 31b and 31c). Locally there is a preferred orientation to the bumps, possibly related to the presence of stress marks on the original glass surface. The alignment is apparent particularly in

Fig. 31. SEM Micrographs of Surface Layer Features on the Bottom of P-V-7. (a) 2900X, (b) 6000X, and (c) 9000X (see text)

Fig. 31c but is also visible in Fig. 31b. Preferential precipitation of the Si-rich "clay" occurs on these aligned bumps. The lower layer shows extensive cracking and puckering from the surface; however, no complete exfoliation has occurred. There are very few precipitated grains on the surface aside from the Si-rich "clay". Traces of S and Cl are occasionally detectable in EDS analyses of the surface layer.

3. Solution Analyses

Elemental releases from the P-V-1 continuous experiment are shown in Fig. 32 and normalized releases for Li, B, and U are given in Table 13. The raw data and background subtracted cumulative releases are included in Appendix I for both the continuous and batch experiments.

The P-V experiments have the smallest element release of any of the parametric experiments. There are, however, several factors that hamper interpretation of the solution data. The most significant problem results from the lack of recovered solution during sampling. When the solution was diluted to obtain enough for chemical analysis (usually 20 times the original volume), many elements including Li, B, and U were sometimes below the level of detection. For the P-V-1 experiment B was below the detection limit on nine occasions (out of a total of 17), while Li and U were below the limit three times. Since the detection limit value is used when computing cumulative release, the magnitude of release must be viewed as a maximum. Similarly, trends also represent maximum rates of release. Another problem involves the observed extrusion of the silicone rubber gaskets into the vessels. It is unknown what contribution, if any, the gaskets made to the amount of Si in solution, but the reported Si values must be suspect for the first 26 weeks.

The concentrations of Ca and Na were always above the detection limit even though both have a net negative cumulative release. This corresponds to the precipitation of Ca- and Na-bearing phases on the WPA. The erratic behavior of Na suggests that precipitation of an Na-bearing phase occurs when little water is available and it is subject to dissolution when more water is present.

Fig. 32. Cumulative Releases of Selected Elements from the P-V-1 Continuous Experiment

Table 13. Normalized Elemental Release for the P-V Series

Test #	Period (weeks)	Normalized Release (g/in ²)		
		B	Li	U
P-V-3	26	0.2	0.6	0.1
P-V-4	52	0.4	1.1	0.3
P-V-5	52	0.3	1.0	0.2
P-V-6	110	0.2	0.9	0.1
P-V-1	26	0.1	0.0	0.0
	52	0.1	0.1	0.0
	110	0.2	0.8	0.1
	156	0.2	1.1	0.1
	182	0.2	1.1	0.1
	208	0.3	1.4	0.2
	234	0.4	1.7	0.3
P-V-2	26	0.1	0.1	0.0
	39.5	0.1	0.5	0.1

^aValues are affected by the Si contributed by the silicone rubber gasket.

4. Discussion

The P-V samples appear to have undergone less alteration compared with the other experiments. This conclusion is based on the smaller quantity of precipitates on the surfaces and the low measured element releases. These samples provide insight into the initial stages of surface layer formation. Initial alteration (hydration and leaching) of the glass surface is nonuniform and may be influenced by the surface roughness. Like the glass, there is no fine-scale texture in altered areas; however, the surface does appear somewhat fuzzy and stress marks are absent. Precipitation of a Si-rich "clay" mat begins at an early stage, even before a continuous hydrated glass layer is completed. This signals the beginning of what will become a composite surface layer. Sample P-V-3 is at this early stage, while P-V-4 already has a partially developed composite layer. The altered layer begins to crack and pull away from the glass. This marks the onset of the process that leads to exfoliation. It is important to note that this process can commence even before the altered layer has completely developed across the surface. Precipitation of the Si-rich "clay" layer appears to be independent of this process. The original surface roughness may be an important factor in the pace and location of exfoliation. Cracks seem to develop first in the rough regions associated with the saw marks. For example,

on the top of P-V-6, where the surface is generally quite smooth, cracking and puckering of the surface layer is restricted to the striations and shallow saw mark traces. As the surface layer ages, coarsening of its texture is apparent. This is particularly noticeable for P-V-7, the 254-week duration experiment. This coarsening may correspond to progressive crystallization of an amorphous layer, but, this is not revealed at the resolution of the SEM.

The top of P-V-6 appears much less reacted than the top of P-V-4 even though its duration was twice as long. This may be the result of the smoother surface on P-V-6 impeding reaction but this is only a hypothesis. The lack of reaction might also result from less water-glass contact during the experiment, perhaps due to evaporation during the experiment.

In all the P-V experiments, Ca is removed from the EJ-13 water. This is consistent with the presence of Ca-bearing phases on the batch samples. On samples P-V-3 and P-V-4 CaSO_4 (either gypsum or anhydrite) is ubiquitous. On samples P-V-6 and P-V-7 calcite is abundant and CaSO_4 is absent. While the availability of sulfate is not well understood, it is unknown why such a difference in mineral occurrence should happen between these samples.

E. P-VIII Experiments

The purpose of these experiments is to examine the effect of sensitization of the stainless steel components on metal-glass-fluid interactions. As the stainless steel pour canisters are anticipated to be exposed to elevated temperatures during filling, the behavior of heat-sensitized steel has direct relevance to waste form performance in the proposed geologic repository.³ The stainless steel used in the experiments is from heat #22841 which contains 0.016 wt% carbon. The components were held at $550 \pm 20^\circ\text{C}$ for 24 hours and were then slowly cooled to room temperature by turning off the furnace. This steel proved very difficult to sensitize, owing to its low carbon content.¹³ The degree of sensitization to the actual samples, while believed to be low based on testing of heat-treated but unreacted steel, has not been measured.

The experiments were initiated on 2/27/86 and have been completed through 195 weeks. Batch experiments were terminated after 13, 26, 39, 52, and 104 weeks. Continuous experiment P-VIII-2 was terminated after 170 weeks because the WPA tipped and would no longer remain upright. The batch sample P-VIII-8, which was first sampled after 104 weeks, is presently being treated as a continuous experiment.

1. General Observations

The WPA had a similar appearance in all the experiments during sampling. The top surface was always dry with some light-colored precipitates often present on the glass in the noncontact areas. Some precipitation of secondary phases occurred on the metal. The bottom surface was always wet with some standing water around the circumference of the glass (sample P-VIII-4 was dry upon termination, however). The extent of standing water was variable.

At termination of P-VIII-7 (104 weeks), the water was about at the level of the bottom of the glass. When P-VIII-8 was first sampled after 104 weeks, the water level was halfway up the side of the WPA indicating that the bottom had been inundated for a significant period of time. These observations must be considered when interpreting the solution composition data from these experiments.

The metal components from all the terminated experiments experienced approximately the same amount of weight gain (Table 14). This is consistent with the observation of secondary phases on the metal. The glass in the short-term experiments (≤ 26 weeks) gained a small amount of weight, while there was a net decrease in the longer experiments proportional to the experiment duration.

2. Component Analyses

The glass from all the terminated batch experiments was examined optically. The top surface of P-VIII-4 and the top and bottom surfaces of P-VIII-6 and P-VIII-7 were investigated by SEM/EDS. The metal components from P-VIII-6 and P-VIII-7 were also examined by SEM/EDS.

a. P-VIII-3, 13-Week Sample

The noncontact areas on the top surface are rather discrete. They have a light gray tint which is in contrast with the brownish background of the contact areas. The central noncontact area, however, has a bluish cast. There are three small light-colored areas, in the contact area, suggesting localized precipitation has occurred.

The bottom surface has a uniform gray color and the noncontact areas are not discernible. There is one light-colored area at the edge of the glass which is similar to the patches on the top surface. Saw marks are readily visible as light-colored streaks on both the bottom and top surfaces. Rougher regions are associated with the saw marks which have a coarse speckled appearance. Finer speckling is visible in the smooth regions at higher magnification.

b. P-VIII-4, 26-Week Sample

Several features stand out on the top surface. Part of the surface has a light gray-blue tint which is mostly associated with the central noncontact area. White precipitates are present in the bluish regions. The other noncontact areas are poorly marked. These are somewhat lighter in color with some white precipitates at their margins. The contact area is generally brownish but light gray tinting occurs around the edge of the glass. Saw marks, visible as white streaks, are present over much of the surface, imparting a coarse-speckled appearance.

Table 14. Experimental Matrix and Weight Change Results for the P-VIII Series

Test No.	Test Period (weeks)	Date Started	Date Stopped	Initial Glass Mass (gm)	Final Glass Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	SA Glass (cm 2)	Initial Top Canister Mass (gm)	Final Top Canister Mass (gm)	Δ Mass (gm $\times 10^{-5}$)
P-VIII-1 ^c		2/27/86	in progress	10.50533			13.88	2.34774		
P-VIII-2 ^a	170	2/27/86	6/01/89	9.99264			13.35	2.37578		
P-VIII-3	13	2/27/86	5/28/86	10.23029	10.23050	210	13.81	2.35705	2.35720	150
P-VIII-4	26	2/27/86	8/28/86	10.37222	10.37225	30	13.86	2.36451	2.36462	110
P-VIII-5	39	2/27/86	11/26/86	10.17771	10.17515	(256)	13.52	2.37383	2.37400	170
P-VIII-6	52	2/27/86	2/26/87	10.27582	10.27524	(580)	13.63	2.36734	2.36774	400
P-VIII-7	104	2/27/86	2/29/88	10.30219	10.30102	(1170)	13.69	2.35248	2.35271	230
P-VIII-8 ^b		2/27/86	in progress	10.37649			13.78	2.37175		

^aContinuous experiments.

^bTreated as a batch experiment up to 104 weeks. Thereafter treated as a continuous experiment.

Cont'd

Table 14 (Cont'd)

Initial Bottom Canister Mass (gm)	Final Bottom Canister Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Initial Total Vessel Mass (gm)	Final Total Vessel Mass (gm)	Δ Mass (gm $\times 10^{-5}$)	Water Added During Testing
3.35091			320.19			
3.34846			327.34			
3.33102	3.36114	120	325.59	327.18	1.59	1.95
3.33765	3.33776	110	320.56	323.70	3.14	3.90
3.33271	3.35291	200	324.34	328.96	4.62	5.85
3.33773	3.39823	500	325.82	331.74	5.92	7.80
3.33328	3.35359	310	325.71	336.98	11.27	15.60
3.33672			325.71			

The bottom surface has a rather uniform dark gray color. The noncontact areas are marked by somewhat lighter colored rings around a central region that looks much like the contact area. There is a patch of whitish precipitates, similar to that observed on P-VIII-3. Saw marks give a coarse-speckled appearance to approximately one quarter of the surface.

Only the top surface was investigated by SEM/EDS. The general appearance is similar to the P-IV experiments. The "as-cut" contours are clearly visible, however, the surface has a fine-scale texture at high magnification indicating that reaction has occurred (Fig. 33a). A Si-rich alteration layer has developed across the glass surface. Its composition is essentially the same as observed for the other experiments. Small precipitates of similar composition occur on the surface (Fig. 33a). In some parts, coverage is extensive, forming a discontinuous upper layer upon the altered surface. That the glass has reacted is also indicated by the preferential etching of stress marks. Short cracks have locally developed in the layer and small portions have raised up from the glass. This phenomenon occurs in both the contact and noncontact areas.

Aside from the Si-rich layer, there are several other secondary phases that have precipitated on the surface. There are colonies of small ($<0.5 \mu\text{m}$) spherical grains distributed over the entire surface (Fig. 33b). These areas are enriched in Fe relative to the surface layer and EDS analyses suggest a very fine-grained mixture of Si-rich "clay" and $\text{Fe} + \text{Mn} + \text{Ni}$ oxide or hydroxide (Fig. 33c/EDS). This is based on the observation that the Si, Al, and Ca peaks have relative intensities approximately equal to precipitated Si-rich "clay" (compare Fig. 33c with Fig. 34c). The Fe peak intensity varies from spot to spot, suggesting its signal is independent of Si, Al, and Ca and that this results from variable proportions of two phases being detected. The phenomenon of coprecipitation is well known.^{14,15}

Other irregular-shaped grains contain Ca and S and are probably either gypsum or anhydrite (see above). A number of large (up to $180 \mu\text{m}$) prismatic grains are present whose EDS spectrum consists of only a Ca peak suggesting it is calcite. Several irregular fluffy masses occur with only Si, Al, and K detectable by EDS (Figs. 33d and 33e/EDS). Their approximate stoichiometry is consistent with K-feldspar, but they have not been analyzed by XRD.

c. P-VIII-5, 39-Week Sample

The noncontact areas on the top surface are easily visible owing to a rather heavy coverage of whitish-gray precipitates. The central noncontact area is gray, and extends into the adjacent contact area. Exfoliation of the altered layer is apparent in the middle of several noncontact areas. The contact areas are brown except in the saw marked regions which have light-colored speckles as observed on most other P-VIII samples. The bottom surface is similar to the top of P-VIII-3. Most of the noncontact areas are only faintly visible with a slight grayish tone. Saw marks and a corresponding rough-speckled appearance covers approximately half the surface.

