Contract
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SIMULATED HIGH-LEVEL WASTE-BASALT INTERACTION EXPERIMENTS

ANNUAL PROGRESS REPORT
FOR THE PERIOD
OCTOBER 1, 1977 to SEPTEMBER 30, 1978

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MATERIALS RESEARCH LABORATORY

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INTRODUCTION

The objectives of the research conducted for FY-1978 under the contract entitled "Simulated High-Level Waste-Basalt Interactions" were to determine the nature of waste-basalt interactions and to begin to establish an understanding of their relevance to radionuclide release rates. The reader will observe that the thrust of this year's program has shifted from the broad scoping studies to more detailed investigations of the resultant interactions and alteration that were observed. The analyses of the solution phases have become increasingly more important for the detailed interaction experiments to complement the solid phase characterization program developed initially during the previous contract year. The importance of this ability to characterize the liquid phase is exemplified in the detailed studies involving spent unreprocessed fuel (SURF) as a waste form. Typically, the chemical conditions of the experiment are such that no detectable changes can be attributed to the solid phase, therefore causing reliance upon our solution analysis capabilities.

The reconnaissance experiments, initiated during FY-1977, were completed during this year as a project milestone. In the progress report that follows, the reader is presented with the generalized stability of each of the waste forms as a function of temperature. These scoping studies have led to the design of long-term experiments designed to study the phase assemblage.

The basic approach to recognizing the characteristic alterations in waste forms was developed with the glass experiments and can now be applied to a more comprehensive study of SURF. The approach to the investigations into the alterations and interactions of SURF has taken two main pathways. The first of these is procedurally similar to that applied to glass; i.e. to hydrothermally treat the closest simulation to a feasible waste form for use in our facility and to follow the progress by careful solution and solid phase characterization. The next step is to extend the experimentation to the two solid component system of SURF and basalt plus water and follow the potential interactions and alterations by both liquid and solid phase characterization. The second pathway is to take the individual component phases, that are known or presumed to be typical of the SURF assemblage, and to examine in detail the interactions and stability of these phases alone and in the presence of basalt minerals. These experiments were conducted under relevant repository conditions typical of the thermal period.

The latter pathway has proven to be very fruitful. Experimentation presented to date indicates that favorable interactions with the country rock mineralogy would occur if the Cs and Sr phases that are present in SURF come into contact with hydrothermal fluids. These interactions would reduce or prevent the movement of the two radionuclides.

Two distinctly different experiments have been designed and initiated to simulate the full repository conditions. These experiments include the waste, the rock, the canister and, potentially in the future, an engineered overpack. One of these repository simulations represents a "closed" system which has been used routinely to ascertain if interactions would occur under designated P,T conditions. The other, a high pressure flow-through experiment, represents a close laboratory approximation of an "open" system repository simulation.

It has been a continuing goal of this program to document the procedures developed and employed within this project so that interlaboratory exchange of results and ideas could be accomplished. The reader is referred to the Annual Report for 1977 (RHO-BWI-C-2) which describes the dry low-pressure experiments, hydrothermal experiments and characterization by optical microscopy, x-ray diffraction, and scanning electron microscopy. The First Interim Progress Report (RHO-BWI-C-12) for 1978 also contains detailed descriptions of preparation of simulated SURF, the Gandolfi method, hydrothermal run solutions: preparation and analysis, description of ETEC microprobe and updated procedural steps for hydrothermal experimentation.

SUMMARY

With the completion of the reconnaissance experiments during this year, the nature of the research effort changed over to a more in-depth, detailed experimental program. The reconnaissance experiments suggested that the observed reactivity of calcine and glass at 300°C would be anticipated at lower temperatures but only after longer times of hydrothermal treatment. With this observation, long-duration experiments at 100° and 300°C were initiated to determine the time dependence of the alterations at lower temperatures. Results of the reconnaissance experiments also suggested that equilibrium conditions were not yet achieved in these closed system experiments. Observations also suggested experimentation time ranging up to one year in duration; these have been initiated.

A major topical report on the alteration of glass as a waste form has been completed as the first step in the systematic examination of waste-basalt interactions. Glass was observed to alter readily with the formation of three recognized crystalline alteration products. These phases are acmite-augite pyroxene; a uranyl silicate, weeksite; and a rare-earth silicate-phosphate hydroxyapatite. Analyses of the solution phase in these closed system experiments revealed that nearly all of the B, ca. 70% of the Mo and ca. 50% of the Na in the original glass were dissolved and were present in the aqueous phase.

A simulated reduced SURF was synthesized and utilized in hydrothermal experimentation. Solid phase characterization of the products from SURF

experiments does not indicate any alteration. However, the analyses of the solutions confirmed that soluble fission products phases would be leached from the UO_2 matrix. Under these circumstances all of the alkali metals were leached from the SURF. In the presence of basalt, however, the released alkalis react with aluminosilicates and are removed from solution almost in totality.

As an alternative approach to establish the stability of SURF in a basalt repository, individual phases that are believed to be present in SURF have been hydrothermally treated individually, with the reference basalts and with the major primary and secondary minerals present in basalt. Again results are very encouraging. $Cs(OH)$, Cs_2MoO_4 and $Cs_2U_2O_7$ were used as potential cesium phases. Results indicate that in some cases as much as 99.9% of the cesium can be removed from solution by interacting with the above rocks and minerals to form pollucite. $SrZrO_3$ is the other phase that is known with more certainty to be present in SURF. The interaction of strontium zirconate under hydrothermal conditions with the above rock and basalt minerals indicates that in all cases 99.9% of the available strontium is retained in the strontium zirconate or as alteration products.

To complement the closed system experimentation, the ability for more control over the physical parameters of the experiment; i.e. P, T, pH, Eh, can be achieved in the open or flow-through system. The direction of the research program over the next year will be toward this experimental area with the repetition of the selected closed system experiments.

RECONNAISSANCE EXPERIMENTS

The objective of this set of experiments was to identify the temperatures, at a fixed relevant repository pressure, where alterations or interactions between simulated waste forms and/or basalts would occur. The identification of individual reaction products in the solid phase was the major thrust of this effort. In addition, the ability to rank the individual waste forms as to their stability and to develop a predictive capability for their alteration was a prime objective.

