MASTER

REACTION OF WATER WITH A SIMULATED HIGH-LEVEL NUCLEAR WASTE

GLASS AT 300°C, 300 BARS

Gregory J. McCarthy
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October 20, 1978

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MATERIALS RESEARCH LABORATORY

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SUMMARY

The hydrothermal stability of high-level nuclear wastes is an important consideration in establishing waste form acceptance criteria for a geological repository in basalt. A detailed examination of the stability of a typical simulated high-level waste glass and pressurized water at 300 degrees Centigrade ($^{\circ}\text{C}$) in a closed system has shown that extensive reaction occurred within a few weeks. The water acted first as a catalyst-solvent in devitrification of the glass and in dissolution, transport and recrystallization of some of its constituents, and, second, as a reactant in forming hydrated and hydroxylated phases. This reaction with water resulted in the conversion of a solid shard of glass into a fragmented and partially dispersed mass of crystalline and noncrystalline material plus dissolved species within two weeks. The major crystalline reaction products were found to be analogs of naturally occurring minerals: $(\text{Cs}, \text{Na}, \text{Rb})_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$ (weeksite) and a series of pyroxene-structure phases, $(\text{Na}, \text{Ca})(\text{Fe}, \text{Zn}, \text{Ti})\text{Si}_2\text{O}_6$ (acmite, acmite-augites). Weeksite, however, is not expected to have long-term stability in the basalt environment. Much of the Na and Mo, and almost all of the B, in the original glass was identified in the product solutions. Of the elements or analogs of long-lived, hazardous radionuclides studied in this work, only Cs was observed in these solutions in substantial amounts. Although the comparatively rapid and extensive reactions at 300°C would appear to require that an acceptable glass would have low waste and heat loading, it is suggested that there is good potential for favorable glass-basalt-water hydrothermal interactions. Favorable interactions would mean that, in the event of a hydrothermal incident, the interaction products would be more stable than the original waste form and would remain in the immediate repository. An example would be the reaction of dissolved Cs released from the glass with Al and Si from the basalt to form the mineral pollucite, $(\text{Cs}, \text{Na})\text{AlSi}_2\text{O}_6 \cdot n\text{H}_2\text{O}$. In any case, it is the glass-basalt-water interaction products that become the "source terms" for long-term radionuclide release studies.

INTRODUCTION

Terminal storage in underground rock formations is presently considered the most feasible method of isolating high-level nuclear power plant wastes from the biosphere. Among the candidates for geologic repositories are the basalt formations underlying the Hanford Site in eastern Washington State. One of the many factors that will need to be considered in repository design and in setting high-level waste form acceptance criteria is the effects of the heat produced by radionuclide decay. Heat would have certain effects on the physical properties of the repository and, especially when combined with water encroachment, heat would promote chemical reactions within the immediate repository (1). Exploring and then carefully defining the effects of hot pressurized groundwaters on simulated waste forms such as spent fuel and high-level waste glass in a basalt repository are the goals of a research project at The Pennsylvania State University (PSU). Research of this type is one of the activities of the Basalt Waste Isolation Program at Rockwell Hanford Operations (2).

An important feature of the PSU research is concern for the products of reactions as well as the reactivity of the waste form. Whether hydrothermal* reactions in a basalt repository would be beneficial or detrimental to waste containment is primarily a question of the long-term stability of the reactions products. As McCarthy *et al.* (1) have pointed out, waste-rock interactions can result in products that are more stable than the original waste form.

The research presented here was the first to deal with the reaction of superheated water and high-level waste glass.** Objectives of the research were

* The term "hydrothermal" is used here to denote reactions involving superheated water; i.e., reactions at any temperature above 100°C where pressure is sufficient to maintain H₂O in the liquid phase. Note that, in strict earth sciences nomenclature, such conditions involving temperatures between 100 and 373°C are "mesothermal."

** This research was initiated prior to April, 1977, when nuclear fuel reprocessing was anticipated and vitrification was the reference process for solidification of high-level liquid waste.

twofold: first, to explore the stability of a typical simulation of this reference waste form near the expected upper limit of hydrothermal conditions in a basalt repository; and, second, to develop and refine the methodology and tools for thorough characterization of both solid and liquid reaction products. A temperature of 300°C was selected for the experiments. This was 100°C below the maximum projected for a reference container (called a "canister") of high-level waste glass* in a basalt repository (3). Pressure was fixed at ~300 bars, a value typical of the overburden pressure at a depth of ~1000 meters. Based on the hydrothermal reactivity of silicate glasses, such as those long used as reactive starting materials in experimental geochemistry (e.g., Reference 4), it was estimated that treatment times on the order of weeks would be sufficient to yield observable glass-water reactions.

Experiments were performed in inert gold capsules. Closed system experiments such as these are ideal for exploring the reactivity of solid-liquid systems and establishing the direction of thermodynamic equilibrium. The experiments simulate the case where superheated water is admitted through a breached canister and reacts with the glass in a region where the chemistry of the glass dominates the course of the reactions. Full simulations of the repository will require open system experimentation and contact of the simulated waste and superheated water with canisters and large excesses of basalt. Such experiments are in progress or planned and will be the subject of subsequent reports.

* Glass from reprocessing of spent fuel 10 years out of the reactor; thermal power, 10 kw per 6-inch diameter by 8-foot high canister (4).

EXPERIMENTAL PROCEDURES

SIMULATED HIGH-LEVEL WASTE GLASS

The simulated high-level waste glass used in these experiments was Pacific Northwest Laboratory (PNL) formulation 76-68 (5). It was supplied by PNL. The glass was formulated according to the projected reprocessing flow sheet of the Nuclear Fuel Services plant in West Valley, NY, and is sometimes referred to as "NFS glass." The composition of PNL-76-68 glass (6) is given in Table I. One notable compositional feature is that the glass contains 62 wt % ($\text{Na}_2\text{O} + \text{Fe}_2\text{O}_3 + \text{SiO}_2$). The glass was colored green-black in massive pieces, but in thin fragments it had an amber brown coloration. It contained numerous vesicles (bubbles), some up to several hundred micrometers in diameter. Also incorporated in the glass were clusters of dull to metallic black crystallites. Studies at PNL (7) have shown that these crystallites consist both of crystalline phases that never dissolved in the molten glass plus phases that crystallize on cooling. In work specific to PNL-76-68, it was shown that the crystalline phases were RuO_2 and a ferrite spinel in the as-prepared glass, with fluorite structure phase, chiefly CeO_2 , formed on heat treatment (7). A small amount of this fluorite phase, along with RuO_2 , ferrite spinel and perhaps Pd metal were identified in diffractograms of the slow-cooled glass received from PNL. The total amount of crystalline products in the glass was reported to be <10 wt % (7).

The glass was received from PNL as several large fragments. The typical specimen used in the present study was a single shard broken from one of these fragments and weighing ~30 mg. Figure 1 is a photograph of one of these shards. The opaque regions are the crystalline inclusions. It should be noted that the ratio of these crystalline phases to glass was not constant

TABLE I

COMPOSITION OF PNL-76-68 GLASS^a

<u>Oxide^b</u>	<u>Wt %</u>	<u>Oxide</u>	<u>Wt %</u>
(waste oxides)		Pr ₆ O ₁₁	0.53
Rb ₂ O	0.13	Nd ₂ O ₃	1.67
SrO	0.38	Sm ₂ O ₃	0.33
Y ₂ O ₃	0.21	Eu ₂ O ₃	0.07
ZrO ₂	1.77	Gd ₂ O ₃	0.05
MoO ₃	2.28	U ₃ O ₈	4.58
RuO ₂	1.07	Fe ₂ O ₃	9.77
Rh ₂ O ₃	0.17	Cr ₂ O ₃	0.41
PdO	0.53	NiO	0.20
Ag ₂ O	0.03	P ₂ O ₅	0.48
CdO	0.03	Na ₂ O	5.02 ^c
TeO ₂	0.26	(glass forming additives)	
Cs ₂ O	1.03	Na ₂ O	7.49 ^c
BaO	0.56	SiO ₂	39.80
La ₂ O ₃	0.53	B ₂ O ₃	9.47
CeO ₂	1.19	CaO	2.00
		ZnO	4.97
		TiO ₂	2.97

^aAfter reference (6); waste loading 33 wt %; fission product loading 12.8 wt %.

^bComposition normalized to these oxides by PNL; the oxide compositions do not necessarily reflect the actual cation valences in the glass.

^cTotal Na₂O = 12.51 wt %.

FIGURE 1

A TYPICAL SPECIMEN OF PNL-76-68 BEFORE HYDROTHERMAL TREATMENT

from specimen to specimen. Because of the variability of the amounts of these inclusions, it is estimated that the actual concentration (or amount) of an element in a particular specimen could vary by as much as 10-20% of the nominal composition given in Table I. Several of the specimens used in the early stages of this study were made into spheroidal shapes by an abrasion technique.