Fig. 33. SEM Micrographs and EDS Spectra from the Top of P-VIII-4.
 (a) 2500X, (b) 1790X, (c) EDS spectrum of material shown in (b),
 (d) 4000X, and (e) EDS spectrum of grain shown in (d)

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 34. SEM Micrographs and EDS Spectra from the Top of P-VIII-6.
(a) 1500X, (b) 300X (see text)

d. P-VIII-6, 52-Week Sample

The glass and metal components were examined optically and by SEM/EDS. Two precipitates were also analyzed by XRD.

(1) Glass

The top portion of the glass has clearly marked contact and noncontact areas. The noncontact areas are lighter in color than the contact areas, being tan rather than gray. This is due to heavier precipitate coverage in the noncontact areas. Some saw marks appear as light-colored, discontinuous streaks. Close optical inspection suggests the color difference is mostly due to the partial separation of the surface layer from the glass in the saw grooves. One region, encompassing approximately one-third of the top surface, has a rusty appearance and seems to have more precipitates on it.

The "as-cut" contours are preserved, although they are subdued (Fig. 34a). The surface has a poorly developed flaky texture at high magnification like that on P-VIII-4, indicating the presence of an altered layer (see Fig. 33a). A coarsening of this texture is locally observable, but this may be the result of precipitation. The layer composition is the same as for samples from other experiments; it is Si rich with some Al, Ca, Fe, * Mg * Mn * Ni, *Na. Only minor cracking of the surface layer is apparent, although such features are present in both the contact and noncontact areas (Fig. 34a). Where cracking has occurred, small pieces of the adjacent layer have raised up from the glass.

There are a number of secondary phases present. The most abundant is a Si-rich material which occurs in numerous morphologies including: ribbons, round grains with flaky surfaces, string-shaped masses, and fine fromboidal masses (Figs. 34b and 34c/EDS). This material has the same composition as the surface layer. The relative uniform Al-to-Si ratio suggests this is a crystalline phase and its composition is consistent with smectite. The Fe, Mn, and Ni content can be quite variable; sometimes Ni content can exceed that of Fe.

The next most abundant phase is Fe oxide or hydroxide which is especially abundant in the rusty region. It occurs as irregular-shaped grains; however, some possess a good geometric form, like the diamond-shaped grain in the left center of Fig. 34b. Fe-rich material is also associated with many of the fine-grained precipitates that are present all over the surface. This may explain, in part, the apparent variability in Fe content of the Si-rich precipitates. Along with Fe, a small amount of Mn is almost always present and Cr and Ni are locally important components (Fig. 34d/EDS).

A Ca- and S-bearing phase, most probably anhydrite or gypsum, is ubiquitous on the glass surfaces. It occurs as very fine fromboidal grains that grow on other phases and are often intimately intermingled with these phases. For example, fromboids are growing on the Fe-rich grain in Fig. 34b.

Several other phases are present in minor quantities which are worthy of note. A silica phase, presumably either quartz or opal, is present as small angular grains. An Al-rich phase occurs in several places. The absence of any other detectable elements, along with its flaky appearance, suggest it is gibbsite or some other Al-hydroxide (Fig. 34e/EDS). Another Ca-rich phase containing Mg and Fe is present which is probably a high-Mg calcite or possibly dolomite (Fig. 34f/EDS). In rare instances, Cl is detectable. These grains often have a complex composition suggesting the presence of numerous phases.

The surface layer and precipitates are well developed on the bottom glass surface. There is only a weak demarkation between the contact and noncontact areas. This is in contrast to the top surface where contact-noncontact areas are well delineated. Saw marks are clearly visible on the bottom surface, marked by light-colored streaks. As with the top layer, this color difference seems to result from buckling and separation of the surface layer from the glass.

The "as-cut" contours are mostly obscured and the surface has a flaky appearance that is much coarser than observed on the top surface (Fig. 35a). This suggests that much of the visible surface may have formed by precipitation, masking the original surface topography. The composition is typical of the altered layer and is probably smectite. An extensive network of cracks has developed across the surface (Fig. 35a). Most have the appearance of shrinkage cracks caused by dessication, presumably after termination of the experiment. However, the glass exposed within the cracks looks altered and has some fine precipitates on it. This suggests cracking must have begun during the experiment. The cracks would then become enlarged as the layer dried after termination of the experiment. Other cracks, where the surface layer has raised up, are associated with the saw marks (Fig. 35b). This represents the initiation of exfoliation of the surface layer.

The types of precipitated phases are essentially the same as described for the top surface with a couple of minor additions. A Ca-bearing phase without any Mg or Fe is present and is probably calcite. One analyzed grain contains only Si, Al, and Na, with Al exceeding the amount found in the surface layer (Figs. 35c and 35d/EDS). It does not have a distinctive morphology, but its composition suggests it is analcime.

(2) Metal Components

The top and bottom steel components generally have the same appearance. They have a dull rusty color where they were in contact with the glass during the experiment. Along the rims and the sides facing away from the glass, little reaction has occurred. There are some small irregular-shaped patches of corrosion on these surfaces. There are, however, small patches of thick precipitates that have developed in both the contact and noncontact areas on the side facing the glass. These are mostly intimate mixtures of Si-rich material, probably smectite clay, and Fe-oxide or hydroxide. The clumps can be stringy in form, similar to that observed on the glass.

Fig. 35. SEM Micrographs of Surface Layer Features from the Bottom of P-VIII-6. (a) 2500X; (b) 200X; (c) a small grain on the surface that contains only Si, Al, and Na (3500X); and (d) EDS spectrum from grain shown in (c)

On the bottom metal piece, there are numerous honey-colored precipitates. These are shaped like open cylinders and cones (Fig. 36a). Analysis of this material by XRD suggests that it is hematite. They occur on both sides of the metal but are most abundant along the edges on the side facing away from the glass. In general, there are more precipitates on the surfaces facing the glass than on the other side. Unlike the glass, there is no complete surface coating on the metal.

Virtually all the phases identified on the glass are also present on the metal components. The most common phases on the metal are the Si-rich clay, Fe-oxide or hydroxide, and calcium sulfate. These are often intimately intergrown with each other. The Si-rich material has the same composition as that found on the glass except that it is generally very poor in Ni. Fe-oxide or hydroxide occurs as the material covering the surface and as open cylinders and cones (Fig. 36a). Tiny dots of gypsum or anhydrite occur all over the metal surface. Chloride-rich grains are present, mostly associated with the welded regions. These grains may contain Na, K, and Ca. XRD analysis confirms the occurrence of NaCl. There is a Cr-rich substance present on both metal components that was not observed on the glass. While spectra from this

Fig. 36. SEM Micrograph (250X) and EDS Spectrum of Fe- and Cr-Rich Deposit on the Bottom Surface of the Metal Component on P-VIII-6

material resemble the metal and Fe-hydroxide, the Cr content is very high (Fig. 36b/EDS). This may be Fe-hydroxide that is for some reason locally very rich in Cr. Considering that the source of the Cr is the metal, the absence of Cr-rich material on the glass suggests that Cr is not very mobile under the conditions of the experiments.

e. P-VIII-7, 104-Week Sample

The glass and metal components were examined optically and by SEM/EDS/WDS.

(1) Glass

The top glass has a general medium gray tone with a smooth, evenly colored region and a rough, mottled region. The roughness is from the saw blade during cutting of the glass cylinder. There is a distinction between the contact and noncontact areas but it is not very pronounced. Precipitates are sparsely scattered over the noncontact areas. A honey-colored mark and a concentration of precipitates are present in one small portion of the contact area, near the edge of the glass.

A well-developed altered layer is present over the entire surface. The "as-cut" contours are not preserved and the layer has a "cardhouse" type morphology reminiscent of clay (this is consistent with its composition). Masking of the contours suggests at least a portion of the layer formed by precipitation, filling in depressions on the rough surface. The surface layer is cracked in many places and appears to be pulling away from the glass (Fig. 37a). Some of the cracks expose etched glass from below. The presence of precipitates bridging the cracks suggests the cracks began to form during the experiments. Some shrinkage after termination of the experiment may have enlarged the cracks. The pulling away of the surface layer from the glass is more pronounced in the rough region. Here, it appears that the layer has variable thickness.

(a)

(b)

(c)

(d)

(e)

(f)

(g)

Fig. 37
SEM Micrograph and EDS Spectra of
Reaction Products on the Top Glass of
P-VIII-7. (a) 3000X (see text)

The most abundant precipitated phase is Si-rich which also contains Al, Ca, Fe, Mn, * Mg * Ni, * Na, * K, in proportions similar to the average surface layer. It occurs as ribbons, flaky grains, and fluffy textured masses of variable size (Fig. 37a). At high magnification, the small fluffy masses have the same "cardhouse" type morphology as the top of the surface layer which suggests that the visible portion of this layer may also have formed by precipitation. The next most abundant phase is very Fe rich and is probably Fe-oxide or hydroxide. This material occurs as irregular-shaped grains and is almost always intergrown with Si-rich "clay". It is otherwise generally quite pure with only a small amount of Mn present.

Other precipitated phases include Ca-rich grains, presumably calcite, which are fairly abundant. Some Ca-bearing grains also contain Mg and Fe, indicative of dolomite. Some grains are very Al-rich and are possibly gibbsite (or bayerite?, or nordstrandite?). Variable small Si and Fe peaks on the spectra suggest this material is intermingled with Si-rich "clay". Tiny Cl- and S-rich grains occur on the surface layer and on many precipitates. Based upon numerous EDS analyses, the phases present are likely to be NaCl, Na₂SO₄, CaSO₄, and possibly CaCl₂ (Figs. 37b/EDS and 37c/EDS). Whether the sulfates are actually hydrated is impossible to determine by EDS. A number of grains contain significant Ti. When EDS spectra from several grains are compared, it is clear that they are a mixture of phases (Figs. 37d/EDS and 37e/EDS). For example, while the spectrum in Fig. 37d has large Si and Ca peaks, that in Fig. 37e has a much smaller Si peak and virtually no Ca. This suggests that the Ti-bearing phase does not contain either of these elements. A plausible interpretation is that these grains contain TiO₂, anatase?, along with Si-rich "clay" and calcite.

Several other phases, while occurring rarely, are worthy of note. A couple elongate, layered grains are present which contain only Si and Mg (Figs. 37f/EDS). Their morphology and composition suggest they are serpentine. Ca-phosphate grains presumably apatite, occur sparingly (Fig. 37g/EDS). Silica, possibly quartz or opal occur very rarely.

The bottom surface has a medium gray color with smooth and rough cut regions. The noncontact areas are generally poorly defined, being only slightly darker gray than the adjacent contact areas. Under the SEM, the surface has a similar texture to that observed on the top surface. Small precipitated grains have the same "cardhouse" type texture and composition as the surface layer. An extensive network of cracks is present and, in places, pieces of the layer have exfoliated, exposing etched glass below (Fig. 38a). It is clear that exfoliation occurred during the experiment because of the presence of fine NaCl threads in some of the cracks and Si-rich precipitates on some of the freshly exposed surfaces (Figs. 38a and 38b). In these exfoliated regions there is a continuum of surface appearance from fresh etched glass, to glass with a few precipitates, to glass with a heavy cover of precipitates. This suggests that exfoliation occurred over a period of time up to the termination of the experiment. In one location, it is apparent that the surface layer is actually composed of two layers (Fig. 38b). Here, a flake of the upper portion of the layer has spalled off, exposing a lower layer which in turn is also in the process

Fig. 38. SEM Micrographs of Surface Layer Features on the Bottom of P-VIII-7. (a) 1600X, irregular-shaped grain in NaCl; and (b) 2000X (see text)

of exfoliating. The glass below has many small dots on it either from precipitation or alteration. Based upon several EDS analyses, there are no significant compositional differences between the two layers. The lower layer is finer grained; however, it has the same texture as the upper layer when viewed at high magnification.

Like the other samples, the surface layer and associated Si-rich precipitates form the dominant alteration product on the bottom surface. The texture and composition is consistent with it being Fe-smectite. The next most abundant phase is NaCl. It occurs as fine threads and blocky grains and may also be intimately associated with the Si-rich "clay". It often occurs with Na_2SO_4 and CaSO_4 (whether these sulfates are hydrated is uncertain). These phases, along with CaCO_3 , calcite, are frequently intergrown with the Si-rich "clay" at a very fine scale. Fe-rich material is also present as irregular blobs on the surface which may contain minor Mn and Ni. This is probably Fe-oxide or hydroxide, although the XRD results from P-VIII-6 suggest it is an oxide.

(2) Metal Components

There is an extensive deposit of precipitates on the metal components. Small patches of corrosion are associated with the welds. Most of the phases found on the glass are also present on the metal. There are two predominant phases: Si-rich "clay" and Fe-oxide or hydroxide. There is a thin Si-rich "clay" mat on the bottom component, but for the most part, the "clay" occurs in clumps with a fluffy texture. The clumps occur on both sides of the components indicating an origin by precipitation. The EDS spectra are often enriched in Fe (and not Cr) suggesting that the clay is intergrown with Fe-oxide or hydroxide, as was observed on the glass. Fe-oxide or hydroxide occurs in irregular clumps and as tiny balls and open cylinders (see Fig. 36a from P-VIII-6).

Ca-rich phases, presumably calcite and dolomite, are quite abundant. Some grains have a rhombohedral form which is characteristic of calcite. Many Si-rich "clay" clumps have detectable Ca and S suggestive of gypsum or anhydrite.