The initial set of scoping runs at 200°C and 400°C was accomplished during FY-1977 under the direction of a contract entitled "High-Level Waste-Basalt Interactions." The remaining components of waste and waste/basalt mixtures were completed at 100°C and 300°C during the first half of FY-1978. The following experimental conditions were characteristic of the hydrothermal scoping runs:

- Temperature: nominally 100, 200, 300 and 400°C;

- Pressure: nominally 300 bars (4300 psi; 29.6 MPa);
- Duration: 28-30 days;
- Simulated waste forms: calcine (PW-7a), SURF (95% UO_2 + 5% PW-4b), supercalcine, glass (PNL-76-68);
- Basalts: DDH-3 (core from Hanford Site) and BCR-1 (USGS standard);
- Hydrothermal fluid: simulated Hanford groundwater (Ames, 1976) added 50% by weight to total solids;
- Sample description: intimate mixtures of -200 mesh (74 μm) powders of waste, basalt, and waste + basalt.

A detailed characterization procedure was developed that employed optical examination to screen alteration or interaction products followed by the use of state of the art instrumentation for solid phase examination. These characterization tools included scanning electron microscopy, microprobe, energy dispersive x-ray fluorescence, bulk x-ray diffraction, and Gandolfi x-ray diffraction techniques. Detailed descriptions of each technique can be obtained in the First Interim Progress Report (RHO-BWI-C-12), Appendix A.

Discussions of the results obtained for the components of the scoping study can be obtained in our FY-1977 Annual Report, First and Second Interim Progress Reports (RHO-BWI-C-2, RHO-BWI-C-12 and RHO-BWI-C-16).

The following generalizations can be made for each of the waste forms:

- Calcine is extremely reactive,
  - reacts with basalts/minerals at all temperatures above 100°C to form pollucite,
  - reacts to form two Mo-scheelite-structure phases of Ca and Ba with limited Sr substitution;
- Glass is altered readily,
  - reacts with basalt to form pyroxenes and several other crystalline phases not yet identified,
  - reacts alone to form weeksite as well;
- Supercalcine is generally unreactive,
  - only minor enhancement of pollucite crystallinity recognized;

- SURF is generally unreactive,
  - no observed reaction between UO_2 and basalt minerals,
  - reaction observed with fission product simulation components of SURF,
  - reaction products are Mo-scheelite-structure phases and separate molybdates of Cs and Na.

The following generalized observations can be reported pertaining to the kinetic effects of reacting the named solids with water at temperatures from 100°C to 400°C for up to two months:

- Only calcine is observed by bulk XRD to react at 100°C;
- Optically, glass and basalt mixtures and glass alone appear to have altered or interacted at 100°C;
- Alteration is limited to calcine and glass at 200°C as characterized by bulk XRD;
- Alteration is observed to be extensive for calcine and glass but only weakly present for SURF and supercalcine at 300°C;
- The extent of alteration at 400°C is similar to that at 300°C.

Observations of the alteration products suggest that over the temperatures spanned in these experiments, reactivities similar to those at 300°C and 400°C could be expected at the lower temperatures for mixtures of wastes and/or waste-basalt, but reaction times will be longer. Clearly the alteration reactions are kinetically limited at the lower temperatures. This observation will be tested when the results of the long-duration experiments are examined.

DETAILED EXAMINATION OF COLUMBIA RIVER BASALTS BEFORE AND AFTER HYDROTHERMAL TREATMENT

In order to gather data for the evaluation of basalt as a host rock for a nuclear waste repository, x-ray diffraction studies were conducted on basalts both before and after hydrothermal treatment. Two basalts were studied: the USGS standard Basalt Columbia River (BCR-1) was used as a generic representative and the other sample was a basalt from a site-specific core sample located on the Hanford Site (DDH-3/A2120/3320.

X-ray powder diffractograms of these basalts showed the minerals labradorite (and/or andesine), augite, glass, and a solid solution of magnetite and ulvospinel. With the exception of the two iron oxides, little change in the bulk x-ray diffraction patterns was observed between the untreated rock and that hydrothermally treated with 50% by weight of synthetic Hanford groundwater for up to 30 days.

Because the ferrous-ferric ratio of the minerals in the basalt is expected to buffer the waste-rock-water system, the oxidation state of the iron-titanium oxides was studied in detail. These minerals were separated magnetically until the diffractograms showed principally spinels. The cell constants were subsequently calculated to determine the fraction of magnetite in the magnetite-ulvospinel mixtures. Compositions varied from 30 to 40 percent magnetite and depended upon hydrothermal treatment. Further information, either the temperature of the rock formation or the composition of the ilmenite-hematite solid solution in equilibrium with the magnetite-ulvospinel phase, will allow calculation of pO_2. The latter method is currently being pursued by experimentation with further magnetic separation. The magnetite-ulvospinel ratios can be used as a monitor of oxidization state in hydrothermal runs on waste-rock interactions.

LONG-DURATION EXPERIMENTS

These experiments were designed to run for up to one year, in order to obtain an understanding of the kinetics involved with those reactions observed in the scoping studies. In addition, the longer duration experiments will also give insight into the assemblage of reaction products that may persist under a situation that more nearly approaches equilibrium conditions.

These experiments were initiated at two temperatures, 100°C and 300°C, and 300 bars pressure. To date, the 300°C full matrices of waste/basalt mixtures were sampled at one month (the reconnaissance experiments) and additionally at two and six months. The results of the two-month experiments will be discussed in detail. The six-month 100°C run was terminated during the preparation of this report but has not yet been fully analyzed.

To summarize the results of the two-month-long duration, 300°C experiments, it can be reported that:

- No evidence of alteration or interactions with UO_2 component of simulated SURF was seen;
- The only interaction of basalt with SURF was with the simulated fission product component;

- Both calcine and glass alter readily;
- Weeksite is not seen to form from any of the basalt-glass interactions;
- "Unknown A," a zinc sodium silicate, is observed in all basalt-glass runs;
- Supercalcine was shown to undergo some crystallization of the approximate 5% amorphous component and a redistribution of some of the cations in the synthetic mineral components.

The following is a detailed tabulation of the 300°C two-month-duration waste-basalt interaction descriptions, which include pertinent SEM photographs and the results of x-ray diffraction studies.

LONG DURATION EXPERIMENT, SERIES #55

BCR-1/calcine - Clusters of small crystals of Ca and Mo composition ($CaMoO_4$?) and very small spherical particles with pollucite chemistry were observed.