HYDROTHERMAL TREATMENT

The inert container chosen for these experiments was fashioned from 5 mm diameter gold tubing. A length of tubing was cut and sealed at one end by electric arc welding or cold welding with a crimping tool. A weighed glass specimen was placed in the capsule along with either deionized water or artificial Hanford groundwater (nominal concentration in $\mu\text{g/ml}$: 168 Na, 0.5 Ca, 0.1 Mg, 90 Cl, 14 (SO_4), 56 (HCO_3), 87 (CO_3), 4 K; pH = 10; water was in contact with amorphous SiO_2) in a water to solid ratio of 10:1 or 30:1 and the capsule was welded shut. The sealed capsules were then weighed, heated for several hours in a vacuum oven and reweighed. Any leaks in the welds would show up as weight losses due to evaporation of the water through the leak.

The experiments were performed in conventional 0.5-in. (12.7-mm) cold-seal pressure vessels (8) using water as the pressurizing medium. In a typical experiment, each vessel contained three to six individual sealed gold capsules. The vessel was inserted into a resistance-heated tube furnace having a solid-state controller/power supply. Temperature was measured with a chromel-alumel thermocouple inserted into a well in the vessel near the level of the gold capsules, and was displayed continuously on a digital readout. The temperature was nominally 300°C , but over the course of the typical experiment it varied between 294 and 306°C . Pressure, measured continuously with a Bourdon gauge, was 300 ± 10 bars. Run durations were 7, 14, 21 and 28 days. At least two runs were made at each duration to evaluate reproducibility of the solid and solution products.

Combined temperature-pressure cooling in air was used at the end of each run. The cooling rate was approximately 10°C/min from 300 to 200°C, 8°C/min from 200 to 150°C and 2°C/min to 90°C. The capsules were removed and reweighed. Any breach of closure would show up as a weight change. The capsules were also examined microscopically for signs of pinholes or stains from leaked contents. Any run that had leaked was repeated.

The gold capsule was cut open at one end and the liquid was poured into a plastic beaker. The outside of the capsule as well as the scissors were gently washed with deionized water using a wash bottle. The capsule was next opened longitudinally and placed in the beaker for about 10 minutes to equilibrate in about 20 ml of water. The solution from the beaker was then quantitatively transferred to a 25-ml volumetric flask. The beaker, the sample and the gold capsule were rinsed, and this solution was also added to the volumetric flasks. Next, 186 mg of KCl were added to make the solution 0.1N in KCl when made up to volume. The use of 0.1N KCl serves two purposes: first it helps in the flocculation of the sample, if any, during centrifugation, and second, it removes the ionization interference during atomic absorption spectrophotometric analysis for cesium, rubidium, and sodium. The solution was next centrifuged in polycarbonate tubes at 2500 rpm to sediment any fine particles in the solution and then pipetted from the polycarbonate tubes into polyethylene bottles without disturbing any sediment at the bottom. A drop of toluene was added to the solution to prevent bacteria from growing.

CHARACTERIZATION OF SOLID PRODUCTS

The solid products, still contained in the cut-open gold capsule, were initially examined under a binocular microscope at up to 40X magnification. The extent of hydrothermal alteration was first estimated at this stage. Because in all cases material had been transported from the original glass specimen onto the inside walls of the gold capsule, solid products characterization was necessary throughout the capsule.

X-ray diffraction was used for crystalline phase identification. Individual clusters of crystals or apparently homogeneous alteration zones were examined by the Gandolfi camera technique (9) and the bulk product was then ground

and studied by conventional x-ray diffractometry. For the Gandolfi studies, individual fragments or crystals were extracted using a sharpened needle and transferred to the tip of a hollow, thin glass fiber which had already been mounted in the normal camera specimen holder. They were cemented to the fiber by various media. Where a cluster of crystals or several fragments of the same material were available, the crystals were crushed between microscope slides and the powder carefully collected into a ball at the tip of the glass fiber. It was important to keep the sample size small and spherical in order to obtain sharp diffraction lines and good line resolution. Having several individual crystals on the fiber was also important, so that all observed Debye-Scherrer reflections of low symmetry crystals would be included on the film.

Qualitative elemental analysis for elements above neon was obtained by energy dispersive x-ray spectrometry (EDX) on a scanning electron microscope (SEM). The microstructures of the alteration zone or microcrystalline products were observed simultaneously by SEM. Quantitative elemental analysis and elemental distributions were studied on a computer-controlled electron microprobe.

Using the x-ray powder data read from the Gandolfi films, plus chemistry from the SEM/EDX, crystalline phase identification could often be made by reference to the Joint Committee on Powder Diffraction File (PDF) standards (10). The Mineral Subfile of the PDF was especially useful in this work.

CHEMICAL ANALYSES OF SOLUTIONS

Solutions were analyzed for eighteen of the elements in PNL-76-68.

All the elements except Cs, Rb, Na, Zn and U were analyzed with a computer-interfaced Atomic Emission Spectrometer (AES). The elements Cs, Rb, Na and Zn were analyzed by Atomic Absorption Spectrophotometry (AAS). Uranium was determined by a fluorometric method. Results of duplicate chemical analyses of the same solution had a mean deviation of $\pm 2\%$.

The objective of the analyses is to determine what proportion of the elements from the glass are present in the product solutions. Because the product solutions are always diluted to a 25-ml analytical solution, the sensitivity of

the analyses to glass dissolution is a function only of specimen weight and the instrumental detection limits. The level of sensitivity is illustrated by the data in Table II. Detection limits are compared to the concentration of selected elements that would be present in the 25-ml analytical solution of a particular glass specimen if it had totally dissolved during the hydrothermal run and there were no insoluble solid phases formed on cooling. For example, the data in Table II indicate that, for this weight of specimen, it would be possible to detect dissolution of 0.003% of the Na, 0.25% of the Mo, 0.4% of the Sr, 0.6% of the Cs or 0.003% of the U present in the original glass. The typical specimen was twice as heavy, so the typical analysis was twice as sensitive to the presence of an element from the glass in the solutions.

RESULTS

Twenty individual experiments were performed at 300°C and 300 bars. The experimental variables and run numbers are listed in Table III. The results of the hydrothermal treatments of the glass will be described first for the solid products and then for the solutions extracted from the reaction capsules.

THE SOLID REACTION PRODUCTS

Reconnaissance experiments described elsewhere (11) had shown that powdered PNL-76-68 glass would be altered by hydrothermal solutions at 200-400°C and would form crystalline phases. More massive specimens were used in this study to enable us to follow the alteration of the glass as a function of time. Spheroidal specimens were chosen for the first few experiments in the expectation that the hydrothermal alteration front might extend only into a small portion of the glass, and thus that measurements of weight and volume changes as a function of time could be obtained. However, upon opening of the first capsule, it became obvious that, even for times as short as 7 days, the alteration of the glass was too extensive, and it would not be possible to employ these techniques. After 7 days (Run GD 59) the alteration had proceeded into approximately one-third of the

TABLE II

COMPARISON OF SOLUTION ANALYSIS DETECTION LIMITS WITH THE "MAXIMUM SOLUTION CONCENTRATION"^a
FOR ONE SPECIMEN

Element in Glass	"Maximum Solution Concentration" for a 19.5 mg Specimen (in µg/ml)	Detection Limits (in µg/ml)		
		Atomic Absorption Spectrophotometry	Atomic Emission Spectrometry	Fluori- metry
Na	73.3	0.002	--	--
B	23.2	--	0.05	--
Si	146.8	0.08	0.2	--
Mo	12.0	0.03	--	--
Cs	7.67	0.05	--	--
Rb	0.94	0.005	--	--
Sr	2.54	0.01	0.01	--
Ba	3.92	--	0.2	--
Ca	11.3	--	0.002	--
Zn	31.5	0.002	--	--
Ni	1.24	--	0.003	--
Cr	2.22	--	0.003	--
Fe	48.5	--	0.005	--
La	3.56	--	0.07	--
Nd	11.3	--	Not available	--
Ti	14.1	--	0.08	--
Zr	10.3	--	0.3	--
U	29.2	--	--	0.001

^aThe concentration that would be present in the 25-ml analytical solution if the specimen had completely dissolved during hydrothermal treatment.

TABLE III
 EXPERIMENTAL PARAMETERS AND RUN NUMBERS
 OF THE 300°C, 300 BARS HYDROTHERMAL TREATMENTS

<u>Run Duration</u>	<u>Run Number</u>	<u>Water Type^a</u>	<u>Water to Solids Ratio</u>
7 days	GD 59 ^b	DW	10:1
	GD 113	DW	10:1
	GH 112	HGW	10:1
	GD 121	DW	30:1
	GD 126	DW	30:1
14 days	GD 68 ^b	DW	10:1
	GD 88	DW	10:1
	GD 124	DW	10:1
	GD 127	DW	10:1
	GH 150	HGW	10:1
	GD 123	DW	30:1
	GD 143	DW	30:1
21 days	GD 80	DW	10:1
	GD 81	DW	10:1
28 days	GD 78	DW	10:1
	GD 79	DW	10:1
	GD 89	DW	10:1
	GD 90	DW	10:1
	GH 111	HGW	10:1
	GD 122	DW	30:1

^aDW = Deionized Water; HGW = artificial Hanford
Groundwater.