Very Al-rich grains are abundant on the top component. These grains are generally only a few microns across with only Al in their EDS spectra, suggestive of Al-hydroxide (Fig. 39a/EDS). Ti-rich grains, which are possibly mixtures of clay and TiO_2 , are also present on the top metal piece. A rare Cr-Mn phase is associated with the metal grain boundaries and is probably the result of corrosion (Fig. 39b/EDS).

3. Solution Analyses

Elemental releases from the continuous experiments are shown in Fig. 40, and the normalized releases of B, Li, and U are presented in Table 15. The raw data and the background subtracted cumulative releases are included in Appendix I for both the continuous and batch experiments. Continuous experiment P-VIII-2 was terminated after 170 weeks because the WPA would not remain in an upright position. Batch experiment P-VIII-8 is currently being treated as a replacement for P-VIII-2, but the data are not presented as such in Fig. 40.

There is good agreement in the trends and magnitudes of elemental release between the two continuous experiments, P-VIII-1 and P-VIII-2. Overall release is low and is comparable to the P-V experiments. The last sampling of P-VIII-2, at 170 weeks, showed a sharp change in all element releases (Fig. 40). The tipped WPA may, in some way, have caused this accelerated behavior. The release from P-VIII-8 is significantly greater than the other two continuous experiments. This is probably attributable to the period prior to the 37-week sampling when the bottom of the WPA was submerged. Comparison of the last two solutions, collected at 170 and 195 weeks, suggests a sharp reduction in the rate of release.

The relative magnitudes of release are $\text{Li} > \text{B} \geq \text{U}$ (Table 15). There is a net negative release of Ca and Mg in all three experiments. This indicates that these elements have been removed from the EJ-13 water and incorporated in secondary phases on the WPA. This is consistent with the occurrence of CaSO_4 and calcite on the batch samples. Release of Si is negative in the P-VIII-1 and P-VIII-2 experiments. It is positive in P-VIII-8, however, the most recent sampling at 195 weeks shows a minor net negative release. The negative Si release correlates with the extensive amount of precipitated clay on the glass and metal components in the batch experiments. Release of Na is erratic in P-VIII-1 and P-VIII-2 which is similar to that observed in the P-II and P-III experiments. Release of Na in P-VIII-8 is positive and mirrors that of Li, B, and U. The erratic behavior of Na is attributable to periodic precipitation of NaCl or Na_2SO_4 followed by subsequent redissolution during later sampling intervals. These Na-bearing phases are commonly observed on the batch experiments.

Fig. 39. EDS Spectra of Precipitates on the Top Metal Component of P-VIII-7

Table 15. Normalized Elemental Release for the P-VIII Series

Test #	Period (weeks)	Normalized Release (g/m ²)		
		B	Li	U
P-VIII-3	13	0.1	0.4	0.10
P-VIII-4	26	0.2	0.9	0.10
P-VIII-5	39	0.2	0.4	0.09
P-VIII-6	52	1.2	2.1	1.24
P-VIII-7	104	1.5	2.6	1.54
P-VIII-8	104*	2.6	4.8	1.63
	170	5.1	8.3	3.17
	195	5.4	8.8	3.40
P-VIII-1	52	0.1	1.0	0.07
	104	0.2	1.4	0.11
	143	0.2	1.6	0.12
	170	0.2	1.8	0.12
	195	0.2	2.0	0.13
P-VIII-2	52	0.2	0.6	0.05
	104	0.2	1.0	0.07
	143	0.2	1.2	0.18
	170	0.3	1.5	0.29

*P-VIII-8 was treated as a batch experiment up to 104 weeks.

Fig. 40. Cumulative Release of Selected Elements from the P-VIII-1 and P-VIII-2 Continuous Experiments

4. Discussion

There are several observations that can be made about the nature of reaction during the experiments. Despite the apparent difference in the conditions between the top and bottom surfaces (i.e., the top may have undergone wet/dry cycling, whereas the bottom remained wet at all times), the secondary phases are the same. The only difference is that the bottom appears to have undergone somewhat more reaction. The bottom has more precipitates and the surface layer may be a little thicker. The Si-rich "clay" is present as the reacted surface layer and as discrete grains on the glass and metal components. This indicates that the Si-rich material forms by both in situ transformation of hydrated glass and by precipitation. Its composition is consistent with Fe-smectite. The flaky texture of the glass surface is the same as observed on the metal which suggests that much of what is visible on the glass developed by precipitation. Most of the precipitates are composed of a very fine scale mixture of Si-rich "clay," Fe-oxide or hydroxide, and gypsum or anhydrite. This suggests that coprecipitation has occurred which lends support to the interpretation that the visible surface formed by precipitation. There appears to be more Fe-oxide or hydroxide associated with the P-VIII experiments indicating that presensitizing the stainless steel has had an influence on the observed secondary phases. However, the amount of metal corrosion is slight.

The structure of the surface layer undergoes changes upon aging. A network of cracks forms and parts of the layer begin to pull away from the glass. As this process continues, pieces of the layer exfoliate and precipitates form on the freshly exposed glass surfaces. The surface layer also seems to have a complex internal structure of multiple layers. These may correspond to portions formed through glass transformation and precipitation.

IV. DISCUSSION AND CONCLUSIONS

A. Parametric Effects

The series of five parametric experiments were designed to investigate the effect of various parameters on the rate of glass reaction. Overall element release is generally similar for the experiments suggesting that release is relatively insensitive to these parameters. However, there are differences in release and the observed extent of reaction which can, at least in part, be attributed to the varied parameters. The normalized releases of Li, B, and U are summarized in Fig. 41 for all the parametric experiments and the N2 standard Unsaturated Test using SRL 165U glass.⁶ Relative release for all the experiments except P-II is $\text{Li} > \text{B} \sim \text{U}$ which suggests either nonstoichiometric dissolution of the glass or that B and U are accommodated in secondary phases. The SIMS profiles from the P-III experiments indicate that B is depleted on the surface and within the altered layer, favoring nonstoichiometric dissolution as the explanation for the observed release behavior (Figs. 10, 17, and 19).

Fig. 41. Normalized Releases of B, Li, and U for the Parametric and "Standardized" N₂ Unsaturated Experiments

The behavior of the experiment without the metal retainer (P-II) is similar to the N2 Test. The major difference between the P-II and the other experiments is the abundance of secondary phases that formed by evaporation (e.g., NaCl) and that B release exceeds Li release. Without the metal component, the glass surface may be more prone to drying out between injections, however, a direct cause and effect is not possible, because of problems with water retention in the vessels during the experiments. These problems may also be the cause of the reversed element release.

The reduction of glass surface area (experiments P-III and P-IV) gives an apparent small increase in the normalized release of Li and U relative to the N2 test (Fig. 41). This is an apparent increase because the geometric surface area was used in the normalization procedure, rather than an effective surface area. Visual observations and the results from SEM/EDS and SIMS examinations all indicate a variable extent of reaction between the top, bottom, and side surfaces, with the sides showing the least reaction. Since the surface area was reduced by shortening the sides of the glass cylinder, the change in the effective surface area (i.e., that part of the surface where reaction takes place) should be minimal. Therefore, the normalized releases for the P-III and P-IV experiments are exaggerated by close to a factor of two relative to the other parametric experiments. This must be considered when comparing releases from different experiments. As the effective surface area is smaller than the geometric surface area, the reported normalized releases for all the parametric experiments, especially those with the "full size" glass, will be underestimates of the "true" release. This must also be accounted for when comparing with other types of experiments such as leach tests where geometric surface area is equal to the effective surface area.

The P-IV experiments have anomalously high element release. There are two modified parameters in these experiments: a reduction in surface area and a reduction in the volume of water injected. Even if account is taken of the effective surface area (see above), the normalized releases are still significantly greater than any of the other experiments. The high release correlates with the extensive reaction observed on the surfaces by SEM. The reason for this anomalous behavior is uncertain. A reduction in injected water volume would seem to be an unlikely cause for a sharp increase in release. Conceivably, reaction could be enhanced by precipitation from a smaller fluid volume that would become rapidly saturated. However, the amount of precipitates on the P-IV samples is not noticeably greater than on samples from other experiments such as P-VIII. The observation that the WPAs in the P-IV experiments were always wet during sampling may provide a clue to the accelerated behavior, but, the reason why these experiments remained wettest is not known. In general, while the extent of reaction in these experiments was large, there was considerable variance in the batch and continuous test results.

Extension of the injection interval from 3-1/2 to 14 days reduces the element release and apparent extent of glass reaction. Observation of dry surfaces during sampling suggest that water is virtually absent for prolonged periods between injections. Consequently, elemental release from the glass is limited to short periods directly following injection.

The fifth parameter investigated is the effect of sensitizing the metal components. Assessment of this parameter is hampered by the poorly constrained degree of sensitization of the stainless steel. The stainless steel used in the P-VIII experiments has a lower C content (0.016 wt %) than the steel used in the standard N2 tests (0.022 wt %) which reduces the ability of the steel to become sensitized (Table 5).^{6,16} In the N2 tests, pervasive metal reaction was observed.⁶ However, in the P-VIII experiments, corrosion of the metal components is of a localized nature suggesting incomplete sensitization. Release is marginally greater for the experiments that exhibit metal reaction, but this is not definitive as these are also longer duration experiments. In addition, element release is much lower than in other experiments where unsensitized metal was used (compare P-VIII release and P-III, P-IV releases in Fig. 41). It is not clear that metal corrosion has any significant influence on glass reaction. At most it appears to be a second order effect. The metal components do act as sites for secondary phase precipitation and probably help to maintain water in contact with the glass by capillary action. These physical effects should act to enhance glass reaction.

B. The Surface Layer and Secondary Phases

The variation in the extent of reaction between individual parametric experiments provides the opportunity to investigate the evolution of the glass surface during reaction. The following discussion is limited because it is based only on SEM examination. Abrajano et al.¹¹ have demonstrated that Analytical Electron Microscopy (AEM) is required to achieve the resolution necessary for thorough characterization of the alteration layer and its relation to the glass surface. Several samples from the parametric experiments are being prepared for AEM examination, and preliminary results are presented in the Addendum. To help track the phases tentatively identified on the reacted test components, Table 16 provides a listing of phases discussed in the text.

An altered layer develops on the glass surface, presumably resulting from hydration and leaching of the glass. Initially, there is very little structure to this layer at least up to 15,000X magnification. Over time there is a progressive coarsening of the layer texture creating a bumpy or flaky surface. This layer is Si-rich and contains Fe, Ca, *Mg, *Na, *Mn, *Ni. It is similar in composition to Fe-smectite and to an amorphous phase called hisingerite. Eggleton et al. indicate that Fe-smectite crystallizes from hisingerite upon aging. It is conceivable that this may also occur in the altered layer. The progressive coarsening of the layer with time supports this hypothesis.

Investigation of extensively reacted samples reveals a complex structure with two to four discrete components to the altered layer. The outermost layer usually has a "cardhouse" or coarse flaky texture and is often not continuous across the surface suggesting it formed by precipitation. Its composition is essentially the same as the other parts of the altered layer, although other phases such as CaSO_4 and Fe-oxide or hydroxide are detectable in some EDS analyses. This intimate mixture of phases is consistent with the interpretation that the outermost layer formed by precipitation because the source for most of the Ca is the EJ-13 water. The lower portions of the altered layer have a variable texture as discussed above. The origin of these sublayers is not clear and awaits AEM examination.

Table 16. Summary of Phases Tentatively Identified in the Parametric Tests

Test #	Time of Reaction	Tentative Phase
P-II	26	Si-rich layer (smectite) Smooth layer (similar to glass composition) Gypsum or anhydrite (CaSO_4) Calcite (CaCO_3)
	52	Si-rich layer (smectite) Calcite Gypsum or anhydrite NaCl
P-III	13	Si-rich layer (smectite) NaCl Na_2SO_4 Na_2CO_3
	26	Si-rich layer (Ca smectite) Gypsum or anhydrite U, Si, Ca grain (uranophane) Na, Ca, S, Cl grains
	39	Si-rich layer Mn, Cr, Fe, Si grains Fe, Mn oxides/hydroxides Gypsum or anhydrite TiO_2 (anatase)
	52	Si-rich layer (smectite) NaCl Gypsum or anhydrite CaCl_2 Fe, Mn oxide/hydroxide
P-IV	25.5	Si-rich layer (smectite) Silica (opal/quartz) Calcite Cr, Fe, Mn oxide/hydroxide
	52	Si-rich layer (smectite) Gypsum/anhydrite Cr, Mn, Fe, Ni oxide/hydroxide

Cont'd

Table 16 (Cont'd)

Test #	Time of Reaction	Tentative Phase
P-V	26	Si-rich layer (smectite) Gypsum/anhydrite Fe, Cr, Mn oxide/hydroxide Silica (opal/quartz) Al-rich grains KCl Calcite Ca-P grains (apatite) Dolomite Mixed Ti-rich grains
	52	Si-rich layer (smectite) Cr, Mn, Fe, Ni oxide/hydroxide
P-VIII	26	Si-rich layer (smectite) Fe-rich grains with Mn, Ni Gypsum/anhydrite Calcite Si-Al-K grains (K-feldspar)
	52	Si-rich layer (smectite) Fe, Mn, Cr, Ni oxide/hydroxide Anhydrite/gypsum Silica (quartz/opal) Al-rich phase (gibbsite or Al-hydroxide) High-Mg calcite (dolomite) Calcite Cl-rich phase Na-Al-Si grain (analcime) NaCl
	104	Si-rich layer (Fe-smectite) Fe oxide/hydroxide Calcite, with Mg/Fe (dolomite) Al-rich grain (gibbsite, bayerite, nordstrandite) Cl- and S-rich grains NaCl, Na ₂ SO ₄ , CaSO ₄ , CaCl ₂ Ti-rich phase (anatase) (Serpentine) (Apatite) Silica (quartz, opal)

The discontinuous nature of the precipitated layer along with its porous appearance of loosely intergrown grains indicate that the precipitates do not form a reliable barrier to fluid infiltration. While the precipitates will influence the local fluid chemistry, they do not physically impede fluid-glass interaction.