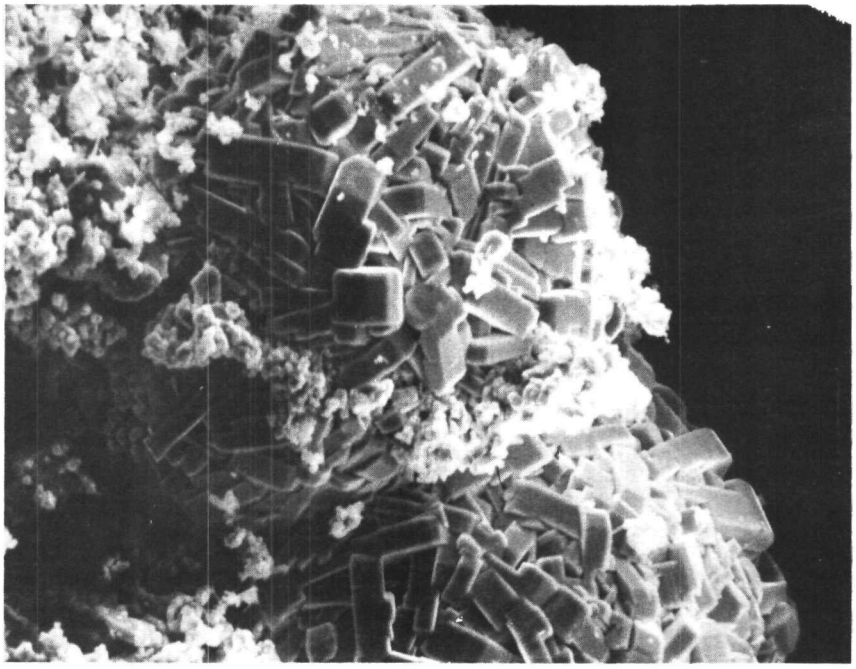
BCR-1/76-68 - The interior surface of the gold tube was heavily encrusted. The charge contains reaction products that consist of spherical clusters of crystals with hexagonal prism faces and basalt termination (Fig. 1) similar to those identified in runs 56-B, 56-D, 56-O and 56-P. The chemistry is composed of Zn, Na, Si, K, Ca and Fe. X-ray methods have found this to be single-phase material that to this date has not been identified. Table I is a listing of the observed d spacing and intensities for this phase which was labeled "unknown A."

- The greenish crust in the ampule has elongate crystals as well as rounded grains. The elongate crystals have a morphology similar to the acmite crystals previously observed; however, the EDX chemistry indicates Fe, Si and an unidentified element, perhaps a rare earth.
- The crust appears to be composed primarily of a Si-containing phase.

BCR-1 - The charge had 0.2 mm growths on the surface that possessed an EDX chemistry of only Ca. This is an unusual observation, and no explanation is given (Fig. 2).

- The charge also contains some small, rounded to hourglass-shaped, crystals with EDX chemistry, Na, K, Al, and Si. This is most likely a mordenite.

DDH-3/calcine - It contains many very small crystals with pollucite chemistry.



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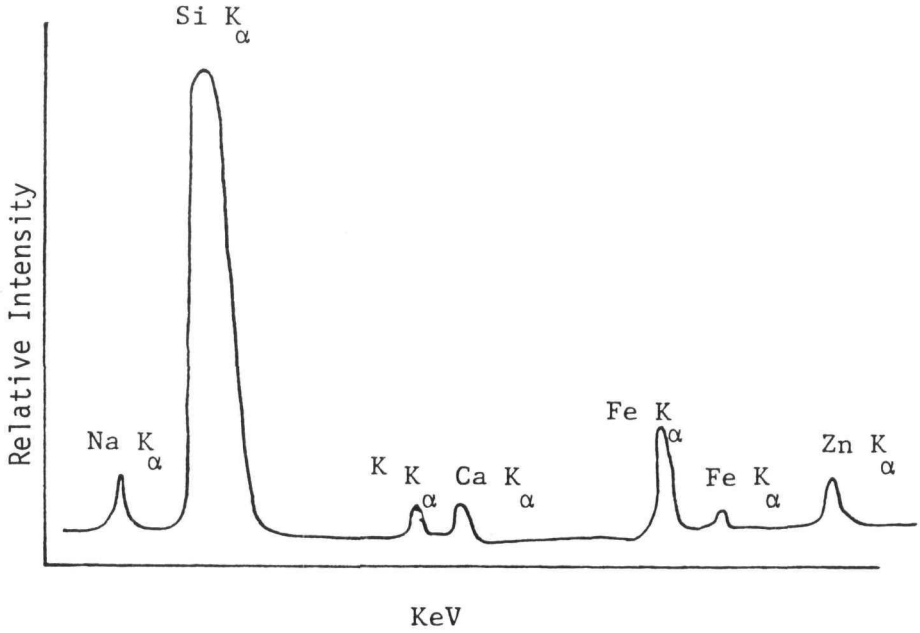


Figure 1. "Unknown A," an interaction product of the hydrothermal treatment of BCR-1 and PNL-76-68 glass.

TABLE I

X-RAY DIFFRACTION DATA FOR "UNKNOWN A"

d	I/I_0
9.1	vvw
7.7	vvw
7.05	m
5.60	m
5.25	mw
4.80	vvw
4.55	w
3.83	s
3.73	vw
3.54	w
3.43	vw
3.35	s
3.32	w
3.21 } 3.20 }	w
3.09	w
3.03	w
2.94	mw
2.88	vvw
2.80	m
2.63	m
2.58	vvw
2.52	vw
2.48 } 2.46 }	w
2.23	w
2.17	w
2.12	w
2.11	vw
2.06	vw