^bThese specimens were spheroids; all others were shards.

specimen and material had been transported from the glass and onto the inside walls of the gold reaction capsule. Figure 2 shows a portion of the cross section of this product mounted in plastic and photographed in reflected light. The white and light blue zones are altered glass, while the black interior zone is apparently unaltered glass. The oval-shaped blue and white features near the interior of the glass could be traced to cracks that permitted access by the solutions. These cracks might have been introduced during the mechanical treatment to form the spheroids. The product from the 14-day experiment (GD 68) had fragmented and was thus not recoverable in its original spheroidal shape. Because of the possibility of mechanical damage from fabrication of the spheroids, it was decided to use the less-damaged glass shards in all further experiments.

The typical appearance of the products from the other eighteen experiments is illustrated in Figure 3. This photograph was taken after the liquid had been removed from the gold capsule and the capsule had been cut open. In all cases, the first observations with the binocular microscope showed abundant yellow needle-like crystals measuring 0.2-2 mm along the needle axis that had grown throughout the capsule and in fissures in the altered shard, plus a light-colored coating covering the inside wall of the capsule. The product was always fragmented. In some cases, a relatively large remnant of the original shard was present, but it was nested in other fragments that had spalled off during the treatment, cooling or opening steps.

The yellow crystals were studied by SEM/EDX and found to contain U, Si, Na, Cs and minor Rb. Figure 4 is a photomicrograph of clusters of these crystals growing on the walls of the capsule. They were rectangular in cross section and had either a pinacoid or a dome for a termination. X-ray examination by the Gandolfi method yielded powder data that gave a very good match to the data of the mineral weeksite, $K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$, pattern 12-462 in the PDF (10). Table IV is a list of the x-ray powder data for these crystals and for the mineral weeksite. The combination of elemental chemistry and x-ray data served to identify these crystals as a weeksite-structure phase with Na, Cs and Rb substituting for the K in

FIGURE 2

CROSS SECTION OF A SPHEROIDAL SPECIMEN OF PNL-76-68 GLASS AFTER HYDROTHERMAL TREATMENT WITH DEIONIZED WATER AT 300°C, 300 BARS FOR 7 DAYS (APPROXIMATE DIMENSIONS 2mm x 4mm)

FIGURE 3

TYPICAL SOLID PRODUCTS AFTER
TREATMENT OF PNL-76-68 GLASS AT
300°C AND 300 BARS

(The Background Is A Cut-Open Gold Capsule)

FIGURE 4

CLUSTERS OF YELLOW NEEDLE-LIKE CRYSTALS
(Length Along the Needle Axis is Typically 1-2 mm)

TABLE IV
X-RAY POWDER DATA FOR THE YELLOW NEEDLE-LIKE CRYSTALS
AND FOR THE MINERAL WEEKSITE

<u>Yellow Crystals</u>		<u>Weeksite (PDF 12-462)</u>	
<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>
8.94	ms	8.98	90
7.14	ms	7.11	100
5.58	s	5.57	90
4.85	vw	4.83	30
4.57	m	4.58	40
		4.48	30
3.84	m	3.84	40
3.57	mw	3.55	70
3.32	m	3.34	40B
		3.30	70
3.20	mw	3.20	50
3.00	vw	2.99	40
2.93	s	2.91	60
2.81	vvw	2.80	30
2.52	vvw	2.51	30
2.41	w	2.41	40
2.38	w	2.37	50
2.30	w	2.28	50
2.24	w	2.29	40
2.18	vvw	2.20	30
2.15	vvw	2.13	40
2.11	vw	2.11	40
2.00	vw	1.994	40
1.982	vw	1.973	30
1.936	vw	1.922	30
1.905	vw	1.905	40

s = strong
 m = medium
 w = weak
 v = very
 B = broad reflection
 d = interplanar spacing
 I = relative intensity

the prototype mineral. Sodium-weeksite, $\text{Na}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$, is known (12), but this is the first report of a weeksite structure phase with the large alkali ions, Cs and Rb, substituting for K. The weeksites (henceforth, the Na-Cs-Rb-weeksite-structure phase will be simply referred to as "weeksite") observed in every experiment, whether for 7 or 28 days, with deionized water or simulated Hanford groundwater and with water to solids ratios of 10:1 or 30:1. In the longer duration runs, the weeksite crystals appeared to be coated or etched and were often nearly colorless near their tips. The x-ray pattern and EDX chemistry were virtually identical for yellow as well as these lighter regions of the crystals. However, these observations suggest that the original alteration product weeksites may be metastable and would themselves alter in much longer duration experiments.

The cream or tan colored phase covering the inside of the gold capsule proved to be made up of 2-10 μm blade-like crystals. Figure 5 is a SEM photomicrograph of these crystals on the gold capsule. Their radiating habit suggests nucleation and growth from solution onto flaws on the surface of the gold. The EDX chemistry of these crystals consisted of primary Si, Fe and Na with very minor Ti, Zn and perhaps several other elements. X-ray powder data obtained with the Gandolfi camera showed a quite good interplanar spacing (d) match and a fair intensity (I) match to the data for the mineral acmite, $\text{NaFeSi}_2\text{O}_6$, PDF 18-1222. This identification is fully consistent with the EDX chemistry. Table V gives the Gandolfi x-ray data and the PDF data for acmite. It is possible that the very small size of the crystals and the potential for some orientation with the mounting fiber could account for the only fair agreement of the intensity data.

The very light color of the acmite crystal coating was somewhat surprising. In nature, acmite is usually green or brown due to minor solid solution substitutions and the partial reduction of Fe^{3+} to Fe^{2+} . The light color requires that the composition be close to stoichiometric $\text{NaFeSi}_2\text{O}_6$ and that the Fe be trivalent. The presence of a Fe^{3+} phase suggests oxidizing conditions inside the sealed capsule. The universal occurrence of the uranyl

FIGURE 5

SEM PHOTOMICROGRAPH OF THE CRYSTALS
COATING THE INSIDE OF THE GOLD CAPSULE

TABLE V

X-RAY POWDER DATA FOR THE CRYSTALLINE COATING
AND FOR THE MINERAL ACMITE

<u>Coating</u>		<u>Acmite (PDF 18-1222)</u>	
<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>
6.37	50	6.369	90
4.42	50	4.416	80
3.62	10	3.614	10
3.20	2	3.188	50
2.998	100	2.983	70
2.912	20	2.900	100
2.536	30	2.5408	50
2.475	20	2.4701	60
2.201	10	2.1995	10
2.122	10	2.1200	30
2.032	10	2.0162	20
1.937	10	1.9350	10
1.834	2	1.8263	5
1.731	5	1.7293	60
1.687	2		
1.664	2	1.6590	5
1.637	5	1.6341	5
1.613	5	1.6120	50
1.598	5	1.5920	50
1.533	2	1.5377	10
1.506	5	1.5290	10
1.475	5	1.4671	20
1.400	5	1.3975	60
1.379	2		
1.328	2	1.3283	20
1.302	5	1.3021	40
1.271	2	1.2687	30
1.230	5	1.2289	20

phase, weeksite, also supports oxidizing conditions. Apparently, PNL-76-68 was an oxidized glass. The color of the acmite crystal coating turns brown after several weeks of exposure to air.

Microstructure and Microchemistry

The microstructure and microchemistry of the bulk products from a 7-day, 14-day and 28-day hydrothermal treatment were studied by SEM and electron microprobe analysis. The 7- and 14-day specimens were from the two runs where glass spheroids had been used. Although they were cracked, these products were not as fragmented as the products from glass shards. Thus, they could be handled, mounted in the plastic, sectioned and polished with less damage to the specimen.

Figure 6 is a secondary electron image (SEI) of the cross sectioned spheroid shown in Figure 2. The brightness of the SEI can be correlated to the mean atomic number of a material and to density. Thus, the apparently unaltered glass core is bright with still further brightness for the crystalline inclusions in this glass. The altered portions of the product give a dull grey SEI. Cracks in the product are black. Note the correlation of the blue-white oval-shaped alteration features in Figure 2 with the grey zones in the bright core in Figure 6. Similarly, the residual crystalline inclusions in the altered glass zone that were blue in Figure 2 are brighter than their matrix in Figure 6.