The surface layer undergoes other changes upon aging. A network of cracks form and parts of the layer begin to pull away from the glass. Cracking begins as a localized phenomenon even before the layer has fully developed across the surface. This process, sometimes referred to as crazing, has been observed during leaching of simple alkali-silicate glasses.¹⁷ The inception of cracking may be influenced by the surface topography. The cause of cracking may be tensional forces at the interface between the hydrated altered layer and the glass. A contributing factor may also be volume changes and tensional forces within the layer as it begins to crystallize upon aging. Once a network of cracks is established, pieces of the layer begin to exfoliate from the surface, exposing patches of glass from below. Eventually, the exposed glass becomes covered with precipitates. The ubiquitous occurrence of cracks indicates that the surface layer cannot retard glass-fluid interaction to any large degree. While the intact layer may (or may not) act as a diffusion barrier, the cracks provide free access to the glass.

There are a number of secondary phases that have precipitated on the surface of both the glass and the metal components. The most common is Si-rich "clay" which has the same composition as the altered layer. Fe-oxide or hydroxide (XRD results suggest it is an oxide) is common especially on samples where the metal components have corroded. Some samples have a Cr- and Mn-rich phase, presumably an oxide or hydroxide. While the source of the Cr is probably the metal, no localized metal corrosion is observable on the samples where this phase occurs.

There are two common Ca-bearing phases: calcite and CaSO_4 . They may occur together but generally only one is present. The net negative release of Ca in all the experiments indicates that Ca is removed from the EJ-13 water. Furthermore, the Ca depletion indicates that CaSO_4 precipitated during the experiment rather than upon cooling during sampling. Being the stable phase at 90°C , anhydrite must have precipitated. This demonstrates the influence of the EJ-13 water composition on the formation of secondary phases. Sodium-bearing phases are abundant on some samples but absent on others. Their occurrence is presumably linked to the availability of water. Phases tentatively identified include: NaCl , Na_2SO_4 , and Na_2CO_3 .

A U-bearing phase was observed on the metal components of the P-III-6 batch experiment. The small clusters of acicular grains contain Si and Ca which is suggestive of uranophane. This is the only observed occurrence of an U-bearing phase in any of the parametric experiments, although U-bearing phases are observed in the N2 tests.⁶

In order to assess the relative effects of an unsaturated environment where water drips onto the waste form, it is informative to compare this study's results with other types of experiments. Two short-term leaching experiments have been performed at 90°C using the same SRL 165U glass.^{18,19} In these experiments, the glass was submerged in EJ-13 water and run both with and without an imposed γ -radiation field. The experiments of Ebert were performed at 0 and 1×10^{-3} rad/hr up to 278 days and those of Abrajano had a 1×10^{-4} rad/hr radiation field and a maximum duration of 182 days.

The normalized releases of B, Li, and U in the 278-day experiments of Ebert are presented in Table 17 along with the releases from selected batch and continuous experiments of similar duration. Element releases in the leaching experiments are only slightly greater than in the P-IV continuous and P-III batch experiments (by less than a factor of two). This difference is much less than

Table 17. Comparison of Normalized Release of B, Li, and U between the Leaching Experiments of Ebert and the Parametric Experiments

Test #	Time (weeks)	Normalized Release (g/m ²)		
		B	Li	U
G308 ^a	39.7	4.93	6.98	4.38
G309 ^a	39.7	4.80	6.89	4.17
G350 ^b	39.7	3.61	5.87	3.56
G351 ^b	39.7	4.08	5.97	3.51
Parametric Experiments				
P-II-1	39	2.2	0.9	0.29
P-II-2	39	1.0	1.1	0.24
P-II-6	39	0.8	1.1	0.27
P-III-1	39	0.5	1.8	0.46
P-III-2	39	0.4	1.6	0.34
P-III-7	39	3.1	4.2	2.11
P-III-8	39	2.0	3.3	1.48
P-IV-1	39	2.9	3.8	2.88
P-IV-2	39	2.2	3.2	2.10
P-V-1	39.5	0.1	0.0	0.00
P-V-2	39.5	0.1	0.5	0.06
P-VIII-1	39	0.1	0.8	0.07
P-VIII-2	39	0.1	0.5	0.05
P-VIII-5	39	0.2	0.4	0.09

^a90°C leach test of Ebert with 1×10^{-3} rad/hr γ -radiation.

^b90°C leach test of Ebert with no radiation.

the order of magnitude range in release obtained for the set of parametric experiments. Furthermore, the normalization procedure underestimates release only for the parametric experiments because the geometric and effective surface areas are equal in the leaching experiments (see above). This suggests that true normalized releases, based upon the effective surface area, would be in even closer agreement between the parametric and leaching experiments.

The release trends of the leaching and parametric experiments do appear to differ. The rates of release in the leaching experiments become progressively reduced through 39 weeks. In contrast, the release rates remain relatively constant in the parametric experiments for at least 300 weeks. This differing behavior may be attributable to the dripping environment where fresh water is periodically added and where evaporation can occur.

Relative release for the leaching (complete liquid submersion) and parametric (drip) experiments is $Li > B \sim U$ (except for P-II) suggesting a similar mechanism of glass reaction for both types of experiments. In the leaching experiments Na and Mg exhibit large positive releases but Ca has only a very small release. In the parametric experiments Na release is often erratic and Mg and Ca have net negative releases. This contrasting behavior is most likely attributable to differences in the secondary phases that precipitate on the glass. Aside from an Fe-smectite-like surface layer, precipitation in the leach experiments is not very extensive. Some Ca-rich precipitates such as calcite are reported by Ebert along with a U-silicate, an Al-rich phase, and rare NaCl. In contrast, precipitates are generally much more abundant in the drip experiments. Ca-rich precipitates such as calcite or anhydrite are common as is NaCl. It appears that in the unsaturated environment of the parametric experiments precipitation is more extensive, which in turn influences the solution chemistry. The development of a clay-like surface layer is common to both types of experiments and the behavior of the elements most indicative of glass reaction (Li, B, and U) is the same.

V. ACKNOWLEDGMENTS

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ADDENDUM

While the SEM provides important information about the nature of glass reaction, it lacks the requisite resolution to understand the detail of alteration layer development. Analytical electron microscopy (AEM) may provide the key to unravelling this process. For example, the AEM study by Abrajano et al. of leached SRL 131 glass reveals a reaction layer with a complex structure, composed of six distinct sublayers and a mixture of amorphous material and crystalline phases.¹² At present two samples from the parametric experiments have been prepared. The following a very brief description of these samples. A thorough AEM investigation will be the subject of a future topical report.

A section through the reacted layer from the bottom glass surface of P-VIII-7 (104 weeks) is presented in Fig. 42. As there is no accompanying glass in this sample, this must be viewed as only a partial section through the upper part of the layer. This part has a complex structure of repeated bands only partially attached to one another. Each band has a fine-grained Fe-rich element with an epitaxial growth of smectite on either side. The structure of the individual bands is reminiscent of that observed for the same glass after 280 days in static MCC-1 leach tests.²⁰ The origin of the multiple bands is uncertain at this time.

A sample from the side of P-III-10 (52 weeks) was taken from near the top surface where prolonged water contact had occurred during the experiment. There is a layer of coarse, loosely packed smectite grains which lies above the glass surface (Fig. 43). No Fe-rich band is observed here. The smectite may have formed by precipitation on the glass. However, etching has caused retreat of the glass surface, resulting in a gap between the smectite layer and the glass.

Much more work needs to be done; however, it is clear that the AEM is an extremely useful tool for investigating the mechanisms of glass alteration. This work is underway. It is comforting that some of the interpretations based on SEM observations are confirmed by the preliminary AEM results.

Fig. 42. TEM Micrograph of the Layer from the Bottom of P-VIII-7. The scale is 7 mm = 500 nm

Fig. 43. TEM Micrograph of the Side of P-III-10. The scale is 9 mm = 200 nm

APPENDIX I

Raw data for the analyses of solutions from the parametric unsaturated experiments (continuous mode) are presented. The data presented include the test number, sample interval (in weeks; both the interval and cumulative time periods are given), sample identifier (TF #), the solution volume in mL submitted for analysis (the original solution volume is diluted with acidified DIW prior to analysis), and the volume of test solution added during the test period (water is injected throughout the test period and a specified volume of water is added to the bottom of the test vessel at the beginning of each test period. The water added at the beginning of the test period is DIW for the P-II experiments and EJ-13 for the other experiments. The volume given in the H₂O Added column is only the volume of EJ-13 or J-13 water and the value is used in the background subtraction process).

The composition of groundwater (ppm) added during the test is given in the first row(s) under the heading of elements. For each sampling period, generally three rows of data are presented. The first row is the total mass of each element in the diluted solution submitted for analysis, the second row is the total mass of each element in solution that can be attributed to the glass (the value is obtained by subtracting from the total elemental mass the mass attributed to groundwater added to the test. The value will be negative if elements are precipitated from solution). The third row is the cumulative mass of each element attributed to the glass.

Test #	Time Period	TF #	Solution Volume	H ₂ O Added	E-J13	Al	B	Ca	Fe	Li	Pg	Mn	Na	Ni	Si	U	I
P11-1a	6	TF-65	20.57	0.900		100 1650 1560	130 18100 17983	13600 4300 -7940	10 2470 2461	49 4320 4276	2130 1070 -847	5 450 446	46700 28400 -13630	28 -25	30900 9460 -18350	0 420 420	4450 0 0
1b	7 13	TF-69	20.75	1.050		10375 10270 11830	16200 16064 34046	3940 -10340 -18280	2280 2270 4730	3110 3059 7334	930 -1306 -2154	280 275 720	28600 -20435 -54065	435 406 380	5800 -26645 -44995	504 504 924	0 0 0
1c	6.5 19.5	TF-72	20.71	0.975		1035 958 12768	9300 9173 43220	5200 -8060 -26340	1850 1840 6571	3300 3252 10587	970 -1107 -3260	410 405 1125	30800 -15532 -49598	400 373 753	8300 -21828 -66822	460 460 1384	0 0 0
1d	6.5 26	TF-79	20.52	0.975		1000 902 13670	8600 8473 51693	2000 -11260 -37600	1370 1360 7931	5130 5082 15669	550 -1527 -4787	160 155 1280	55860 10348 -39250	400 373 1126	4500 -25628 -92450	615 615 1999	0 0 0
1e	7 33	TF-91	20.80	1.050		1500 1395 15065	6000 5864 57556	3950 -10330 -47930	1620 1610 9540	4035 3984 19652	330 -1906 -6694	395 390 1670	44300 -4735 -43985	600 571 1696	12200 -20245 -112695	565 565 2564	0 0 0
1f	6 39	TF-97	24.92	0.900		1200 1102 16175	5200 5083 62640	2750 -9490 -57420	1050 1041 10582	4500 4456 24108	125 -1792 -8486	350 346 2016	64000 21970 -22015	2050 2025 3721	14000 -13810 -126505	570 570 3134	0 0 0
1g	6.5 45.5	TF-111	21.28	0.975		1200 1102 17278	2800 2673 65313	2100 -11160 -68580	1600 1590 12172	1210 1162 25271	250 -1827 -10312	340 355 2351	16400 -29132 -51148	425 398 4119	7000 -23128 -149632	147 147 3281	0 0 0
1h	6.5 52	TF-123	25.5	0.975		1300 1202 18480	2370 2243 67556	2500 -10760 -79340	5870 5860 18032	1000 962 26223	180 -1897 -12209	870 865 3216	19100 -26432 -77560		5360 -24768 -174400	242 242 3523	0 0 0
1i	6.5 58.5	TF-141	20.57	0.975		1000 902 19382	2900 2773 70329	11300 -1960 -81300	5140 5130 23162	1770 1722 27945	1200 -877 -13086		27000 -18532 -96112		9050 -21078 -195478	245 245 3768	0 0 0
1j	7 65.5	TF-152	21.11	1.05		1050 945 20328	3800 3664 73993	7600 -6680 -87980	2100 2090 25252	3380 3329 31274	1370 -866 -13952	510 505 3716	103200 54165 -41948		24700 -7745 -203222	443 443 4211	0 0 0
1k	5.5 71	TF-180	20.44	0.825		2000 1918 22245	2250 2143 76136	2050 -9170 -97150	715 707 25958	3470 3430 34703	350 -1407 -15360	960 956 4672	81600 43072 1125		6100 -19392 -222615	382 382 4593	0 0 0