d = interplanar spacing

I/I_0 = relative intensity

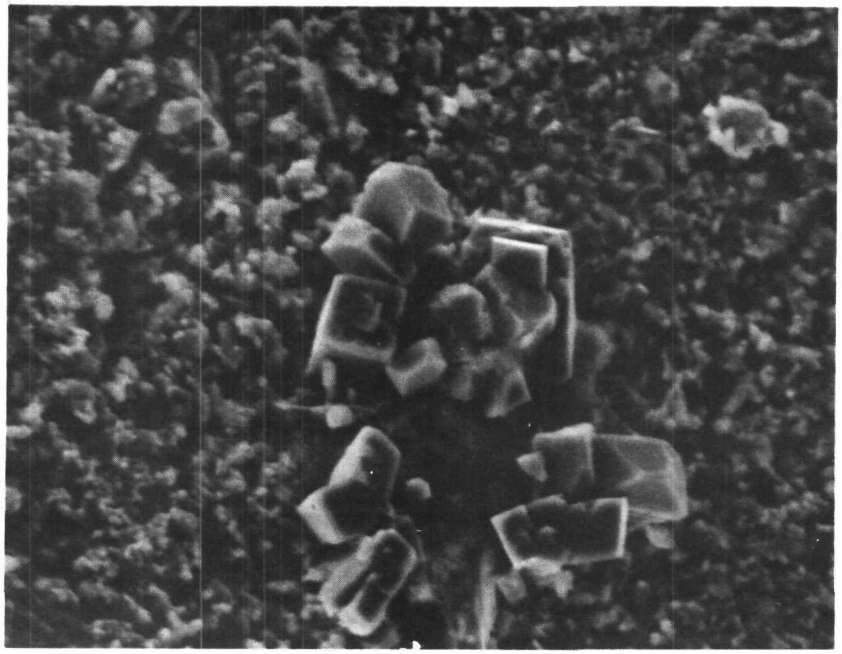
s = strong

m = moderate

w = weak

vw = very weak

vvw = very very weak



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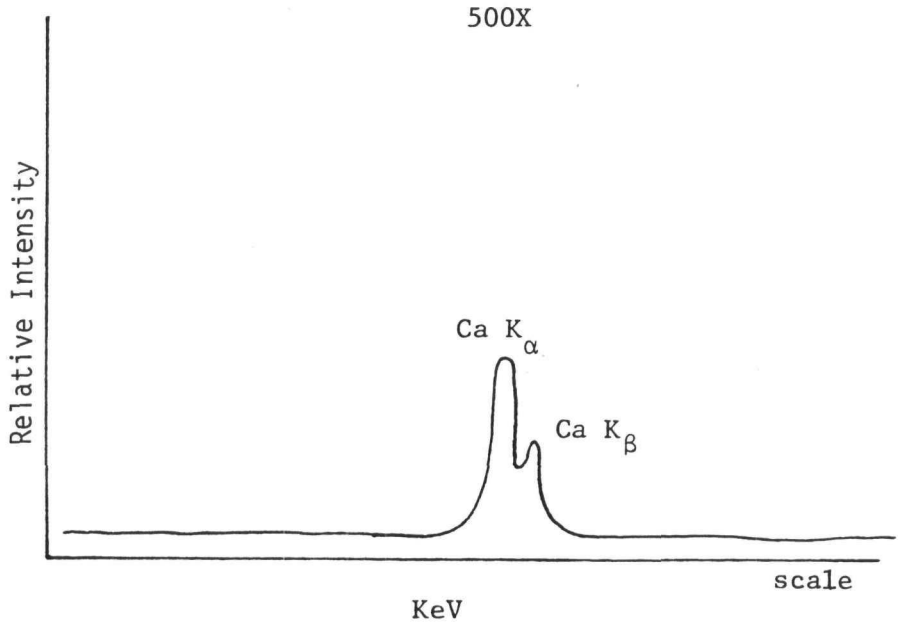


Figure 2. An unidentified phase which is most probably a calcium carbonate observed in the hydrothermal reaction products of BCR-1.

DDH-3/76-68 - The crust on the inner surface of the gold ampule had large elongate crystals with EDX chemistry similar to acmite Na, Fe, and Si.

- The small needle crystals appear to be a silica phase (Fig. 3).
- Aggregates of unknown A are present.

DDH-3/SPC-2 - Crust on inside of the gold ampule is mainly a silica phase.

- Rectangular lath-like crystals with an equant cross sectional area are composed of Na, K, Ti, Al, and Si as analyzed by EDX. The phase identity has been speculated upon.
- Clusters of spherical crystals of approximately 5 μm diameter have EDX chemistry of silica phase.
- Clusters of platelet-like crystals with a maximum 40 μm dimension and composed of Ca and Si are most probably truscottite (Fig. 4).
- Very small spherical clusters with EDX chemistry containing Na, K, Ca, Zn, Si as determined by EDX analysis were observed. No identification is speculated upon.

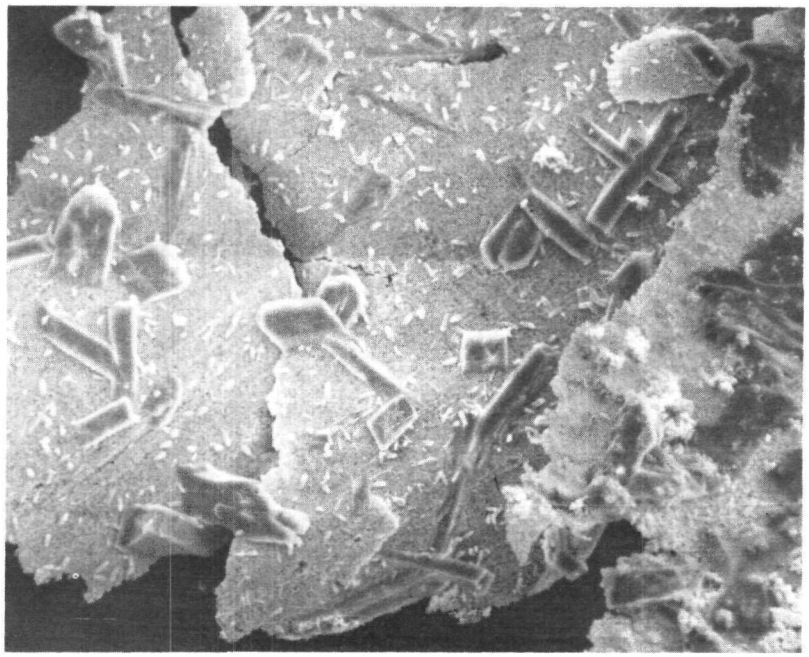
DDH-3/SURF - 40 μm crystals of a phase containing Cs and Mo, most probably Cs_2MoO_4, were present (Fig. 5).

Calcine - A bright green crust formed upon evaporation of the mineralizing solution. This was found to contain $Na_2MoO_4 \cdot 2H_2O$, see Table II.

- 76-68 - Large growth of weeksite crystals formed on the charge and on the gold capsule.
- The surface of the sintered charge has large, dark dendritic growths with EDX chemistry Na, Si, Ca and Fe.
- The surface of the sintered charge is a mass of fine needle crystals with chemistry similar to the dendrites, with perhaps Zr.

SPC-2 - Large aggregates of platelets with Ca, Si chemistry were observed. X-ray methods have identified this as truscottite, Table III (Fig. 4).

- Dark green crust with several different grains was observed that contained small crystals with an unidentifiable EDX chemistry and small spherical aggregates with Ca, RE, Al and Si, perhaps an apatite structure.