A thin skin or rind not evident in Figure 2 is observed in Figure 6. This was a characteristic feature in all products. Under the binocular microscope, this skin was seen to consist of at least two bands, an outer band of white and almost spherical material covering an orange-brown inner band. Figure 7 is an electron backscatter (EBS) image with accompanying Na, Si and Fe x-ray maps for a near-surface portion of a two-week run, GD 68. Two features are notable. First, the skin is enriched in Fe and, second, there is a bright area to the right that has Na, Fe and Si concentrations. This area is probably unaltered or only partially altered glass. A cross section of the skin is shown under higher magnification in Figure 8,

FIGURE 6

SEM-SEI PHOTOMICROGRAPH OF A SECTION THROUGH THE PRODUCT FROM A 7-DAY HYDROTHERMAL TREATMENT
(Run GD 59)

FIGURE 7

X-RAY MAPS OF THE NEAR-SURFACE ZONE OF THE PRODUCT FROM RUN GD 68 (160 X).

Na	EBS
Si	Fe

FIGURE 8

X-RAY MAPS OF A PORTION OF FIGURE 7 (800X).

Sr	EBS
Fe	Ca

along with Sr, Fe and Ca x-ray maps. It is clear from this figure that the outer band of the skin is rich in Ca and Sr, while the adjoining band is Fe-rich. The x-ray emission traces across this banded skin shown in Figure 9 confirm the enrichment of Ca and Sr in the outer band and indicate that Si is associated with Fe in the adjoining band.

Samples of each band were examined by Gandolfi x-ray diffraction, and crystal-structure types for these phases were obtained. The outermost band of white material had the apatite structure type. (This phase identification was based on crystals obtained from the surface of the products from longer duration [three- to four-week] treatments. It is not certain that the apatite structure band in the one- and two-week products were crystalline.) X-ray data for this phase and for hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, are given in Table VI. A U x-ray map of the EBS image in Figure 8 showed that U was crystallizing in this apatite phase. Examination of the material in the SEM showed these spheroids to be actually made up of aggregates of randomly oriented fibrous crystals. Their EDX chemistry was quite complex, with Ca, Sr, Ba, rare earths (Ln), Si, U and P as the primary elements. Thus, the material should be assigned to the generalized solid solution formula:

The orange-brown band gave x-ray data typical of a pyroxene (single chain silicate) near the acmite-augite, $(\text{Na}, \text{Ca})(\text{Fe}, \text{Mn}, \text{Zn}, \text{Mg}, \text{Ti})(\text{Al}, \text{Si})_2\text{O}_6$, composition (see PDF 18-1221 and 19-1). In Figures 8 and 9, it was shown that this band had high-Fe concentration and in x-ray emission traces the presence of Na, Zn and Ti was observed. A generalized solid solution formula for this phase is:

In the EBS image from Figure 8, it is seen that there is a third, innermost, band to the skin. Both x-ray maps and x-ray traces across the skin (Figure 9) indicated that this band was especially enriched in U relative to the adjoining altered glass zone. This U concentration was higher than that in the apatite phase

FIGURE 9

X-RAY EMISSION PROFILES
OF THE NEAR-SURFACE ZONE

OF THE PRODUCT FROM

RUN GD 68

(Arrows Indicate The Positions
Of Cracks. Dashed Lines At The
Left Mark The Approximate
Boundaries Of The Three Bands
Of The "Skin" And The Line Near
The Center Marks The Boundary
Between Less Altered And More
Altered Glass)

CPS = counts per second.

TABLE VI

X-RAY POWDER DATA FOR THE WHITE OUTER BAND
AND FOR HYDROXYAPATITE

White Band		Hydroxyapatite (PDF 9-432)	
<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>
3.45	60	3.44	40
3.18	10	3.17	12
2.814	100	2.814	100
2.714	20	2.778	60
2.637	10	2.720	60
2.522	5	2.631	25
2.276	10	2.528	6
2.071	10	2.262	20
2.006	5	2.065	8
1.949	10	2.000	6
1.903	5	1.943	30
1.848	10	1.890	16
1.725	10	1.841	40
		1.722	20

constituting the outermost band. Titanium also appeared to be concentrated in this high-U band. No phase identification has as yet been made for this innermost band.

Element distributions among the various altered and unaltered glass regions were further characterized by electron microprobe analysis. Results were obtained in the form of characteristic x-ray emission traces through these regions and quantitative elemental analyses at selected spots on the product. In Figure 6, the traverse of a microprobe scan is marked by the black line starting at the banded skin and passing through a region of generally altered glass, then into the unaltered core and terminating in the oval-shaped alteration feature. X-ray emission traces for nineteen elements monitored during this scan are shown in Figures 10, 11, and 12.

The enrichments in Na, Ca, Sr, Fe, Ti and U in the banded skin have already been discussed. Except for Mo and Na, the x-ray traces did not display further major fluctuations (the sharp dips that occur in all traces in the same place are due to cracks). The broad maximum in Mo and the sharp fluctuations in Na occurring between 500 and 700 μm correlate with the traverse of the beam out of an altered zone, into unaltered glass and then back into the oval-shaped alteration feature. This correlation suggested the use of Mo and Na as "marker elements" for the presence of alteration.

The numbers in Figure 6 mark individual point analyses with the computer-interfaced microprobe. Calibration standards were those available in PSU's Mineral Constitution Laboratory for silicate rock and mineral analyses. The results presented in Table VII are for thirteen of the elements in the glass (plus K, which was not reported to be a constituent of the glass). Note that the available computer code calculated concentrations as oxides. The U analyses were suspect because a U standard with a suitably high U concentration in an appropriate matrix was not available. There also appeared to be a problem with the Na analyses, perhaps due to the familiar difficulty with Na vaporization in the electron beam. Analyses for the thirteen elements for a specimen of the as-received PNL-76-68 glass

FIGURE 10

X-RAY EMISSION TRACES FOR Na, Cs, Ca, Sr AND Zn
ALONG THE TRAVERSE SHOWN IN FIGURE 6

FIGURE 11

X-RAY EMISSION TRACES FOR Fe, Y, Zr, Ti, U, Si and Mo
ALONG THE TRAVERSE SHOWN IN FIGURE 6

FIGURE 12

X-RAY EMISSION TRACES FOR THE LANTHANIDES
ALONG THE TRAVERSE SHOWN IN FIGURE 6

TABLE VII
ELECTRON MICROPROBE ANALYSES OF THE PRODUCT SHOWN IN FIGURE 6
(Run GD 59)

Oxide	W e i g h t P e r c e n t				
	PNL-76-68 Nominal Composition ^a	PNL-76-68 Microprobe Analysis	Unaltered Glass ^b	Alteration Zones	
				I ^c	II ^d
CaO	2.0	2.0	1.9	2.0	2.0
Cs ₂ O	1.0	1.3	1.0	1.0	0.9
TiO ₂	3.0	3.2	2.9	2.9	3.0
CeO ₂	1.2	1.6	2.3	2.3	2.9
Nd ₂ O ₃	1.7	1.8	1.7	1.5	2.0
FeO	8.9	9.3	8.9	8.8	5.8
ZnO	5.0	4.8	5.5	5.3	5.2
SiO ₂	40.3	39.0	38.2	42.1	34.2
SrO	0.4	0.2	0.1	0.1	0.1
ZrO ₂	1.8	2.3	2.0	1.9	2.7
MoO ₃	2.3	2.4	2.4	0.2	0.8
UO ₂	4.5	7.2 ^f	5.4 ^f	5.8 ^f	4.3 ^f
K ₂ O	0.0 ^e	0.1	0.1	0.3	0.1
Na ₂ O	12.7	8.6	10.5	3.1	2.1
	84.8%	83.8%	82.9%	77.3%	66.1%

^aModified from Table I to show Fe as FeO and U as UO₂.

^bAveraged from points 1-8 in Figure 6.

^cAveraged from points 9-11, the oval-shaped alteration zone in Figure 6.

^dAveraged from points 12-14 in Figure 6.

^eNo K was reported in the composition of PNL-76-68.

^fThe U standards were designed for lower U concentrations, so these values may be in error.

were within 5% of the compositions reported by PNL for Ca, Ti, Nd, Fe, Zn, Si, and Mo. Analyses differed by greater amounts for Cs, Ce, Sr and Zr, as well as for the previously discussed U and Na. The importance of these compositional variations is not known because the glass is an inherently inhomogeneous product and the PNL composition is nominal (i.e., based on the starting batch) rather than the result of an actual chemical analysis.

The microprobe data for the various zones in the product are averages of multiple analyses. The core of apparently unaltered glass gave an analysis averaged from eight points that compares moderately well to that of the original glass specimen. Note their correspondence in Mo concentrations. In alteration zones I and II the Mo and Na concentrations were appreciably lower. The data for zone I were averaged from three analyses in the oval-shaped feature in Figures 2 and 6. Three analyses from the more heavily altered outer region occurring between the skin and the core constitute zone II. Here, somewhat lower Fe, Si and U concentrations were noted in addition to the heavy depletion in Mo and Na. One of the most consistent and useful observations from the study of this specimen was that Mo and Na appear to be early and sensitive indicators of hydrothermal alteration in the glass.