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
11	7.5 78.5	TF-203	16.13	1.125	1600 1488 23732	3200 3054 79189	1300 -14000 -111150	400 389 26347	3550 2495 38198	260 -2136 -17496	145 139 4811	77100 24562 25568	320 288 4300	13400 -21362 -243978	448 448 5041	0 0 0
1m	5 83.5	TF-224	20.12	0.75	2000 1925 25658	1700 1602 80792	1600 -8600 -119750	1400 1392 27740	2150 2113 40311	260 -1338 -18833	260 256 5067	47300 12275 37962	560 539 4839	12100 -11075 -255052	356 356 5397	0 0 0
1n	7.5 91	TF-237	22.33	1.125	2200 2088 27745	1500 1354 82146	1100 -14200 -133950	330 319 28058	3750 3695 44006	200 -2196 -21030	130 124 5192	94000 41462 79425	450 418 5258	21900 -12862 -267915	431 431 5828	0 0 0
1o	6.5 97.5	TF-256	23.49	0.975	2300 2202 29948	700 573 82719	1200 -12060 -146010	230 220 28279	460 412 44418	110 -1967 -22996	110 105 5297	1200 -44932 35392	460 433 5690	2300 -27828 -295742	0 0 5828	0 0 0
1p	6.5 104	TF-268	20.97	0.975	2100 2002 31950	1300 1173 83892	2700 -10560 -156570	1000 990 29269	3550 3502 47921	300 -1777 -24773	400 395 5692	101700 56168 91260	420 393 6083	30000 -128 -295870	0 0 5828	0 0 0
1q	6.5 110.5	TF-290	15.71	0.975	2200 2102 34052	700 573 84465	4400 -8860 -165430	1600 1590 30859	960 712 48833	800 -1277 -26050	520 515 6207	12100 -33432 57828	520 493 6576	10400 -19728 -315598	0 0 5828	0 0 0
1r	6.5 117	TF-316	19.13	0.975	1900 1802 35855	550 423 84888	2900 -10360 -175790	950 940 31800	520 472 49305	460 -1617 -27666	80 75 6282	10100 -55452 22395	540 513 7089	4200 -25928 -341525	384 384 6212	0 0 0
1s	6.5 123.5	TF-334	17.69	0.975	1700 1602 37458	530 403 85292	1900 -11360 -187150	800 790 32590	1200 1152 50457	350 -1727 -29393	200 195 6477	32500 -13032 9362	350 323 7411	8500 -21628 -363152	459 459 6671	0 0 0
1t	5.5 129	TF-349	20.46	0.825	2500 1918 39375	600 493 85784	1100 -10120 -197270	600 592 33182	2200 2160 52617	360 -1397 -30790	180 176 6653	70000 31472 40835	473 -23 7388	9000 -16492 -379645	473 473 7144	0 0 0
1u	26 155	TF-317	15.55	3.900	1500 1110 40495	450 -57 85728	2300 -50740 -248010	800 761 33942	420 229 52846	370 -7937 -38728	140 120 5774	8200 -173930 -133095	430 321 7709	3400 -117110 -496755	312 312 7456	0 0 0

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
Iv	36.5 191.5	TF-501	22.71	5.475	2200 1652 42138	5320 4608 90336	6400 -68060 -316070	2200 2145 36088	11100 10832 63677	2140 -9532 -48249	840 813 7586	319200 63518 -69577	2450 2247 9956	175100 5922 -490832	4434 4434 11890	26800 2436 2436
Iw	18.5 210	TF-577	21.17	2.775	100 2117 1840 43977	44 931 571 90906	250 5292 -32448 -348518	47 995 967 37055	34 720 584 64261	31 656 -5254 -53504	5 106 92 7678	1340 28368 -101225 -170802	36 762 684 10640	200 4294 -81514 -572346	6.5 105 195 11995	300 6351 -5998 -3561
Ix	14.5 224.5	TF-639	18.38	2.175	1800 1582 45560	12130 11847 102754	8500 -21080 -369598	800 779 37833	1800 1693 65955	350 -4283 -57786	400 389 8067	104400 2828 -167975	680 619 11259	22800 -44408 -616754	239 239 12234	23200 13521 9960
Iy	11.5 236	TF-680	31.52	1.725	3200 3028 48587	146568 146344 249097	13200 -10260 -379858	1900 1883 39716	400 315 66270	1000 -2674 -60461	600 591 8659	7200 -73558 -241332	1000 952 12211	32500 -20802 -637556	117 117 12351	9500 1824 11784
Iz	20.5 256.5	TF-748	34.26	3.075	3400 3092 51680	45600 45200 294298	7500 -34320 -414178	1300 1269 40985	3600 3449 69720	550 -1473 -61933	340 325 8993	156200 12598 -228735	690 604 12815	79100 -15918 -653474	120 120 12471	38000 24316 36100
Iaa	5.5 262	TF-767	24.41	0.825	2400 2318 53997	10000 9893 304190	1500 -9720 -423898	800 792 41777	390 350 70069	270 -1487 -63421	120 116 9099	16800 -21728 -250462	730 707 13532	22400 -3692 -656566	24 24 12495	6600 2929 39028
Ibb	13 275	TF-820	18.28	1.95	5500 5305 57382	5500 5246 309437	1300 -25220 -449118	3800 3780 45557	370 274 70344	180 -3974 -67394	180 170 9270	7100 -83965 -334427	1650 1595 15117	25800 -34455 -691021	12 12 12507	16500 7822 46851
Icc	26 301	TF-864	15.04	3.90*	1500 1400 60702	2250 2120 311557	1350 -12250 -461368	890 880 46437	180 131 70475	420 -1710 -69104	500 495 9765	4210 -42490 -376917	450 422 15539	25870 -5030 -696051	23 23 12530	4510 60 46911

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mo	Mn	Na	Ni	Si	U	K
PII-2a	6	TF-64	20.60	0.900	J-13											
					100	130	13600	10	49	2130	5	46700	28	30900	0	4450
					3900	8650	1850	1440	1100	560	160	8240		2680	250	0
2b	7 13	TF-71	20.76	1.050	3810	8533	-10390	1431	1056	-1357	156	-33790	-25	-25130	250	0
					12250	5400	2000	1300	3100	460	150	23700		4150	378	0
					12145	5264	-12280	1290	3049	-1776	145	-23335	-29	-28295	378	0
2c	6.5 19.5	TF-73	20.88	0.975	15955	13796	-22570	2720	4104	-3134	300	-59125	-55	-53425	628	0
					1040	6050	2100	1670	9200	540	100	71000	410	18150	837	0
					942	5923	-11160	1660	9152	-1537	95	25468	383	-11978	837	0
2d	6.5 26	TF-80	20.99	0.975	16898	19720	-33830	4381	13257	-4670	395	-33658	328	-65402	1465	0
					2900	2500	2000	900	3800	340	100	31500	420	5700	233	0
					2802	2373	-11260	890	3752	-1737	95	-14032	393	-24428	233	0
2e	7 33	TF-92	20.99	1.050	19700	22093	-45090	5271	17009	-6407	490	-47690	721	-89830	1698	0
					1600	4000	2300	2400	10500	480	300	118100	900	51400	865	0
					1495	3864	-11980	2390	10449	-1756	295	59065	871	18955	865	0
2f	6 39	TF-98	22.40	0.900	21195	25956	-57070	7660	27457	-8164	785	21375	1591	-70875	2563	0
					1100	1120	2200	1650	1200	150	100	24400	450	2900	73	0
					1010	1003	-10040	1641	1156	-1767	95	-17630	425	-24910	73	0
2g	6.5 45.5	TF-112	19.08	0.975	22205	26960	-67110	9302	28613	-9930	881	3745	2016	-95785	2636	0
					950	860	1900	800	1240	170	115	23100	400	7100	66	0
					852	733	-11360	790	1192	-1907	110	-22432	373	-23028	66	0
2h	6.5 52	TF-124	25.15	0.975	23058	27693	-78470	10092	29806	-11837	991	-18688	2389	-118812	2702	0
					1300	900	4000	1500	1400	500	1500	27400		7000	101	0
					1202	773	-9260	1490	1352	-1577	1495	-18132	-27	-23128	101	0
2i	6.5 58.5	TF-140	20.24	0.975	24260	28466	-87730	11582	31158	-13414	2486	-36820	2362	-141940	2803	0
					1200	770	3240	3440	1500	485		22500		9300	79	0
					1102	643	-10020	3430	1452	-1592	-5	-23032	-27	-20828	79	0
2j	7 65.5	TF-153	20.48	1.05	25362	29109	-97750	15012	32610	-15006	2481	-59852	2334	-162768	2882	0
					1020	610	7800	2250	1820	1660	1150	67400		23600	108	0
					915	474	-6480	2240	1769	-576	1145	18365	-29	-8845	108	0
					26278	29583	-104230	17252	34379	-15582	3626	-41488	2305	-171612	2990	0

Test #	Time Period	TF #	Solution Volume	H ₂ O Added	Al	B	Ca	Fe	Li	K ₂	Mn	Na	Ni	Si	U	K
2K	5.5 71	TF-181	19.25	0.825	1900 1818 28095	620 513 30096	2700 -8520 -112750	2300 2292 19544	2900 2863 37238	500 -1257 -16840	620 616 4242	70800 32272 -9215	-23 2282	11550 -13942 -185555	179 179 3169	0 0
2I	7.5 78.5	TF-204	16.77	1.125	1700 1588 29682	855 709 30804	4700 -10600 -123350	600 589 20132	3520 3465 40703	440 -1956 -18796	130 124 4366	78500 23962 16748	340 308 2590	13600 -21162 -206718	116 116 3285	0 0
2M	5 83.5	TF-223	20.64	0.75	2000 1925 31608	660 562 31367	1900 -8300 -131650	370 362 20495	660 623 41326	270 -1328 -20123	100 96 4462	14700 -20325 -3578	600 579 3169	4300 -18875 -225592	31 31 3316	0 0
2N	7.5 91	TF-238	22.69	1.125	2200 2088 33695	680 534 31900	1300 -14000 -145650	250 239 20734	450 395 41721	230 -2166 -22290	110 104 4567	8200 -44338 -47915	450 418 3583	2300 -32462 -258055	22 22 3338	0 0
2O	6.5 97.5	TF-257	22.84	0.975	2300 2202 35898	690 563 32464	1800 -11460 -157110	250 240 20974	460 412 42133	500 -1577 -23866	110 105 4672	23100 -22432 -70348	460 433 4020	2300 -27828 -285882	0 0 3338	0 0
2P	6.5 104	TF-269	21.51	0.975	2200 2102 38000	1600 1473 33937	5800 -7460 -164570	1660 1650 22624	5160 5112 47246	860 -1217 -25083	430 425 5097	185000 139468 67120	420 393 4413	74900 44772 -241110	0 0 3338	0 0
2Q	6.5 110.5	TF-291	15.71	0.975	1700 1602 39602	1020 893 34830	2400 -10860 -175430	850 840 23464	740 692 47938	360 -1717 -26800	190 185 5282	25600 -21932 47188	380 353 4766	12400 -17728 -258838	0 0 3338	0 0
2R	6.5 117	TF-317	22.65	0.975	2200 2102 41705	450 323 35154	1700 -11560 -186990	960 990 24354	680 632 48670	320 -1757 -28556	110 105 5387	10900 -34632 12555	450 423 5189	5000 -25128 -283965	0 0 3338	0 0
2S	6.5 123.5	TF-335	18.92	0.975	1900 1802 43508	570 443 35597	2100 -11160 -198150	700 690 25345	380 332 48902	380 -1697 -30253	230 225 5612	4900 -40632 -28078	360 353 5541	3600 -26528 -310492	989 989 4327	0 0
2T	5.5 129	TF-350	17.11	0.825	1700 1618 45125	500 393 35990	20700 9480 -188670	2000 1992 27036	800 760 49662	1200 -557 -30810	430 426 6038	25200 -13328 -41405	670 847 6388	9600 -15892 -326385	640 640 4967	0 0

Test #	Time # Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
2u	26 155	TF-318	15.94	3.900	1600 1210 46335	320 -187 35802	1200 -51840 -240510	640 661 27638	480 289 49951	220 -8087 -38898	80 60 6099	7700 -174430 -215835	320 211 6599	3500 -117010 -443995	1190 1190 6157	0 0
2v	36.5 191.5	TF-502	17.91	5.475	1800 1252 47588	950 238 36041	9700 -54760 -305270	8400 8345 35983	230 -38 49912	1250 -10412 -49309	1700 1673 7771	49600 -206082 -421918	3220 3067 9686	84100 -85078 -528472	150 150 6307	5400 -18964 -18964
2w	18.5 210	TF-578	19.85	2.775	100 1985 1708 49295	340 6749 6388 42429	1220 24217 -13523 -318793	110 2184 2156 38138	190 3772 3636 53548	50 993 -4918 -54228	15 298 284 8055	12900 256065 125473 -295445	56 1112 1034 10700	1970 39104 -46643 -575116	14 278 278 6585	420 8337 -4012 -22976
2x	14.5 224.5	TF-649	19.24	2.175	1900 1682 50978	14400 14117 56546	10400 -19180 -337973	2100 2078 40217	3800 3693 57241	900 -3733 -57960	290 279 8334	215200 114528 -180818	600 539 11239	62700 -4508 -579623	231 231 6816	25400 15721 -7254
2y	11.5 236	TF-681	31.20	1.725	3100 2928 53905	25600 25376 81922	4200 -19260 -357233	1000 983 41200	3100 3015 60257	340 -3334 -61294	160 151 8486	7500 -73058 -253875	620 572 11810	29300 -24002 -603626	296 296 7112	9400 1724 -5530
2z	20.5 256.5	TF-749	33.36	3.075	3300 2992 56852	20000 19600 101464	4000 -37820 -401173	700 669 41864	500 349 60584	330 -6220 -68473	160 145 8628	12700 -130902 -495792	620 534 12332	58700 -36318 -653848	37 37 7149	10000 -3684 -9214
2aa	5.5 252	TF-768	23.99	0.825	2400 2318 59170	6000 5893 107356	700 -10520 -411693	500 492 42356	2400 2360 62944	240 -1517 -69990	120 116 8744	6000 -32528 -438320	220 197 12529	19700 -5792 -659640	24 24 7173	4800 1129 -8086
2bb	13 275	TF-821	17.77	1.95	5300 5105 64275	96600 96346 203703	2300 -24220 -435913	22700 22680 65036	350 254 63198	200 -3954 -73944	10000 9990 18734	8700 -82365 -520685	3000 2945 15474	35900 -24355 -683996	18 18 7191	16300 7322 -763
2cc	26 301	TF-865	15.07	3.90	1500 1110 65385	8740 8233 211936	770 -52270 -488183	590 551 65388	500 309 63507	200 -8107 -82050	150 130 18865	220000 37870 -462815	450 341 15815	104740 -15770 -69766	41 41 7232	39480 22125 21362