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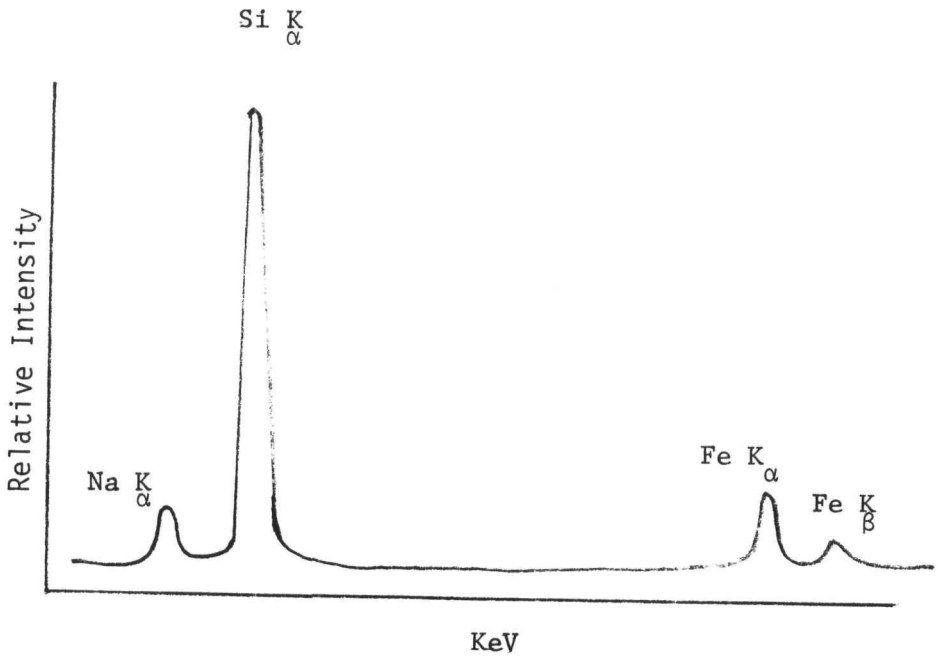
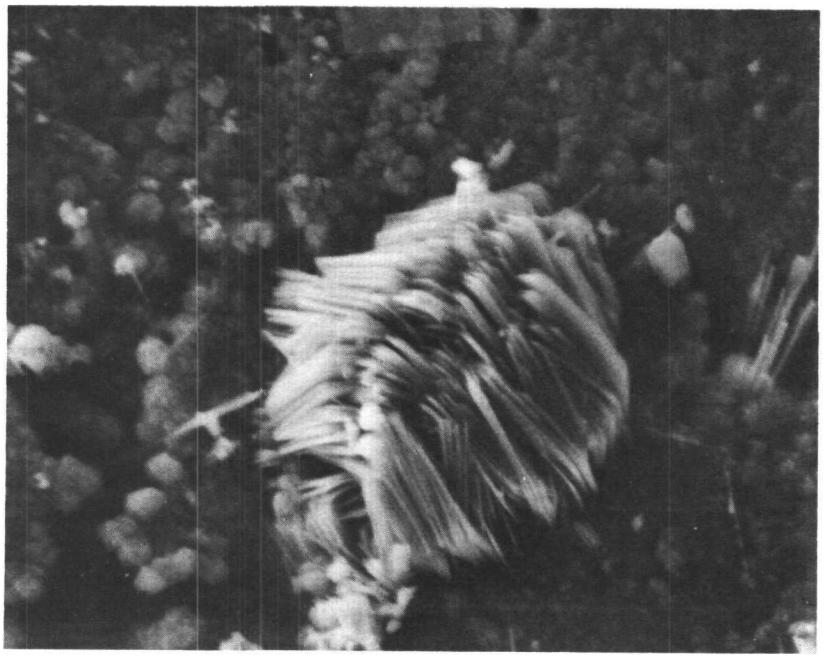


Figure 3. Lath-like crystals of a pyroxene-like phase in the reaction products of DDH-3 and PNL-76-68 glass.



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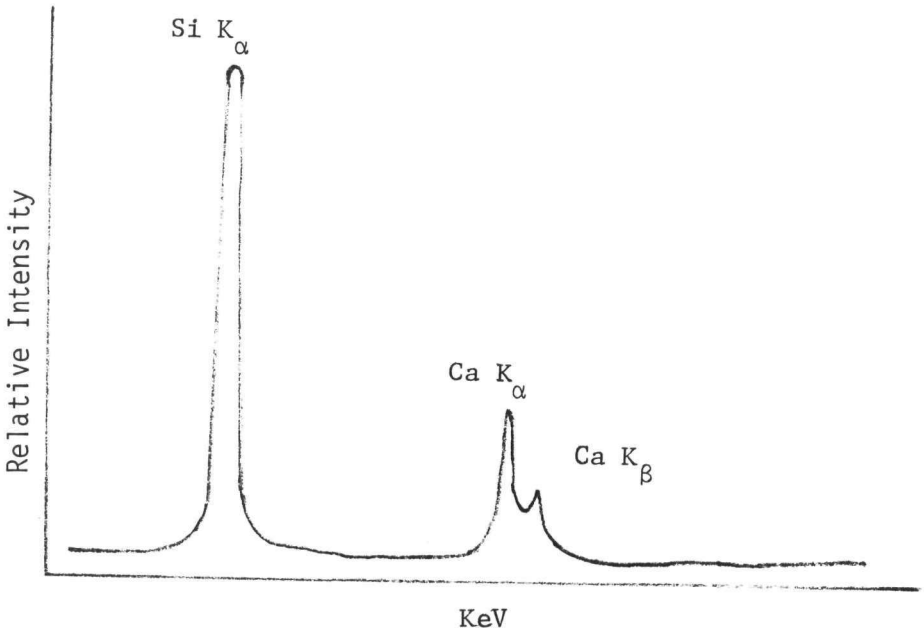
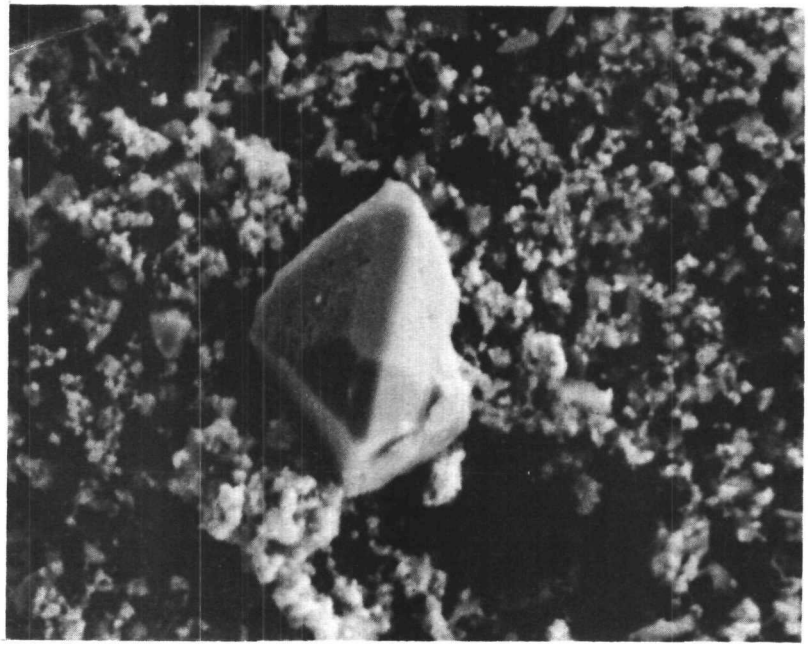