The partially altered product just described for the one-week treatment differed markedly from the products from longer treatments. For specimens treated for two to four weeks, there appeared to be at least partial alteration throughout the solid. One of the four-week products was sufficiently intact after the treatment that a partial cross section could be prepared for examination by SEM and the microprobe. In Figure 13, it can be seen that major fragments of the product had separated and parts of the surface had spalled off prior to specimen preparation; yet, enough of the product was retained that all of the typical alteration features were displayed in one cross section. The alteration has been divided into four zones and microprobe analyses (Table VIII) have been obtained from each of them.

The least altered of the zones was the "core." In reflected light, it retained its original green-black coloration and it appeared to have become more transparent as a result of the treatment. The core zone had the

FIGURE 13

SEM PHOTOMICROGRAPH OF A SECTION THROUGH THE PRODUCT OF A FOUR-WEEK HYDROTHERMAL TREATMENT

TABLE VIII

ELECTRON MICROPROBE ANALYSES OF THE PRODUCT SHOWN IN FIGURE 13
(Run GD 78)

Oxide	PNL-76-68 Microprobe Analysis	W e i g h t P e r c e n t			
		Alteration Zones			
		Core Zone ^a	Exterior Core Zone ^b	Interior Zone ^c	Outer Zone ^d
CaO	2.0	2.1	2.1	2.5	1.6
Cs ₂ O	1.3	1.4	3.1	0.4	1.5
TiO ₂	3.2	3.1	2.9	4.3	2.6
CeO ₂	1.6	1.4	1.4	0.9	2.0
Nd ₂ O ₃	1.8	2.1	1.9	1.2	3.2
FeO	9.3	9.6	8.7	13.2	3.7
ZnO	4.8	4.3	4.5	5.3	3.8
SiO ₂	39.0	39.1	38.9	46.3	28.0
SrO	0.2	0.4	0.3	0.4	0.4
ZrO ₂	2.3	2.2	2.1	1.5	3.1
MoO ₃	2.4	1.1	0.1	0.0	0.1
UO ₂	7.2	6.1	5.3	5.5	2.0
Na ₂ O	8.6	2.0	2.4	5.2	0.7
	83.6%	74.9%	73.7%	86.8%	52.7%

^aAveraged from points 1-11 in Figure 13.

^bAveraged from points 12-14 in Figure 13.

^cAveraged from points 18-20 in Figure 13.

^dAveraged from points 15, 21, 22, 26 in Figure 13.

bright secondary electron image typical of unaltered glass in Figure 6, but the microprobe analyses (Table VIII) indicated that this zone was heavily depleted in Mo and Na. An "exterior core zone" differed only slightly from the core in optical and SEM image characteristics, but microprobe analysis indicated almost total depletion in Mo and a distinct enrichment in Cs compared to the adjoining alteration zones.

The outer core zone was at least partially crystalline because an x-ray diffraction pattern consisting of broad reflections was obtained from it. The data, listed in Table IX, have not been matched to any phase or mixture of phases in the PDF.

In reflected light, the region labelled "interior zone" in Figure 13 was cream-white, porous and rich in opaque microcrystalline inclusions. These inclusions were dull black and were often surrounded by a purple hue; they were less abundant in the core and outer zones; also, their orientation in the interior zone seemed to be related to the external morphology of the original glass shard. These two observations suggest transport and recrystallization of the opaque phases. X-ray diffraction analyses indicated that the opaques consisted of several phases, a Fe-rich spinel, $(\text{RuO}_2)_{\text{ss}}$ and, usually, $(\text{Pd})_{\text{ss}}$. The spinel had a unit cell parameter of $8.40\text{\AA}$ and its powder data corresponded closely to those of the Fe-spinel magnetite, Fe_3O_4 , PDF 19-629. The Ru-rich phase has been designated as $(\text{RuO}_2)_{\text{ss}}$, a solid solution phase, because its powder data indicated a slightly larger unit cell than is found for pure RuO_2 , PDF 21-1172. Similarly, in those products where Pd-rich crystalline inclusions were identified, the unit cell parameter, $3.92\text{\AA}$, was larger than the $3.89\text{\AA}$ parameter of pure Pd, PDF 5-681. No fluorite structure CeO_2 -rich phase was detected in any products.

The microprobe data for the "interior zone" indicated a depletion of Cs, Zr and lanthanides, and enrichment in Na, Ca, Fe, Ti, Zn and Si, in comparison to adjoining zones. The enrichment was most pronounced in those features in the interior zone that are brighter in Figure 13. X-ray analysis of these features gave a pyroxene-like pattern with moderately broad reflections corresponding to those of the acmite-augites described earlier. The microprobe and x-ray powder data are consistent with a pyroxene-structure

TABLE IX

X-RAY POWDER DATA FOR ADDITIONAL ALTERATION ZONES OR PHASES

Outer Core Zone		Orange Vesicle Crust ^a		White Spherical Aggregates ^b	
<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>	<u>d</u>	<u>I</u>
4.11	m	4.13	50	7.03	80
3.99	m	3.68	5	6.56	30
3.75	ms	3.47	20	5.13	50
3.49	w	3.18	20	4.82	10
3.24	w	2.978	20	4.53	5
2.998	ms	2.940	20	4.15	100
2.894	m	2.84	10	3.90	5
2.629	vs	2.515	60	3.75	10
2.543	m	2.259	100	3.58	5
2.455	m	1.961	50	3.45	10
2.380	m	1.684	5	3.24	50
		1.637	10	3.18	20
		1.480	20	3.11	50
		1.388	10	2.940	30
		1.182	10	2.814	30
		1.130	5	2.652	20
		1.088	5	2.536	20
		0.9022	5	2.380	10
				2.067	10
				1.892	5
				1.852	5
				1.734	5
				1.578	5

^aNoted only in products of two-week treatments.

^bNoted only in one product of a four-week treatment; morphologically similar to the apatite phase.

phase having a generalized solid solution formula, $(\text{Na,Ca})(\text{Fe,Ti,Zn})\text{Si}_2\text{O}_6$. X-ray patterns of representative samples from the interior zone showed that there was a considerable amount of an x-ray amorphous phase mixed with the pyroxene and opaque crystalline phases.

The region labelled "outer zone" in Figure 13 consisted of light-colored translucent material lying just below the skin. In reflected light, this material has distinct opalescence. With the typical product, much of this zone and the skin were found to have spalled off. X-ray examination of random samples from this zone indicated that it was generally non-crystalline. A few broad pyroxene-like reflections were noted. Microprobe data (Table VIII) indicated major depletion of Na, Fe, Si and U. These are the key elements of the skin and the two phases crystallized after transport, acmite and weeksite. Note that the analyses of the oxides listed in the table sum only to ~56%. This fact, when combined with the characteristic opalescence of this zone, suggests that hydrated or hydroxylated, perhaps gel-like, material has been formed in this zone by the hydrothermal treatment of the glass.

The skin, seen as a thin bright layer on some of the more intact segments in Figure 13, was again made up of a white crust of small spheres overlying an orange band. X-ray diffraction confirmed that, here also, the orange band was a pyroxene phase and, with one exception, the white crust was an apatite phase. In that one exception, aggregates looking very much like the apatite phase (the spheres were even made up of tiny needle crystals) had quite dissimilar x-ray powder data (see Table IX).

Two other alteration features were noted. Often, fissures or veins in the altered glass were filled with a translucent pale yellow material. This phase had both the elemental chemistry and characteristic (although broad) x-ray reflections of the pyroxene phase. Another feature was an orange crust lining one of the vesicles from the original glass. It looked quite like the orange pyroxene band observed on the skin, but its x-ray data, given in Table IX, were distinctly different.

The "white spherical aggregates" and "orange vesicle crust" features were two examples of the need for utilizing multiple methods of characterization in this work. If visual or SEM appearance had been used alone, then the phases would have been mis-identified as apatite and pyroxene, respectively.

Bulk X-Ray Diffraction

At least one product treated at each different set of conditions (time, water type, water to solid ratio) was studied in bulk specimens by routine x-ray diffractometry. All of the solids were collected from inside of the gold capsules and were ground together to make up the diffractometer specimen.

The resulting diffraction patterns were remarkably similar to each other and to patterns of products from other hydrothermal experiments involving PNL-76-68 glass. The diffractogram of the original glass specimen is compared to that of the products of a typical alteration product (Run GH 111) in Figure 14. The glass is x-ray amorphous except for a few weak reflections of $(\text{RuO}_2)_{ss}$, $(\text{CeO}_2)_{ss}$ and the Fe-spinel(s), while the alteration product has strong reflections from crystalline phases. The broad hatched reflections are due to the various acmite and acmite-augite-pyroxene phases and all but a few of the remaining reflections are those of the weeksite-like phase. One of these extra reflections is consistent with the strongest apatite phase reflection, but, in general, the other phases that were so clearly discernible as tiny crystals by the Gandolfi technique are apparently below the level of detection by bulk x-ray diffraction.