Test #	Time Period	TF	Solution Volume	SEC Added	Al	S	Ca	P ₂	Li	K ₂	Mn	Na	Hi	Si	U	I
1k	6.5 71.5	TF-272	10.27	1.175	1090	1040	3000	11600	1800	250	300	51400	2500	68200	522	0
					166	840	-1618	11588	1717	-178	354	-590	2470	22142	517	0
					7832	11954	-14830	251672	33641	-2122	37256	13460	29974	105550	4803	0
1l	6.5 75	TF-321	20.42	1.175	2000	940	3700	32700	2100	250	1700	64500	6500	125400	318	0
					1166	740	-1118	32558	2017	-168	1674	9510	6270	62042	313	0
					8995	12674	-15948	284360	35678	-2350	40390	25370	36270	187392	5116	0
1m	13.0 91	TF-245	11.19	2.150	1450	1340	7500	23800	3700	680	1500	99200	3110	111700	866	0
					-76	1454	-1815	23778	3547	-158	1489	-821	3157	23062	632	0
					3821	14169	-17262	306133	38225	-2559	42479	25150	35428	215953	5574	0
1n	13.0 104	TF-393	11.00	2.150	1650	1800	6800	40800	3300	540	1200	103000		78500	526	0
					1134	1454	-8572	40778	3188	-25	1189	-2720	-45	6190	526	0
					10855	15643	-25835	348917	42413	-2534	43669	22370	39384	222088	6500	0
1o	13.0 117	TF-424	11.33	2.150	1100	1200	7000	3580	3700	240	600	120100	900	85500	598	0
					584	1554	-8572	5878	3588	-305	589	14320	857	12330	796	0
					10639	17196	-54288	354756	46002	-2840	44258	36650	40242	234418	7450	0
1p	13.0 130	TF-453	15.24	2.150	1500	2300	7500	13000	3500	260	600	110200	1200	79300	706	14500
					984	1954	-7472	12978	3388	-305	589	4420	1157	630	764	5558
					11623	18150	-41680	367774	49390	-3155	44847	41110	41358	225648	8240	3853
1q	14.0 144	TF-486	16.50	2.150	1700	1340	5400	4300	3500	80	450	90100	870	72800	607	13700
					1148	970	-11045	4277	3380	-525	419	-23060	824	-5860	605	2400
					12771	20130	-52725	374031	52770	-3670	45266	18050	42222	229188	8865	5950
1r	12.0 156	TF-525	17.05	2.000	1900	1500	5100	9100	2700	210	475	85400	1300	62500	487	8000
					1420	1178	-7200	9080	2356	-316	465	-13000	1250	-5408	455	-2000
					14181	21259	-61925	381131	55366	-3786	45731	36550	43481	223588	9350	3950
1s	13.0 159	TF-580	20.25	2.150	180	47	120	220	89	20	9	2600	34	1400	21	300
					2825	952	2430	4455	1682	465	182	52650	739	28350	425	6075
					1507	606	-12742	4434	1650	-160	172	-53130	636	-44320	425	-4675
					15700	21904	-74868	385565	57057	-4146	45902	-42080	44148	179266	9775	-725

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Hg	Mn	Na	Ni	SI	U	X
1t	12.0 182	TF-627	20.25	2.15	2000 1484 17164	3320 3554 25457	6100 -5272 -24140	3400 2376 388943	5300 5186 62245	200 -365 -4512	180 167 46071	111200 5420 -42660	600 537 44726	50300 17630 196856	1542 1560 11313	16000 5250 4325
1u	12.5 195.5	TF-633	20.91	2.225	2100 1566 18750	3600 3242 28699	2500 -13409 -97549	5000 4978 393721	5400 5284 67529	200 -385 -4897	190 179 46250	111600 9330 -33350	630 586 45311	80100 4875 201792	1350 1368 11310	12300 1675 6200
1v	12.5 208	TF-733	22.17	2.075	100 2217 1719 20469	160 3547 2213 51712	260 5764 -9072 -106621	270 5986 5965 395586	250 5542 5435 72564	10 222 -324 -5221	12 266 256 46306	4720 104642 2552 -30778	40 887 845 46156	3380 74935 4800 206572	62.2 1377 1377 12687	57 13080 2705 3995
1w	13 221	TF-771	20.57	2.15	2100 1584 22053	4600 4254 36166	6500 -8672 -115693	4400 4378 404245	5500 5388 78352	360 -295 -5427	210 199 46705	113500 8120 -22656	1800 1757 47913	66500 -7030 199562	1266 1264 13751	16200 6050 14755
1x	13 234	TF-830	11.37	2.15	1950 1414 23457	5340 4994 41160	6370 -9002 -124496	6370 6348 410613	6250 6136 84490	254 -269 -5626	455 444 47149	114800 9020 -13638	970 927 48640	7530 -68000 132562	1615 1613 15564	18870 3120 16075
1y	26 260	TF-866	17.55	4.1	5150 2176 25665	11080 10420 51566	7200 -22115 -146611	4050 4009 414622	12540 13327 97817	316 -762 -6726	229 208 47355	209200 7480 -6156	1560 1498 50335	145000 9380 142442	3709 3755 19265	28830 8230 24405

[illegible]

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	X
2k	6.5 71.5	TF-293	9.87	1.175	1000	1825	3000	16100	2700	220	500	71300	3900	86600	615	0
					166	1675	-1818	16088	2617	-195	494	16310	2976	43242	611	0
					7762	11239	-15650	345672	31041	-2262	42666	29810	34004	147880	4580	0
2l	6.5 78	TF-322	20.30	1.175	2000	930	2300	45700	1460	180	1480	13000	800	30900	254	0
					1166	730	-2818	45688	1277	-273	1594	-41990	775	47542	250	0
					8928	11267	-16468	391360	32416	-2540	44260	-12160	34780	195422	4830	0
2m	13.0 91	TF-346	10.55	2.150	1100	1400	3300	14300	2250	260	870	65200	1300	84800	567	0
					-426	1034	-5515	14276	2097	-578	859	-55320	1257	5465	561	0
					8501	13004	-25982	405639	34515	-3119	45119	-47500	36038	200388	5392	0
2n	13.0 104	TF-354	11.16	1.500 ***	1100	330	2300	28200	1750	190	1600	61360	-30	58100	392	-7500
					740	68	-8425	28185	1872	-204	1592	-12500	390	6800	396	-7500
					9241	13072	-32408	433824	36367	-5323	46712	-60600	36006	207688	5782	-7500
2o	13.0 117	TF-425	11.56	1.150 ***	1200	600	2300	10300	1400	160	500	44460	2100	24600	193	-5750
					924	415	-5922	10288	1340	-142	494	-12160	2077	-14530	192	-5750
					10165	13507	-38330	444112	37727	-3466	47206	-72180	38084	193158	5974	-13250
2p	13.0 130	TF-454	15.71	2.150	1600	2800	6300	13500	5500	250	400	176000	1700	87000	1175	21800
					1084	2454	-9072	13478	5388	-335	389	70220	1657	14330	1173	11050
					11249	15961	-47402	457591	43116	-3801	47595	-1960	39742	207488	7147	-2200
2q	14.0 144	TF-487	16.30	2.300	1600	1960	5200	3900	3400	80	160	95500	2000	68000	647	14800
					1048	1590	-11245	3877	3280	-525	165	-17660	1754	-10660	645	3300
					12297	17551	-58648	461466	46396	-4325	47764	-19620	41696	196828	7791	1100
2r	12.0 156	TF-550	20.17	1.050 ***	2200	1900	3600	9100	2400	340	540	68400	3800	44200	637	7900
					1664	1676	-6338	9086	2228	-26	359	12	3772	-3338	636	950
					15964	19227	-64966	470554	46724	-4352	48097	-19608	45462	193490	8427	2050
2s	13.0 165	TF-521	20.71	1.100 ***	160	110	270	240	170	110	24	5220	56	3630	38	630
					2671	2278	5592	4970	3521	267	497	11077	746	75177	787	13047
					1607	2101	-2273	4959	3464	-82	492	56057	724	37557	786	7547
					15771	21228	-67289	475513	52167	-4434	45728	36446	46171	231047	9213	9597

Test #	Time Period	TF	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	SI	U	X
21	12.0 182	TF-632	12.75	1.315 ***	1970 1586 17556	1600 1335 22717	2200 -7166 -74426	5800 5757 481300	2600 2532 54719	180 -115 -4558	150 193 48772	88700 4542 40657	1000 874 4.165	25200 -15002 215445	712 711 9824	9400 2850 12447
22	13.5 195.5	TF-689	22.11	1.625 ***	2200 1811 17167	2600 2039 24756	3300 -8283 -82707	18800 18784 500084	3500 3216 57935	310 -116 -4714	1300 1292 50064	75300 15586 58293	3360 3268 55453	42000 -13404 202941	3000 755 19722	11401 2250 14747
23	12.5 208	TF-754	24.62	2.075	2500 2602 21169	1600 1266 26022	2500 -12386 -95045	9400 9379 509463	2300 2192 68127	240 -306 -5020	370 360 50423	62000 -40950 16203	1400 1353 51771	31300 -57685 162375	926 924 11646	5800 -1775 12371
24	13 221	TF-772	21.01	2.15	2100 1564 22753	3400 3054 29076	4600 -10772 -105818	6100 6078 515542	5000 4885 65015	270 -295 -5316	480 469 50893	144600 38820 53023	2630 2587 54378	68700 -4830 157546	1414 1412 13658	22500 11750 24722
25	13 234	TF-831	15.26	2.15	1460 944 23697	3710 3364 32440	5570 -9802 -115620	10740 10718 528260	3850 3738 68753	380 -185 -5501	650 639 51592	107300 1520 56543	2390 2347 56725	59300 -14230 145316	1591 1589 14647	15250 4500 29222
26	26 250	TF-869	17.4	4.1	1740 756 24453	4520 3660 36300	4000 -25815 -140555	5050 5009 531269	6055 5877 74630	209 -865 -6370	1860 1660 52591	135550 -66179 -7827	1220 1138 57863	73800 -86433 76856	2875 2871 17616	16630 -1500 27522

Test #	Time Period	TF #	Solution Volume	H ₂ O Added	Al	S	Ca	Fe	Li	Hg	Mn	Na	Ni	Si	U	K
PIV-1a	13	TF-154	21.00	1.475	E-J13 710	170	4100	10	71	390	5	46800	20	36900	4	5900
					E-J13 -40	161	7150	10	52	263	5	47200	20	34200	1	
1c	13.5 35.5	TF-154	21.00	1.475	7100	16800	4400	27900	22500	945	12600	136700	-30	140100	4850	0
					6053	16349	-1648	27385	22395	370	12793	67870		85672	4845	
1c	13.5 39	TF-199	17.19	1.4375	3400	13400	3400	32100	14900	530	2400	117400	5200	104900	5947	0
					2379	13156	-2494	32866	14698	-31	2393	50125	5171	51856	5942	0
1c	13.5 39	TF-239	18.30	1.5125	8452	25395	-4141	59971	37093	339	15185	117995	5142	137529	10787	0
					3600	12100	3400	10200	13600	360	500	116200	1500	95500	5300	0
1c	13 52	TF-270	21.97	1.475	2726	11843	-2801	10155	13693	-230	492	45415	1470	39489	5295	0
					11158	41348	-6842	70156	50786	109	15678	163410	6612	177015	16081	0
1c	13 52	TF-270	21.97	1.475	4600	15800	5300	11000	16400	640	1000	135300	2300	117000	5954	0
					3553	15547	-748	10595	16295	65	993	68279	2270	62572	5949	0
1c	13 65	TF-314	18.49	1.475	14711	56357	-7690	81141	67081	174	16670	227660	8862	239590	22030	0
					3000	17800	3900	18700	18900	330	3200	125200	1800	117600	5140	0
1c	13.5 80.5	TF-347	10.39	1.6675	1953	17549	-2148	18685	18795	-245	3193	56170	1770	63172	5135	0
					16664	74446	-9338	59826	85876	-71	19963	253850	10652	302762	27165	0
1c	13.5 91	TF-391	15.41	1.2875	6300	34100	4300	14800	33400	350	800	197500	2809	244200	8832	0
					5116	36817	-2337	14763	33282	-300	792	121461	2767	182669	8826	0
1c	13.5 91	TF-391	15.41	1.2875	21780	108263	-12374	114610	119158	-372	20655	407311	13419	485432	35991	0
					1800	17000	7900	10500	10600	750	1200	105600	15601	76400	2927	0
1c	13 104	TF-420	13.52	1.475	886	16781	2621	19487	10509	246	1194	45345	1474	28891	2922	0
					22666	125044	-9753	125097	129667	-124	21848	452656	14893	514323	38913	0
1c	13 104	TF-420	13.52	1.475	3290	17600	4300	9200	18600	270	300	136600	15001	119000	4813	-7375
					2646	17563	-6246	9165	18723	-116	293	64030	1470	68555	4612	-7375
1c	13.5 117.5	TF-449	14.54	1.5125	25512	142406	-15999	134262	148390	-242	22141	516366	16364	582878	43725	-7375
					2900	18300	4500	3600	20500	260	190	143200	400	129800	6179	10600
1c	13.5 132	TF-484	15.56	1.5375	2557	18056	-6314	3565	20421	-138	182	63785	370	78072	6177	3038
					26049	160463	-22314	137367	168811	-373	22323	565471	16734	660750	49902	-4335
1c	14.5 132	TF-484	15.56	1.5375	20200	53800	7000	8000	65300	180	660	347000	760	467500	17927	16500
					20519	53544	-4351	7984	65217	-238	672	262595	748	413508	17925	8561
					48568	214067	-26664	145351	234029	-617	22995	845066	17462	1074458	67628	4515