Figure 4. Crystals of truscottite, $Ca_5Si_4O_9(OH)_2$, identified in the reaction products of DDH-3 and supercalcine.



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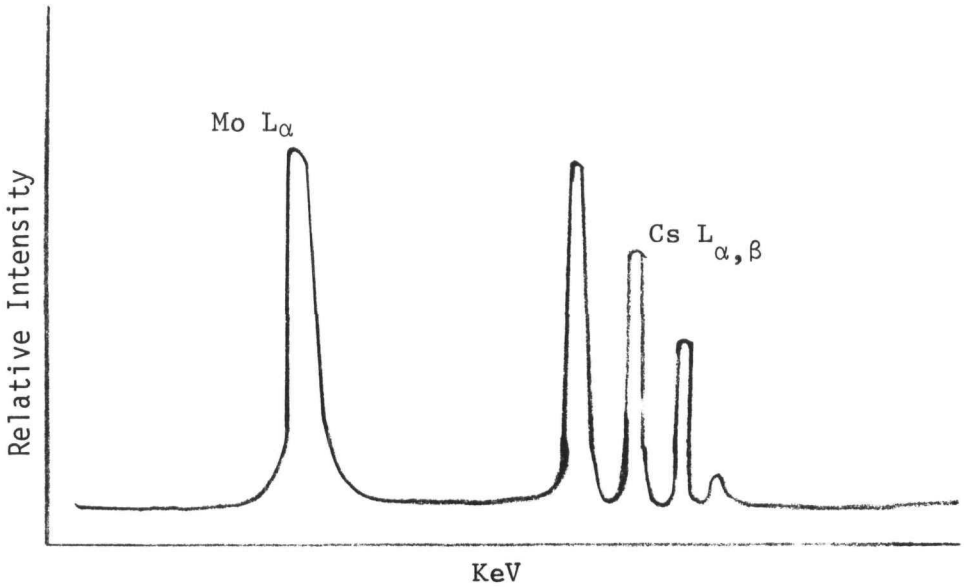


Figure 5. Crystals of a cesium molybdate formed most probably from the fission products of simulated SURF reacted hydrothermally at 300°C.

TABLE II

X-RAY DIFFRACTION DATA FOR LIGHT OLIVE GREEN GLOBULES COMPARED TO $Na_2MoO_4.2H_2O$

light olive green globules		$Na_2MoO_4.2H_2O$ 13-236	
d	I/I_o	d	I/I_o
6.90	ms	6.91	100
5.95	w	5.95	8
5.25	w	5.26	12
4.75	w	4.77	6
4.45	m		
		4.22	22
4.18	m	4.19	30
		3.92	2
3.78	vw	3.78	12
3.63	m	3.60	75
3.45	vw	3.46	22
		3.41	8
		3.41	6
3.30	m	3.30	40
3.21	vw	3.21	26
3.17	s	3.16	60
3.07	w	3.06	40
2.98	mw	2.982	45
		2.976	45
		2.935	2
2.90	w	2.890	22
		2.740	28
2.67	mw	2.674	26
		2.652	16

d = interplanar spacing
I/I_o = relative intensity
s = strong
m = moderate
w = weak
vw = very weak
vvw = very very weak

TABLE III

X-RAY DIFFRACTION DATA FOR WHITE GLOBULES COMPARED TO TRUSCOTTITE

55M white globules		Truscottite $Ca_2Si_4O_9(OH)_2$ 19-229	
d	I/I_o	d	I/I_o
		19.0	100
		9.48	
9.5	w		100
		7.73	20
		6.31	30
		5.05	10
4.75	w	4.72	40
4.30	vw		
4.20	vw		
		4.11	20
3.88	w	3.84	40
		3.76	40
3.53	mw	3.50	40
		3.44	10
3.16	s	3.14	100
		3.01	30
		2.98	10
		2.94	20
2.85	m	2.84	100
		2.69	10
2.65	m	2.64	80
		2.57	10
		2.52	10
		2.43	10
2.44	vw		
2.25	vw		
		2.09	10
2.07	vw	2.05	20
		1.922	10
1.855	m	1.838	40
1.82	vw	1.802	10

d = interplanar spacing; I/I_o = relative intensity; s = strong; m = moderate; w = weak; vw = very weak; vvw = very very weak

- Several grains have been hand picked for x-ray examination and been found to be $BaMoO_2$ (Table IV) and $Na_2MoO_4 \cdot 2H_2O$ (Table II).

BCR-1/76-68/stainless steel - A great deal of interaction was observed.

- Large spherical aggregates, similar to unknown A were observed.
- Fine needle bundles with chemistry Fe, Si, with minor Na, K, Ca and Ti were present.
- Rectangular laths containing U and Si with Na and Fe were observed.
- Portions of the surface are covered with a 3-D mud-crack-like texture that perhaps could be a desiccated gel.

BCR-1/SPC-2 - 70 μm long clusters of euhedral $(Ca,Sr)MoO_4$, most likely a scheelite structure, have been observed (Fig. 6).

- In direct association crystals of $(Ba,Sr)MoO_4$ are present; in both cases the amounts of detected Sr are by far the highest to date.