The same basic diffractogram was obtained for six other run products where a 10:1 water to solids ratio had been used. The major difference between one and four weeks of treatment was in the sharper and more intense pyroxenes reflections observed for the longer treatments. In the diffractograms of the four-week, 30:1 water to solid ratio product, the weeksite reflections were just as evident, but those of the pyroxenes were much less intense. There was also a larger diffuse scattering halo which suggested a higher proportion of x-ray amorphous phases in this product.

FIGURE 14

PORTIONS OF THE X-RAY DIFFRACTOGRAMS FOR PNL-76-68 GLASS BEFORE HYDROTHERMAL TREATMENT AND AFTER TREATMENT WITH ARTIFICIAL HANFORD GROUNDWATER AT 300°C, 300 BARS FOR 28 DAYS (Run GH 111)

The weeksite plus pyroxenes phase assemblage was also observed in another set of hydrothermal treatments described elsewhere (11). In these, a 200-mesh powder of PNL-76-68 glass had been treated at 300°C, 300 bars for an extended period of time. The water to solid ratio was 0.5:1 rather than 10:1 or 30:1. Diffractograms of 4-, 8- and 24-week products were very similar to that of the altered glass in Figure 14.

In another series of experiments with the powdered glass and the 0.5:1 ratio, the weeksite plus pyroxenes assemblage was well crystallized after only 2.5 days at 400°C, 300 bars, and was seen to be starting to crystallize after the same 2.5-day treatment at 200°C, 300 bars (13).

CHEMICAL ANALYSES OF SOLUTIONS

The product solutions from each gold capsule were analyzed for eighteen of the elements present in PNL-76-68 by the techniques described above. These analyses covered all of the elements whose oxides were present at >1 wt %, except Ru (see Tables I and II). More than 96 wt % of the oxide composition of the glass was included.

There are two potential contributions to these solutions. First, there are the elements that had been extracted from the glass during the hydrothermal treatment and had remained in solution during the cooling of the run. A second contribution could come from any solid products that were sufficiently soluble to have dissolved during either the 10-min equilibration of the capsule in 20 ml of water or the subsequent washing of the solid products. This second contribution might include such salts as sodium molybdates or borates that either had formed as solids at temperature because the solution was already saturated or that precipitated from solution during the cooling of the run. In the discussion that follows, both contributions will be considered under the "solutions" portion of the products.

Solutions From Runs Using Deionized Water

The analyses of the solutions from twelve of the runs using deionized water

are given in Table X. Because every specimen had a different weight, the concentrations have been normalized to a specimen weight of 0.1g to facilitate comparisons among runs. The elements present in the solutions in the greatest concentrations were Na, B and Mo. Reproducibility among replicate runs that used glass shard specimens (i.e., all but GD 59 and GD 68) was within 10% of the amount present for these three elements. This was about that expected from the variation in specimen composition due to variable content of crystalline inclusions. Note, for example, the Cr analyses in the two-week runs. In GD 124, there was none detected; while in GD 127, there were 42 $\mu\text{g/ml}$ of Cr in solution. Chromium is thought to be present in PNL-76-68 in the spinel(s) (5,7), so GD 124 may have contained less of this crystalline inclusion than GD 127. Other important constituents of the solutions were Si and Cs. Reproducibility among replicate analyses for these elements was only within a factor of 2 to 3 times the amount present.

The most notable aspect of the data in Table X is that (with the exception of GD 59 discussed later) the concentrations are roughly the same for the four run durations. This aspect becomes even more evident when analyses from the replicated runs are averaged. In Table XI, these averaged concentrations are given along with the percentage of the particular element from the original glass represented by these concentrations. It should be noted that this percentage is only the amount of an element detected in the analytical solution and not the total percent of an element "extracted" or "leached" from the glass. The latter would include at least the components of the weeksite and acmite phases that were dissolved, transported and crystallized on the inside walls of the gold capsule. The concentrations of Na, Mo and Cs in solution were nearly constant for all four durations at $\sim 45\%$, $\sim 70\%$ and $\sim 5\%$ of the amount available in the glass. The B and Rb concentrations increased gradually with time of treatment. Some Si, $\sim 4\%$, was observed. Very little of the available alkaline earths, Ca, Sr and Ba, was found in the solutions. There was virtually no detectable Ti, Zn, Zr, La or Nd in the solutions. Only a very small percentage of the available U was present in solution and that percentage decreased with longer treatment times.

TABLE X
SOLUTION CONCENTRATIONS^a PER 0.1g OF GLASS
(10:1 deionized water to glass)

	1 week		2 weeks				3 weeks		4 weeks			
	GD 59 ^b	GD 113	GD 68 ^b	GD 88	GD 124	GD 127	GD 80	GD 81	GD 78	GD 79	GD 89	GD 90
Na	1800	4300	3900	3900	3900	4700	4000	4300	4300	4400	4200	3900
B	1300	2500	3000	2500	2500	2800	2500	2800	2600	2900	2800	2700
Si	750	510	710	1070	430	620	1280	1140	1180	1290	450	550
Mo	1300	1100	1100	1100	1100	1100	1100	1000	1100	1200	--	--
Cs	19	42	110	58	33	74	50	40	50	48	--	--
Rb	ND ^c	ND	6	3	2	ND	5	3	10	11	--	--
Sr	0.8	2.0	ND	0.3	2.4	2.8	0.6	0.8	ND	ND	1.2	0.7
Ba	0.7	7.4	--	0.5	11.6	13.1	0.4	0.1	0.8	ND	0.6	0.4
Ca	2.4	7.4	ND	2.8	9.8	10.9	15.4	2.4	9.0	10.0	30.5	20.3
Zn	ND	0.8	7.8	0.7	1.5	0.9	1.0	1.0	ND	ND	0.8	0.1
Ni	--	1.5	29.0	2.5	2.6	3.1	ND	2.3	12.4	9.8	1.3	1.9
Cr	ND	66	--	--	ND	42	47	53	--	--	73	80
Fe	ND	3	ND	--	3	4	ND	ND	--	--	1	1
La	ND	4	ND	ND	4	ND	ND	ND	ND	ND	3	3
Nd	--	ND	ND	ND	ND	ND	--	--	--	--	ND	ND
Ti	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Zr	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
U	2.6	5.6	4.8	1.1	0.6	6.2	0.9	1.5	0.6	0.9	1.8	0.9

^aIn µg/ml.

^bThese specimens in the form of spheroids.

^cND = None detected.

TABLE XI

AVERAGE SOLUTION CONCENTRATION^a AND PERCENT OF ELEMENT IN SOLUTION
(10:1 deionized water to glass)

	1 week ^b		2 weeks ^b		3 weeks		4 weeks	
	µg/ml	%	µg/ml	%	µg/ml	%	µg/ml	%
Na	4300	46	4200	45	4100	44	4200	45
B	2500	84	2600	87	2700	89	2800	93
Si	510	2.7	700	3.7	1210	6.4	870	4.6
Mo	1100	72	1100	72	1100	72	1100	72
Cs	42	4.3	55	5.6	45	4.6	49	5.0
Rb	ND	--	2	1.4	4	3.4	11	8.7
Sr	2.0	0.62	1.8	0.55	0.7	0.22	0.5	0.15
Ba	7.4	1.47	8.4	1.67	0.2	0.04	0.5	0.1
Ca	7.4	0.51	7.9	0.55	8.9	0.62	17.4	1.20
Zn	0.8	0.02	1.0	0.02	1.0	0.02	0.2	0.005
Ni	1.5	0.94	2.8	1.76	1.1	0.69	6.3	3.96
Cr	66	23	21	8	50	18	77	27
Fe	3	0.05	4	0.06	ND	--	1	0.02
La	4	0.88	1	0.24	ND	--	2	0.48
Nd	ND	--	ND	--	--	--	ND	--
Ti	ND	--	ND	--	ND	--	ND	--
Zr	ND	--	ND	--	ND	--	ND	--
U	5.6	0.15	2.6	0.07	1.2	0.03	1.0	0.03

^aNormalized to 0.1g of glass; in µg/ml.

^bGlass spheroid runs GD 59 and GD 68 were not included in the average.

^cND = None detected

It is instructive to consider the total concentration of the elements in solution as a percentage of the available concentrations of the eighteen elements from the glass that were included in the chemical analyses. After first converting elemental into oxide concentrations, it was found that 17-19 wt % of the glass was observed in solution after any one of the four hydrothermal treatments. [Note that the elements included in the chemical analyses accounted for only 96.2 wt % of the glass. This percentage might change by 0.5-1 wt % if, at some later time, the remaining elements in PNL-76-68 (Ru, Y, Rh, Pd, Ag, Cd, Te, Pr, Sm, Eu, Gd, P) were included in the chemical analyses.] There was a small increase in percentage with time of treatment:

1 week	16.8%
2 weeks	17.2%
3 weeks	18.5%
4 weeks	18.5%.