Fast #	Time Period	TF #	Solution Volume	H ₂ O Added	Al	B	Ca	Fe	Li	Nb	Mn	Na	Ni	Si	U	K
				E-J13	710	179	4100	10	71	390	5	43300	20	36500	4	
				E-J13	240	161	7150	10	52	263	5	49200	20	34530	1	5000
1K	11	TF-523	19.74	1.325	11300	48700	11600	9700	36000	1300	1100	186200	1300	262600	10716	9200
	143				11432	48487	2126	6687	37931	1452	1053	123910	1474	217285	10715	2575
					60050	262494	-24538	155338	271960	835	24069	971076	18955	1291745	78542	7100
11	13	TF-555	20.16	1.475	540	1760	250	470	1910	29	57	10100	81	14500	471	410
	156				10586	35462	5043	9475	38506	535	1149	203416	1633	295304	9455	8266
					10532	35244	-3503	9460	38429	157	1142	131045	1663	229569	9474	891
					70582	297738	-30044	164598	310289	1031	25231	1132122	20559	1531602	88036	7991
1m	13	TF-636	19.82	1.475												
	169				5200	23000	3400	4400	27730	300	700	188300	1000	209200	7313	10100
					4846	22763	-7146	4595	27623	-88	693	115730	970	149753	7312	2725
					75428	320501	-37190	169583	338012	943	25923	1217852	21529	1681357	75346	10716
1n	15	TF-670	19.37	1.475												
	182				2300	10700	5600	5000	14900	390	300	116000	1400	107700	4474	6600
					1946	10463	-4946	4985	14823	2	293	45430	1370	57255	4473	-775
					77374	230963	-42137	174369	352835	945	26216	1263282	22900	1738612	99820	9941
1o	13	TF-765	20.30	1.475												
	195				4500	15400	6300	9900	20900	590	1500	144100	2800	142900	5501	9300
					4146	15165	-4246	9985	20833	202	1493	71530	2770	97455	5500	1925
					81520	346126	-46353	184254	373657	1148	27708	1534812	25670	1831067	105320	11866
1p	15	TF-758	19.27	1.475												
	208				2300	8900	6000	8700	7200	540	1400	61100	1800	78200	2563	7300
					1946	8663	-4546	8885	7123	152	1393	8530	1770	27755	2562	-75
					83466	354782	-50929	193139	380752	1300	29101	1343542	27441	1858322	107891	11751
1q	13	TF-801	19.92	1.475												
	221				4200	2600	5300	8900	1200	300	600	46600	2000	55700	1022	12500
					3846	2365	-5246	5285	1728	-88	593	-26570	1770	5285	1021	5115
					67312	357151	-56176	202024	382505	1212	22694	1316772	29411	1864077	108902	16916
1r	26	TF-855	18.37	2.45												
	247				1800	2570	6200	5200	5150	400	510	51670	720	76050	1160	7500
					1212	2176	-11268	5856	5023	-244	495	-25570	671	-7740	1035	-4350
					88524	359526	-67443	207680	387528	967	30191	1267562	30062	1856357	109999	12566

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
19	13	TF-155	20.92	1.475	E-J13 710	170	4100	10	71	590	5	48600	20	36500	4	
					E-J13 240	161	7150	10	52	263	5	49200	20	34200	1	5000
20	13.5	TF-200	17.66	1.4375	1670 623	3140 2689	5630 -395	35600 35795	9450 9315	900 325	15700 15693	77700 8670	-50	43100 -11523	2030 2025	0
					2600 2579	15400 15156	4100 -1794	22500 22486	19500 19658	540 -21	3500 3893	153000 85725	5400 5371	110600 56956	5611 5866	0
21	13.5	TF-240	20.27	1.5125	3202 4528	18045 29386	-2191 -4672	55271 66656	25013 42306	304	17565	94395	5342	45625	7821	0
					2400 1324	11600 11343	3700 -2501	8400 8385	13400 13293	350 -240	670	112200	1400	80500	3728	0
22	13	TF-271	24.16	1.475	5681 1353	38137 9749	-7140 -2448	76041 9385	50901 8395	-151	20246	156310	6712	70316	11613	0
					2400 6534	10900 46766	3600 -9038	9400 100426	8700 60696	360 -405	680	90400	1300	77100	3141	0
23	13	TF-315	17.07	1.475	1700 653	7900 7649	4100 -1949	24400 24385	9500 9795	320	1300	84000	2200	65700	2680	0
					720 6534	19617 46766	-3016 -9038	13583 100426	10482 60696	-248	742	18195	3167	21154	2903	0
24	15.5	TF-348	11.32	1.6625	7253 1900	57604 11100	-12104 3600	114010 13600	71178 10800	-655	23475	159545	15319	125416	20327	0
					720 1086	19617 1581	-3016 -179	13583 95867	10482 9609	-248	742	18195	3167	21154	2903	0
25	10.5	TF-392	15.52	1.2875	8339 2900	71185 13800	-12262 5100	212677 95900	60737 9700	-427	25768	224190	14574	156608	23064	0
					1086 1346	1581 11263	-179 -6246	95867 14285	9609 12523	229	2294	33645	1274	31191	2757	0
26	13	TF-419	14.62	1.475	9795 1800	82447 11500	-18529 4300	227182 14300	93310 12600	-615	26251	244520	15564	195062	26622	-7375
					1346 9795	11263 82447	-6246 -18529	14285 227182	12523 93310	-188	523	40330	1270	38455	3598	-7375
27	13.5	TF-450	13.79	1.5125	2200 1837	12300 12056	5100 -5714	14200 14185	14200 14121	410	580	127700	550	140700	4440	8100
					11622 3500	94504 17100	-24243 4700	241367 3700	107432 15500	-602	26663	317805	16384	254035	31060	-6238
28	14.5	TF-485	14.77	1.5875	14741 3119	111346 16544	-30694 -6351	245051 3664	126649 19417	-830	27056	350400	17552	353642	36957	-5175
					11622 3500	94504 17100	-24243 4700	241367 3700	107432 15500	-602	26663	317805	16384	254035	31060	-6238

Test #	Time Period	TF #	Solution Volume	H2O Added	E-J13	Al	B	Ca	Fe	Li	Hg	Mn	Na	Ni	Si	U
PIV-3	26.5	TF-201	18.99	1.59	E-J13	710 7690 6471.1	170 19800 15529.7	4100 9700 3181	10 46100 46084.1	71 30200 30067.11	390 1500 679.9	5 25100 25092.95	46800 205100 130688	20 4900 4868.2	36900 163100 104429	4 7748 7742.339
PIV-4	26.5	TF-202	15.3	1.51		9300 8227.9	16800 16543.3	6570 2379	62900 6692.79	23800 6692.79	1700 1111.1	20809 26792.45	185100 114432	6900 6869.8	155800 100081	7435 7429.624
PIV-5	52	TF-202	24.66	2.72		12800 10868.6	42200 41737.6	13300 2148	39700 39672.8	50160 49704.88	1700 637.2	12100 12036.4	372400 245104	4300 4245.6	350200 249832	15190 15180.31
PIV-6	52	TF-273	23.36	2.85		9300 7276.5	24400 23915.5	14100 2415	101000 100971.5	40200 39997.65	3400 2288.5	46200 46185.75	370200 236820	10300 10243	272900 167795	7358 7347.854

Test #	Time Period	TF #	Solution Volume	Added	E-J13	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	I
2V-1a	15.5	TF-225	22.12	0.8000	E-J13	710	170	4100	10	71	350	5	46800	20	36900	4	5500
						240	161	7150	10	52	263	5	49200	20	34200	1	
						2230	660	3540	94000	660	330	6000	15000	3330	79600	20	
						1632	524	260	93992	603	18	5995	-20640	3284	50020	17	0
1b	10.5	TF-253	20.60	0.5750		2030	1030	1700	26600	400	230	1130	10700	3300	123800	20	0
	26					1592	902	-658	26594	359	6	1697	-16410	3288	102582	18	0
						3224	1426	-398	120586	962	24	7093	-87130	6572	152662	35	0
1c	13.5	TF-282	14.47	0.7250		1400	910	2700	43800	350	450	8000	15800	5900	34300	22	0
	39.5					885	787	-272	43793	299	167	7996	-18130	5886	7548	19	0
						4109	2213	-670	164379	1261	191	15090	-55380	12458	160210	55	0
1d	12.5	TF-323	22.29	0.6500		2200	650	1400	7400	600	160	360	14300	850	20500	53	0
	52					1738	540	-1265	7394	554	-94	297	-16120	837	-3485	51	0
						5848	2752	-1935	171772	1815	98	15386	-71500	13295	156725	105	0
1e	16.0	TF-355	13.07	0.8000		1300	400	2600	18800	2600	250	600	29300		22100	45	-4000
	68					1108	271	-3120	17992	2558	40	596	-10060	-16	-5260	44	-4000
						6956	3024	-5055	189764	4373	137	15982	-81560	13279	151465	149	-4000
1f	12.0	TF-403	9.38	0.6500		900	280	1900	10100	820	250	450	14100		7500	54	-3250
	80					744	175	-2748	10094	786	79	447	-17880	-13	-14730	53	-3250
						7700	3199	-7802	199858	5159	216	16429	-99440	13266	136735	203	-7250
1g	12.0	TF-426	12.69	0.6500		1200	380	2300	5700	1400	140	140	17900	380	11500	28	-3250
	92					1044	275	-2348	5694	1366	-31	137	-14080	367	-10730	27	-10500
						8744	3474	-10150	205552	6526	185	16566	-113520	19633	126005	230	-10500
1h	18	TF-455	16.72	0.8750		1700	830	3800	4000	14700	170	150	140100	1100	69600	281	15200
	110					1490	689	-2456	3991	14654	-60	146	97050	1082	39675	280	10825
						10234	4164	-12606	209543	21180	125	16711	-16470	14716	165680	510	325
1i	7.5	TF-498	14.12	0.5000		1400	420	2800	3100	2000	230	230	19800	1400	11300	138	7100
	117.5					1280	340	-775	3095	1974	98	228	-4800	1390	-5800	138	4600
						11514	4503	-13381	212538	23154	224	16939	-21270	16106	159880	648	4925
1j	12.5	TF-532	19.28	0.6500		1900	580	2500	3900	190	210	190	11500	770	7700	19	5800
	130					1744	475	-2148	3894	156	39	187	-20380	757	-14530	18	2550
						13258	4978	-15529	216531	23310	253	17126	-41650	16662	145350	666	7475