A very careful dissection of the run DDH-3 and glass has produced a list of unusual and at this point anomalous phases as well as some previously recognized phases; these were identified from small crystals or grains by Gandolfi XRD techniques. The phase designated unknown A is common to all basalt-glass runs as are the frequent appearance of borate phases, borax and tincalconite. These borate phases were recognized previously in experiments where solutions were allowed to evaporate over the solid charge. It was found that boron is present almost totally in solution. Boltwoodite, $K_2(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$, was identified as yellow-green crystals, topaz, $Al_2SiO_4(OH)_2$, was recognized as colorless crystal and α-quartz has also been identified. The identifications of the latter three phases represent the first time that any of them were recognized as alteration or interaction products. A series of experiments was designed and implemented that will analyze the solid as well as the solution phases of basalt/glass and basalt/SURF mixtures in an attempt to obtain an understanding of the interaction products.

OBSERVED TRENDS

Tentative trends are beginning to develop within the long-duration experiments. The most obvious is the absence of the uranyl silicate phase, weeksite, in the presence of basalt and the formation of a yet unidentified sodium zinc silicate phase. The absence of weeksite was confirmed in the 1, 2 and 6 month basalt/glass mixtures both with and without stainless steel. The formation of an apparent trigonal or hexagonal sodium

TABLE IV

X-RAY DIFFRACTION DATA FOR BROWN PRISMATIC CRYSTALS COMPARED TO $BaMoO_4$

55M Brown Prismatic crystals		8-455 $BaMoO_4$	
d	I/I_0	d	I/I_0
		5.11	2
3.33	s	3.357	100
3.17	w	3.202	20
2.78	m	2.789	25
		2.557	4
		2.487	4
		2.449	4
		3.329	2
		2.154	4
2.08	ms	2.104	30
1.97	vvw	1.9721	10
1.86	w	1.8779	18
1.69	w	1.7007	25
1.675	vvw	1.6787	12
		1.6024	2
		1.3946	2
1.39	vvw	1.3899	8
1.355	vw	1.3606	10

d = interplanar spacing

I/I_0 = relative intensity

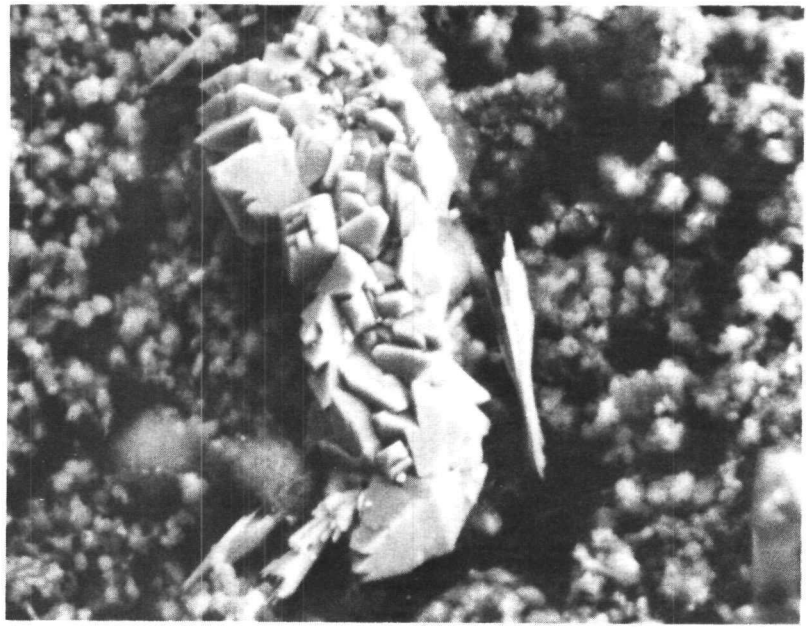
s = strong

m = moderate

w = weak

vw = very weak

vvw = very very weak



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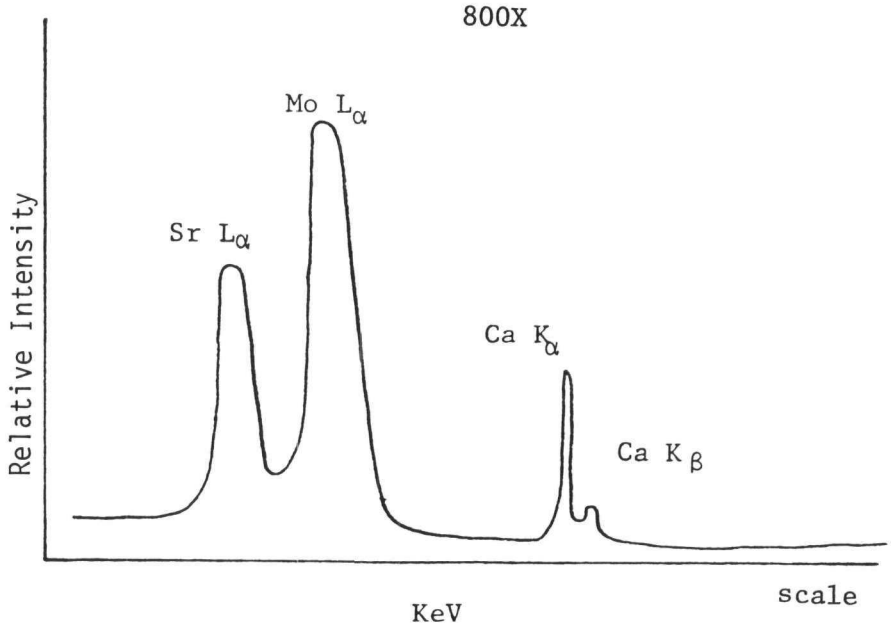

Figure 6. Alkaline earth molybdate crystals identified in the reaction products of BCR-1 basalt with supercalcine.

zinc silicate was confirmed in the one-month and two-month experiments and recognized but not yet confirmed in the six-month run.

Weeksite has formed from the alteration of glass alone in all three experiments. Colorless crystals which possess a chemistry that is in concert with the composition of pollucite were identified in the one- and two-month experiments and similar but yet unconfirmed crystals are present in the six-month experiments.

The trends observed at this early date suggest that there is little major deviation in the course of the alterations or interactions. Alterations will be expected to appear as subtle product formations and will require careful dissections of the samples for use with the Gandolfi x-ray diffraction techniques.

HYDROTHERMAL ALTERATION OF PNL-76-68 GLASS

An extensive study of the hydrothermal alteration of the glass waste form PNL-76-68 has been carried out.