The results of the analyses from GD 59, the one week run that used a spheroidal specimen, appeared to be anomalous when compared to the trend of the other analyses. The concentrations of Na, B and Cs were only half those found for the runs with the glass shard specimens. Also, the Cs analysis in GD 68, the other glass spheroid run, was high. Although the possibility of a systematic analytical error cannot be ruled out, it seems likely that the radical difference in the surface condition between the two types of specimens was responsible for different amounts of alteration and, thus, the apparently anomalous solution analyses.

One explanation for the approximate constancy of solution concentrations after only one week of treatment might be that the solutions have simply become saturated in various elements. In order to test this explanation, five runs were made where the deionized water to glass ratio was increased to 30:1. Analyses from these runs, again normalized to a 0.1g glass specimen, are listed in Table XII. The Na concentration did increase sharply. For example, after four weeks, Na was 6300 $\mu\text{g/ml}$ or 68% of the available Na. The Si

TABLE XII
 SOLUTION CONCENTRATIONS^a PER 0.1g OF GLASS
 (30:1 deionized water to glass)

	1 week		2 weeks		4 weeks
	GD 121	GD 126	GD 123	GD 143	GD 122
Na	5100	5200	5400	5000	6300
B	2300	2500	2900	2600	2700
Si	2550	1780	1550	1570	1460
Mo	800	800	900	800	700
Cs	21	31	68	31	35
Rb	ND	ND	ND	ND	ND
Sr	4	ND	ND	ND	ND
Ba	19	ND	ND	ND	2
Ca	12	ND	--	ND	--
Zn	1.0	1.8	3.9	1.0	5.2
Ni	2.6	ND	ND	ND	2.6
Cr	21	93	82	75	36
Fe	1	ND	ND	ND	ND
La	ND	ND	ND	ND	ND
Nd	ND	ND	ND	ND	ND
Ti	ND	ND	ND	ND	ND
Zr	ND	ND	ND	ND	ND
U	11.6	3.6	5.1	3.1	8.6

^aIn $\mu\text{g/ml}$.

^bND = None detected.

concentrations increased somewhat, B remained about the same, but Mo showed a substantial decrease. These results are consistent with the solid products characterization and this correlation will be discussed in a later section. From these five experiments, it appears that only with Na was there a major solution saturation effect.

Solutions From Runs Using Artificial Hanford Groundwater

All of the experiments discussed so far have utilized deionized water (DW). At first it would appear that to make the experiment more "relevant," Hanford groundwater should have been used. However, it can be shown that groundwaters typical of those beneath the Hanford Site are so low in total dissolved solids (TDS) that, in these closed system hydrothermal experiments, soon after the experiment begins the solutions would contain far greater concentrations of TDS released from the glass than were present in the original HGW. For example, when a 0.1g specimen of glass releases 17% of its constituents into 1.0 ml of solution, that solution would contain 17,000 $\mu\text{g/ml}$ of total dissolved solids. This compares to the 420 $\mu\text{g/ml}$ of TDS in the artificial HGW described in the experimental procedures section. The HGW would make a contribution of less than 3% to the TDS in such a run. Three experiments were performed to test the validity of this argument.

The results of chemical analyses for solutions from one-, two- and four-week treatments of the glass with an artificial HGW are given in Table XIII. Footnote (b) to this table gives the results of a concurrent cation analysis of the HGW. After subtracting the contribution of Na from the HGW, it is evident that the range of Na concentrations duplicates the results of the comparable DW experiments. Similarly, with the other major constituents of the solutions, B, Mo and Cs, the concentration ranges were in good agreement with the corresponding DW experiments. Among the minor elements, Cs and Cr concentrations were somewhat higher and Si was lower. In general, these results support the position that deionized water is a quite satisfactory generic stand-in for low-TDS groundwaters in closed system experiments.

TABLE XIII

SOLUTION CONCENTRATIONS^a PER 0.1g OF GLASS
(10:1 Artificial Hanford Groundwater^b to glass)

	<u>1 week</u>	<u>2 weeks</u>	<u>4 weeks</u>
	<u>GH 112</u>	<u>GH 150</u>	<u>GH 111</u>
Na	4600	4100	4400
B	2600	2800	2700
Si	430	350	190
Mo	1200	1200	1200
Cs	86	85	44
Rb	2	ND ^c	ND
Sr	2.0	ND	ND
Ba	8.4	2.2	6.1
Ca	7.5	ND	32.2
Zn	ND	ND	0.4
Ni	0.9	ND	ND
Cr	149	126	132
Fe	ND	ND	ND
La	5	ND	ND
Nd	ND	ND	ND
Ti	ND	ND	ND
Zr	ND	ND	ND
U	4.6	3.5	ND

^aIn $\mu\text{g/ml}$.

^bAnalyzed concentrations in $\mu\text{g/ml}$: 170 Na, 60 Si, 6.8 K, 0.4 Mg, no Ca detected.

^cND = None detected.

DISCUSSION AND CONCLUSIONS

The results presented show that, in the laboratory setup, radwaste glass reacts with water under the temperature-pressure regime of 300°C and 300 bars. Reaction for times on the order of weeks resulted in the conversion of a solid shard of glass into a fragmented and partially dispersed mass of crystalline and non-crystalline material plus dissolved species. The more massive solid products were compositionally banded and zoned which is a common indication of the non-attainment of equilibrium. Yet, the solid crystalline products and the species retained in the solutions did not vary greatly over the four reaction times used. It appears that there is a rapid initial reaction of the water with the glass to form a variety of recrystallization products, followed by a much longer time of near steady-state conditions. Although final thermodynamic equilibrium was not reached for the system as a whole, many of the crystalline phases are likely stable under the P-T conditions of the experiments.

Water plays three distinct and important roles in the degradation of the glass:

- (i) As a solvent and catalyst for glass recrystallization (long known to geochemists who use glasses as reactive starting materials for hydrothermal phase equilibrium experiments [8]);
- (ii) As a transport medium carrying elements extracted from the solids to different parts of the capsule and redepositing them as the observed crystalline capsule lining phases;
- (iii) As a component for the formation of hydrated or hydroxylated phases such as wecksite and apatite.

OCCURRENCE OF KEY ELEMENTS IN SOLID AND SOLUTION PRODUCTS

The "key elements" are those that have potentially hazardous and relatively long-lived radionuclides. In high-level nuclear wastes from light water reactors, these elements (radionuclides) would include: Cs (¹³⁷Cs), Sr (⁹⁰Sr), Np (²³⁷Np), Pu (²³⁹Pu), Am (^{241,243}Am), Cm (^{243,244}Cm), I (¹²⁹I) and Tc (⁹⁹Tc).

Only two of these elements, Cs and Sr, are present in the simulated high-level waste glass used in this investigation. However, there is considerable (though certainly not complete) analogy between the crystal chemistry and solution speciation of Np and Pu with U, and Am and Cm with the lanthanides (Ln). Thus, U and the Ln's will be included among the key elements to be discussed below.

Concerning the solutions, it should be noted again that only those elements remaining in solution or forming in readily soluble solid phases during the cool-down from 300°C would be observable in the product solutions. There were certainly other species in solution at temperature that either grew into crystals during the course of the run or precipitated on cooling to form phases that were not dissolved during the subsequent procedures used to separate solids from solutions. The weeksite and acmite phases and, probably, the multiphase banded skin are examples of such solid phases.

Table XIV is a compilation of the occurrences of each PNL-76-68 element in solid alteration products and in solutions of the 10:1 water (DW or HGW) to solid ratio experiments. The occurrences in solids are based on SEM-EDX observations and microprobe x-ray maps and x-ray emission traces. The assignment of structure types and generalized solid solution formulae resulted from x-ray diffraction studies. The key elements are underlined.

Cesium was observed in weeksite and in certain of the non-crystalline solid (NCS) alteration zones. Some 4-9% of the Cs available in the glass was found in the product solutions. Only traces of Sr were found in solution and its occurrences in the solid products were in the apatite band of the skin and in various NCS alteration zones. Uranium was found in many of the solids, but only in trace quantities in solutions. X-ray emission traces of the lanthanides showed that they were relatively well distributed among the NCS alteration zones. The only crystalline host for the Ln elements was the apatite structure phase that made up the outermost band of the skin. Less than 1% of (La+Nd) was observed in any of the various solution analyses. Thus, of the key elements, only Cs occurs in the product solutions in greater amounts.