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	O	I
				E-J13	110 240	170 161	4100 7150	10 10	71 52	390 263	5 5	46800 49200	20 20	36900 34200	4 1	5000
Ik	13.0 143	TF-582	19.23	0.5875	100 1923 1758 15016	30 577 466 5445	150 2884 -2031 -17560	250 4808 4801 221332	22 423 387 23698	12 231 50 313	9 173 170 17295	720 13846 -19979 -61629	53 1019 1005 17868	270 5192 -18320 127030	2 29 28 694	300 5769 2332 9806
Il	13.0 156	TF-642	18.06	0.6875	1800 1835 16550	600 489 5934	2500 -2416 -19976	2200 2193 223525	4300 4264 27962	180 -1 312	90 87 17382	61900 28075 -35554	360 346 18214	25600 2088 129117	81 80 775	9400 5962 15769
Im	13.0 169	TF-690	18.96	0.6875	190 25 16676	570 459 6393	1900 -3316 -22991	6400 5393 229918	1000 964 28926	190 9 321	300 297 17678	12700 -21125 -54678	600 586 18800	7800 -15712 113405	132 131 906	5700 2262 18032
In	13.0 182	TF-737	21.01	0.6875	210 45 16720	630 519 6913	2300 -2616 -25607	4400 4393 234311	1400 1364 30290	210 29 360	190 187 17865	23100 -10725 -65404	1100 1086 19887	15100 -8412 104992	95 94 1000	6300 2862 20894
Ic	14.0 196	TF-773	20.00	0.7250	200 26 16746	1800 1583 8596	2900 -2284 -27890	5400 5393 239704	5800 5762 36053	200 9 359	260 256 18121	90000 54332 -11072	600 586 20472	56400 31605 136597	570 569 1569	13600 9975 30869
Ip	12 208	TF-832	9.31	0.6500	930 774 17520	930 825 9421	2800 -1848 -29738	3900 3894 243596	1400 1366 37419	230 59 419	280 277 18398	25700 -6280 -17354	870 857 21329	19200 -30340 133567	257 256 1826	3458 200 31059
Iq	26 234	TF-870	15.48	1.1750	1550 1258 18788	2475 2285 11707	3715 -4686 -34424	6200 6188 249786	6650 5389 44008	200 -109 369	294 288 18686	86850 29040 11686	1080 1056 22386	62850 22665 156232	1145 1144 2970	12990 6505 37574

Test #	Time Period	TF #	Solution Volume	R20 Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
FVIII-1a	13	TF-316	21.93	2.150	E-313	710	170	4100	10	390	5	4650	20	36900	4	5000
					E-313	240	161	7150	10	283	5	4500	20	34200	1	
1b	13	TF-342	19.42	2.150	E-313	280	2800	4800	9600	420	5300	76500	8000	44500	465	0
					E-313	874	2434	48578	9447	-418	5389	-25800	8257	-39126	457	
1c	13	TF-388	12.16	2.150	E-313	1900	1500	3700	8500	270	3600	197200	8900	103900	253	0
					E-313	374	1134	-5115	43676	-563	3589	6760	8857	24565	244	0
1d	13	TF-401	14.17	2.150	E-313	1047	3589	-9730	92557	-967	5876	-17240	17114	-14570	702	0
					E-313	1290	360	2200	69900	260	2600	60700		42800	98	0
1e	13	TF-451	13.72	2.150	E-313	-326	-6	-6615	60676	-576	2589	-15920	-43	-26526	89	0
					E-313	720	3564	-16345	153436	-1566	11466	-37160	17071	-51105	791	0
1f	13	TF-451	14.17	2.150	E-313	1400	720	3100	8100	270	570	92100		52100	56	0
					E-313	-126	364	-5715	8078	-568	559	-8520	-43	-26235	49	0
1g	13	TF-451	13.72	2.150	E-313	554	3518	-20660	161514	-2134	13027	-45660	17028	-77340	841	0
					E-313	1400	720	4400	9600	410	480	141300	1000	77100	56	18500
1h	15	TF-489	17.86	2.450	E-313	884	574	-10472	9578	-155	467	35320	957	3570	56	7750
					E-313	1476	4352	-38032	171092	-2269	12496	-10160	17865	-79770	885	7750
1i	15	TF-515	18.61	1.750	E-313	1300	570	5400	5200	210	770	111500	1500	68000	259	17500
					E-313	1212	176	-12118	5176	-434	768	-6740	1451	-15770	257	5230
1j	15	TF-515	18.61	1.750	E-313	2650	4467	-43150	176268	-2724	13254	-15560	19436	-89560	1153	13900
					E-313	1900	740	6000	9100	860	760	66700	2000	59700	27	10400
1k	15	TF-572	18.61	2.025	E-313	1473	453	-4727	9662	352	771	-576	1964	-976	25	1500
					E-313	4153	4921	-49577	185350	-2332	14025	-1776	21400	-90536	1176	15500
1l	15	TF-572	18.61	2.025	E-313	190	30	150	770	11	42	5110	100	3540	3	680
					E-313	1000	565	3576	14491	247	790	59170	1862	62859	56	17750
1m	15	TF-572	18.61	2.025	E-313	1346	266	-12353	14469	-376	775	-13300	1838	-13336	54	1675
					E-313	5511	5127	-32210	195819	-2710	14804	-33776	2238	-193772	1732	16175

Test #	Time Period	TF #	Solution Volume	H ₂ O Added	Al	S	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
11	13.0	TF-624	20.54	2.150	719	170	4100	10	71	370	5	48500	20	3690	4	5040
	117				240	161	7150	10	52	263	5	49200	20	34200	1	
					2100	600	4300	45300	3700	270	10050	141500	35000	7220	25	15500
12	13.0	TF-625	18.74	2.150	1554	254	-11072	43278	3588	-255	10285	36230	5737	45	27	9050
	130				7075	5381	-72252	243098	40977	-3006	25094	2944	6795	-48912	1259	25723
					2000	600	3400	9400	1860	200	300	82400	860	47200	20	10600
13	13.0	TF-731	18.51	2.150	1484	254	-11772	5378	1668	-365	259	-23380	837	-24330	18	-150
	142				8579	5635	-85235	252476	42645	-3071	26363	-20426	63602	-175002	1277	23073
					1500	560	260	55610	1500	150	2200	77500	6200	46100	26	17500
14	13.0	TF-735	22.71	2.15	1354	214	-15112	59522	1662	-375	2289	-27320	6157	-27430	24	150
	156				5763	5849	-109367	312065	44353	-3746	27372	-45316	69759	-157002	1301	25023
					2260	650	3100	20900	2700	220	800	110400	2300	57400	45	16100
15	14.0	TF-827	19.11	2.20	1624	334	-12572	30678	2562	-345	789	4630	1157	-15630	41	5250
	170				11647	6183	-112540	332743	46941	-4072	28461	-45696	72046	-162702	1242	36573
					1500	575	3630	7260	2100	229	500	107780	2675	56450	57	16440
16	14.0	TF-827	19.11	2.20	1346	265	-12515	7237	1960	-376	488	-5360	2625	-20150	57	4540
	170				12995	6387	-125455	340180	48922	-4468	28550	-49076	74675	-166472	1359	35513
17	15.0	TF-866	18.20	3.95	2375	850	5675	40080	3640	240	1100	115470	4400	12260	57	3520
	175				1427	214	-22565	40040	3635	-795	1080	-74570	451	-10350	53	15570
					1422	661	-116022	380221	52556	-5257	30030	-11154	7695	-109602	1452	51023

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
FVIII-2a	13	TF-319	20.34	2.15	E-313 710	170	4100	10	71	360	5	46800	20	34900	4	5000
					E-313 240	161	7150	10	52	263	5	47200	20	34200	1	
					2000 474	2700 2334	3100 -5715	13600 15576	7700 7547	350 -482	1500 1457	73300 -27420	3500 3457	52900 -26435	351 352	
25	15 25	TF-315	19.23	2.15	1500 374	2000 1634	6900 -1915	79400 79378	5700 5547	1700 862	5500 6485	94400 -8220	15400 15357	87300 7865	172 163	0
					847	3569	-7630	92567	13055	313	5776	-33640	18514	-18470	546	
					1300 -225	400 34	1500 -7315	22400 22378	270 117	150 -888	1100 1085	10500 -90120	-43	7000 -7235	11 2	
26	13 52	TF-422	13.60	2.15	630	4004	-14945	115336	13212	-316	11068	-123760	18771	-90805	548	0
					1400 -126	775 410	3100 -5715	9500 9478	3500 3147	270 -568	980 969	103000 7380	-45	57800 -19525	52 45	
					494	4413	-20660	124814	16359	-884	12057	-116380	18725	-110340	552	
2e	13 65	TF-452	14.37	2.15	5600 5084	720 374	4500 -10872	6600 6578	5200 5088	430 -135	570 359	188200 82420	900 657	95600 22070	67 65	24600 13850 13850
					5572	4787	-31532	131392	21448	-1019	12376	-33960	15385	-88270	656	
					1800 1212	650 476	5300 -12218	8800 8776	2600 2473	260 -384	840 828	112900 -7640	2600 2551	69000 -14740	27 25	
2f	15 60	TF-450	17.51	2.45	6790	5252	-43750	140168	25720	-1404	15224	-41600	27136	-103080	681	17200
					2000 1573	600 313	5600 -7127	7600 7552	1700 1697	260 -188	660 591	96200 8624	2000 1364	65300 4424	28 18	
					8363	5576	-50877	147750	25528	-1552	13515	-52776	24100	-98636	699	
29	10.5 90.5	TF-526	20.04	1.76	2000 1573	600 313	5600 -7127	7600 7552	1700 1697	260 -188	660 591	96200 8624	2000 1364	65300 4424	28 18	12600 3700 20900
					8363	5576	-50877	147750	25528	-1552	13515	-52776	24100	-98636	699	
					1900 1822	30 548	180 2825	790 14441	49 876	10 183	53 603	2540 53743	56 1024	1720 31442	2 33	
3h	13.5 104	TF-574	18.28	2.225	9657	5756	-63861	162169	26308	-1994	14407	-58705	25080	-143289	730	15442
					1294	159	-12984	14419	760	-402	572	-55127	979	-44652	31	
					9657	5756	-63861	162169	26308	-1994	14407	-58705	25080	-143289	730	

Test #	Time Period	TF #	Solution Volume	H ₂ O Added	Al	S	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
				E-J13	710	170	4100	10	71	350	5	46800	20	36900	4	
				E-J13	240	161	7150	10	52	260	5	49200	20	34200	1	5000
21	13.0 117	TF-635	18.88	2.150	1950	640	3000	9600	2300	230	300	118900	1800	23700	774	17000
					1384	294	-12372	9578	2188	-365	289	13120	1757	5170	772	6250
					11041	6080	-76233	171746	28496	-2360	14676	-75383	26837	-128119	1502	21692
23	13.0 130	TF-657	23.19	2.150	2360	700	2800	25000	1000	230	1200	66800	3200	34800	20	8600
					1784	354	-12572	24978	888	-335	1189	-39180	3157	-38730	18	-2150
					12825	6434	-88806	196726	29384	-2655	15886	-114763	29994	-166649	1520	19542
24	13.0 143	TF-732	22.28	2.150	2200	670	2900	52800	1800	220	1200	101600	6000	75000	403	14000
					1684	324	-12472	52778	1688	-345	1189	-4180	5957	4470	401	3250
					14509	6758	-101278	249505	31072	-3041	17075	-118943	35951	-162379	1920	22792
25	13 156	TF-770	21.85	2.15	2270	660	2900	18400	1800	220	1600	134600	5700	53500	26	17000
					1664	314	-12472	18378	1688	-345	1589	28820	5857	-20230	24	6250
					16193	7071	-113751	267883	32760	-3366	18664	-90123	41608	-182609	1944	29042
26	14 170	TF-828	19.58	2.30	4100	2550	19200	18600	5680	740	1760	280000	2940	144500	1155	40530
					3546	2160	2755	18577	5560	135	1748	166840	2574	65840	1153	29030
					19741	9251	-110956	286460	38321	-3251	20413	76717	44502	-116785	3097	58072

Test #	Time Period	TF #	Solution Volume	H2O Added	Al	B	Ca	Fe	Li	Mg	Mn	Na	Ni	Si	U	K
				E-J13	710	170	4100	10	71	362	5	46800	20	36900	4	
				E-J13	240	161	7150	10	52	263	5	49200	20	34200	1	5000
PVIII-3	13	TF-320	21.42	2.15	2100	2700	4300	9900	11800	450	1300	118900	2800	72000	1101	0
					574	2334	-4515	9678	11647	-388	1289	18280	2757	-7335	1093	
PVIII-4	26	TF-344	18.23	4.10	2600	6700	7700	117700	25200	800	4700	29000	13200	220300	1105	0
					-311	6003	-9110	117659	24909	-799	4650	-163860	13118	69010	1090	
PVIII-5	36	TF-370	14.05	6.05	3600	7400	15500	8600	23900	770	6400	323200	-121	156000	984	0
					-1286	6372	-9305	8540	23470	-1550	6370	43060		-67245	962	
PVIII-6	52	TF-423	13.63	8.00	6700	34500	12900	39700	54800	845	5700	520700	-160	396600	13766	0
					1020	33440	-15900	39620	54232	-2275	5660	146300		101400	13738	
PVIII-7	104	TF-572	25.90	15.60	4500	46600	32600	5200	70000	500	1000	886400	1300	751100	17120	85000
					-2510	44018	-55150	5044	69041	-4593	922	139600	988	196520	17084	6000*
PVIII-8	104	TF-576	25.91	15.60	17990	77200	8600	24400	128500	1500	4100	1110000	2200	966100	18200	75400
					10490	74618	-79150	24244	127541	-3593	4022	361200	1888	411520	18164	-2640*
Bb	66 170	TF-529	14.38	9.90	13370	75200	10070	23580	94330	546	5160	750640	2010	651410	17256	40840
					10994	75606	-60715	23481	93815	-2058	5110	265560	1812	312850	17246	-8660
					21484	145224	-139865	47725	221356	-5651	9132	624760	3700	724350	35411	-11260
Ec	25 195	TF-567	18.70	3.95	1870	8230	4300	26370	14590	300	1600	211310	5800	131460	2525	19075
					922	7594	-23942	26330	14385	-739	1530	16770	5721	-3630	2521	-675
					22406	155818	-163806	74056	235740	-6390	10713	641730	9421	720720	37932	-11535

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