TABLE XIV

OCCURRENCE OF ELEMENTS IN SOLIDS AND SOLUTIONS

Element	Solids	Solutions ^a
Na	Acmite ^b , Acmite-Augites ^c Weeksite ^d , NCS ^e	44-47%
Si	Acmite, Acmite-Augites, Weeksite, Apatite ^f	1-6 %
B	- - -	84-93%
Ca	Acmite-Augites, Apatite NCS	0.5-2%
Zn	Acmite-Augites, NCS	0.2-0.05%
Ti	Acmite-Augites, NCS	ND ^g
Rb	Weeksite	ND-9%
<u>Sr</u>	Apatite, NCS	0.2-0.6%
Zr	NCS	ND
Mo	NCS	68-78%
Ru	(RuO ₂) _{ss}	- -
Pd	(Pd) _{ss}	- -
<u>Cs</u>	Weeksite, NCS	4-9%
Ba	Apatite, NCS	0.04-2%
<u>Ln</u> ^h	Apatite, NCS	0.2-0.9% (La, Nd)
<u>U</u>	Weeksite, Apatite, NCS	0.03-0.15%
Fe	Acmite, Acmite-Augite, Spinel ⁱ , NCS	ND-0.06%
Cr	Spinel	18-54%
P	Apatite	- -
Ni	Spinel	0.7-4%
Te, Rh, Ag, Cd	(not included in any of the analyses)	

^a Percent of the amount of the element present in PNL-76-68 that was detected in solutions from the 10:1 water to solid ratio runs.

^b Acmite = NaFeSi₂O₆.

^c Acmite - Augite = (Na, Ca)(Fe, Zn, Ti)Si₂O₆.

^d Weeksite = (Na, Cs, Rb)₂(UO₂)₂(Si₂O₅)₃·4H₂O.

^e NCS = Non-Crystalline Solids; general designation of the x-ray amorphous-alteration zones.

^f Apatite = (Ca, Sr, Ba, Ln, U)₅[(Si, P)O₄]₃(OH).

^g ND = None Detected.

^h Ln = Y, La, Ce, Pr, Nd, Sm, Eu, Gd.

ⁱ Spinel = (Zn, Ni, Fe)(Fe, Cr)₂O₄.

It is interesting to look at the behavior of some of the other elements. Approximately 62 wt % of PNL-76-68 glass consisted of $(\text{Na}_2\text{O}+\text{Fe}_2\text{O}_3+\text{SiO}_2)$; so, it was not surprising to find that the major crystalline phases in the 10:1 water to solid ratio experiments were Na-Fe-rich pyroxenes. Note that nearly half of the available Na was observed in the product solutions. When the amount of water was tripled, the Na in solution increased to as much as 68% in the four-week run, while the amount of pyroxenes in the solid products decreased. Apparently, Na is a key constituent of these high- Fe^{3+} pyroxenes and with more Na going into solution, less was available to form the pyroxenes. This trend suggests that when water to solid ratios are less than 10:1, less Na would go into the solutions and the formation of crystalline pyroxenes in the altered products would be greater.

Boron is apparently extracted from the glass as one or more species of borate ions and molybdenum as the molybdate ion. When the solutions extracted from PNL-76-68 glass are allowed to evaporate to dryness at room temperature, SEM-EDX and x-ray diffraction characterization of the residual solids revealed the presence of a hydrated sodium molybdate and the borate mineral tinalconite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ (13).

The occurrence of the other major constituent of the glass, Fe, was almost completely confined to the solid products; it was found in the pyroxene, NCS, and spinel phases. A substantial portion of the original spinel crystalline inclusions interacted with the hydrothermal solutions. Much of the Fe content of the glass originally present in these inclusions was recrystallized in the pyroxene phases. This mechanism may also account for the large amounts of Cr in solution. Chromium occurs with Fe in the spinels. When the spinel is altered and Fe is recrystallized in the pyroxenes, the Cr might be remaining behind in solution.

The preceding discussion illustrates that, with the multiple tool characterization used in this study, it is possible to describe alteration of this complex glass in near mass balance detail for many of its elements.

GLASS CRYSTALLIZATION AND REPOSITORY DESIGN

Solution and recrystallization of the prototype radwaste glass takes place so readily that some cognizance of the potential for this effect must be taken during the repository design. Because many of the observed reactions require water only as a catalyst, some of the recrystallization and transport could be expected in the presence of only small amounts of water. One can either view the hydrothermal reactions as a "problem" in need of a solution or one can simply incorporate the potential for hydrothermal reactions as part of the overall waste storage concept. There are some fairly obvious engineering solutions to the "problem" and also some potentially interesting ways of incorporating the reactions as a positive benefit, although data are too sparse at present to make definitive statements about the latter.

First, an obvious requirement for hydrothermal conditions is a certain amount of heat. The heat output of the canisters can be adjusted by adjusting the waste loading. Loadings could be adjusted downward until the skin temperature of the canister was below the temperature at which the reactions would be a problem. The cost of this approach to the "problem" is that much larger volumes of material would be created for the disposal of a given volume of waste.

Second, it may be remembered that heat comes from the decay of mostly short-lived isotopes. The thermal period of the repository is short, a few hundred years at most. One expedient is to retain the canisters in controlled and cooled surface storage for a few tens of years before removal of the material to the repository. Temperatures fall rapidly with time out of the reactor and even a few years of storage improves the thermal heat output greatly. Alternatively, the canister design could be improved in such a way that breaching of the canister during the thermal period became unlikely.

A completely different approach is to examine the implications of waste, rock, and water as a chemical system (2). The results reported in this

paper dealt with a glass waste form in a closed system in the presence of water only. This situation would surely obtain if invading waters came into contact with the surface of the glass ingot or penetrated into cracks and flaws in the material. The initial chemical reactions would be completely dominated by the composition of the glass. As the solutions carrying dissolved species or the solid reaction products themselves came into contact with the surrounding wall rock, the chemistry would come to be dominated by the rock. If the repository wall rock were of basalt, granite, or shale, new reactions would take place that would greatly modify the final phase assemblage. It is the final assemblage, when the waste has come into steady-state conditions with the rock, that must be regarded as the source term for further transport and dispersal of the waste elements by slow processes over the functional life of the repository (2). The paragraphs below outline some of the possibilities based on new but not final experimental results from current waste-rock interaction studies at PSU (11,13).

Strontium and Lanthanides

Much of the Sr and Ln in the original glass was found with the NCS alteration products. Equilibration with hydrothermal solutions could well result in crystallization of apatite phases similar to that identified as one of the skin phases. Apatites are a common accessory mineral in basalts and other igneous rocks and, once formed, they may remain in, or close to, thermodynamic stability, with the rock throughout the thermal period. Mixed phosphate-silicate apatites of Ca, Sr, Ln and U (britholite) such as those formed on the product skin are known.

Uranium

Small amounts of the U in PNL-76-68 crystallized in the apatite phase as has already been noted. The other well-characterized crystalline host for U was weeksite. Uranium in weeksite is in the hexavalent state. Host rocks containing Fe^{++} , sulfides, organic, materials would buffer the oxygen activity well into the reducing range where the U^{+6} would not be stable. In one of a series of experiments designed to explore this stability question, the authors have treated weeksite crystals gathered from glass alteration

products with HGW in contact with a sixty-fold excess by weight of crushed Columbia River Basalt. The water to solids ratio was 30:1 and the experimental conditions were 300°C, 300 bars, four weeks. The resultant crystals had turned black and gave an x-ray powder pattern of uraninite, UO_{2+x} , with a cubic cell parameter typical of a composition near $\text{UO}_{2.25}$. As long as the conditions remain reducing, uraninite should remain a stable and insoluble phase (14). It is possible that the U in the NCS alteration zones would be converted to uraninite through long-term equilibration with basalt-saturated hydrothermal solutions.

Cesium

This element was observed in alteration product solutions, in wecksite and in various NCS alteration zones. (Note that the Cs would be released from wecksite by the decomposition mechanism just described.) The authors have completed numerous experiments in which solutions containing Cs were reacted with Columbia River basalts, with individual basalt phases, and with shales and constituent clay minerals (14). Under conditions of 200-300°C, 300 bars, virtually all of the Cs was removed from the solutions. Intense reflections analogous to those of the mineral pollucite, $(\text{Cs},\text{Na})\text{AlSi}_2\text{O}_6 \cdot n\text{H}_2\text{O}$, were present in x-ray diffractograms of many reaction products. Pollucite occurs in hydrothermally formed pegmatites and may well be stable in contact with basalt and shale under hydrothermal conditions. Results to date indicate that Cs would react with alumino-silicate minerals and become immobilized as pollucite.

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LIST OF ABBREVIATIONS

AAS = Atomic Absorption Spectrophotometry
AES = Atomic Emission Spectrometry
d = Interplanar Spacing (in x-ray data)
DW = Deionized Water
EBS = Electron Backscatter
EDX = Energy Dispersive X-Ray Spectrometry
HGW = Hanford Groundwater
I = Intensity (in x-ray data)
Ln = Lanthanides
NCS = Non-Crystalline Solids
ND = None Detected
PDF = Powder Diffraction File
PNL = Pacific Northwest Laboratory of Battelle Memorial Institute
PSU = The Pennsylvania State University
P-T = Pressure-Temperature
SEI = Secondary Electron Image
SEM = Scanning Electron Microscopy
SS = Solid Solution
TDS = Total Dissolved Solids
wt% = Weight Percent

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