It was shown that at 300°C and 300 bars of fluid pressure, the formulation of PNL-76-68 readily alters. Careful solid phase characterization revealed that three crystalline phases persist as alteration products. These phases are a weeksite analog $(Cs,Na,Rb)_2(UO_2)_2Si_6O_{15}\cdot 4H_2O$, a series of pyroxene structure phases $(Na,Ca)(Fe,Zn,Ti)Si_2O_6$ and a rare earth phospho-silicate apatite. Additionally, several phases were formed as minor alteration products that have no counterparts in the current compilations of x-ray diffraction data. Iron spinel phases were reported to be present in the glass either as constituents that have never dissolved or as components that have dissolved and then precipitated during the heat treatment of the waste form. The predominant phase has been confirmed to be an Fe-spinel similar to magnetite with a cubic cell constant of a_o = 8.40Å admixed with RuO_2 and Pd metal.

The elements sodium and molybdenum were readily leached from the glass and were used as benchmark elements for identifying the spacial extent of alteration. Solution analyses indicate that after the second week of hydrothermal treatment a steady-state between the solid charge and dissolved species was obtained. Virtually all (93%) of the boron present in the original glass is present in solution at the end of four weeks of hydrothermal treatment. Molybdenum is present to the extent of 72% of all of the available molybdenum while sodium is present at 45% of the total Na in the solid charge. Sodium molybdate dihydrate, $Na_2MoO_4\cdot 2H_2O$ was recognized in the scoping studies as a phase that forms when the fluid phase of the reaction is allowed to evaporate while still in contact with the solid charge. The hazardous near-term radionuclides, Cs, Sr and U were present in solution at 5%, 0.15% and 0.03% respectively. The cesium and the uranium were

incorporated into the solid phase formation of weeksite and the strontium was most probably incorporated into the apatite-like structure. Of the 38 components of the initial glass formulation, 96% by weight can be accounted for as redistributed into known solid phases or identified in solution.

HYDROTHERMAL ALTERATION OF GLASS-BASALT MIXTURES, SURF, SURF-BASALT MIXTURES

A logical follow-up to the systematic study of the alteration of PNL-76-68 glass was the examination in detail of glass-basalt alteration interactions. Experimental runs from this series of mixtures of basalt in a 1:1 ratio with glass and a 10:1 excess of water to glass are just being completed. Principally, the alteration or interaction was extensive at the end of four weeks of treatment under hydrothermal conditions. The alteration phase that was observed in glass as a massive white zone of a pyroxene composition is a gray-green color in the presence of basalt. The experiment was designed to separate single chunks of basalt and glass by wrapping the basalt in a loose-fitting gold bag. Weeksite is not observed in these reactions although if mixtures of powders were used instead of chunks weeksite did form. Both solid and solution phase analyses are in process but neither is yet near completion.

Similarly, a simulated spent unreprocessed fuel is being hydrothermally treated both alone and in the presence of an equal mass of basalt and a ten-fold excess of water. These experiments are currently being hydrothermally treated at 200°C and 300 bars pressure. A number of these experiments have been completed and analyses of both the solid and liquid phases completed. Solid phase characterization by optical microscopic observation and bulk XRD reveal no identifiable alteration of interaction products. Solution analyses detected the total amount of Cs and Rb that was present in the simulated SURF in the solution phases at both 200°C and 300°C. Molybdenum was also detected in the solution at approximately 50% of the total amount in the SURF. The only other element that was identified in solution was trace quantities (less than one one-hundredth of a percent) of uranium. Analyses were conducted for zirconium, lanthanum, barium and strontium but none were detected.

When SURF was hydrothermally treated with samples of basalt (BCR-1 and DDH-3) only approximately 1% of the total Cs in SURF could be detected in solution and no Rb, Mo or U were observed in the 200°C samples. At 300°C, the solutions did not contain any Cs, Sr, Rb, Mo or U, at least to the detection limits of the analytical instrumentation. These initial results are encouraging, for the potential retention of the near-term hazardous radionuclides.

HYDROTHERMAL INTERACTIONS OF Cs AND Sr PHASES IN SURF WITH BASALT AND BASALT MINERALS

Spent unreprocessed fuel (SURF) is the leading candidate nuclear waste form. Once SURF is emplaced into basalt, hydrothermal interactions between the basalt minerals and various Cs and Sr phases in SURF may be anticipated under certain scenarios during the first few hundred years. These conditions could occur as the result of overburden pressure and temperature generated by the radioactive decay of the waste. The results from these interaction studies will be relevant to the development of an engineered over-pack in any geological repository.

The exact Cs and Sr phases in SURF are not known with certainty, but Cs_2MoO_4, $Cs_2U_2O_7$ and $SrZrO_3$ are frequently cited as possibilities. For this study, cesium molybdate was obtained from a chemical company while β-$Cs_2U_2O_7$ and $SrZrO_3$ were synthesized in this laboratory.

Cs-IN-SURF/BASALT INTERACTIONS

Two basalts, BCR-1 and DDH-3, and three basalt mineral constituents, labradorite, a pyroxene and a synthetic glass possessing the composition of the mineraloid phase described by Ames (1976) were mixed with either Cs_2MoO_4, CsOH or β-$Cs_2U_2O_7$. Water was added 50% by weight to these mixtures and the contents were sealed into gold capsules which were hydrothermally treated at 200°C and 300 bars for 60 days. Cesium hydroxide is not a SURF component (although Cs_2O is mentioned as an active component of zircaloy corrosion) but it is more reactive, allowing a more complete reaction over the time frame of the experiment. The three sets of runs were completed. The solid and solution phases from the gold capsules were separated as described in the First Interim Report (RHO-BWI-C-12). The solutions were analyzed for unreacted Cs while the solid phases were characterized by x-ray diffraction. Results for two sets of runs involving cesium molybdate and cesium hydroxide are given herein while the analyses of the set of runs with beta cesium diuranate are presently being completed.

X-ray diffraction analysis of various cesium phase-basalt interaction products indicated that pollucite, $(CsNa)AlSi_2O_6$, was the major reaction product but $CaMoO_4$ was also observed along with unreacted or hydrothermally altered basalt minerals.

Measuring the Cs concentration of the product solutions permitted the determination of the partitioning of Cs between the liquid and solids (Table V). Results varied with the particular Cs source and basalt mineral but the fixation of up to 99.9% of the Cs in the solids was observed in certain cases. The two basalts and labradorite reacted readily with Cs_2MoO_4 while the pyroxene and the synthetic basalt glass were slow in reacting with Cs_2MoO_4.

TABLE V

CESIUM FIXATION AS A RESULT OF HYDROTHERMAL INTERACTIONS BETWEEN TWO Cs SOURCES AND TWO BASALTS PLUS BASALT MINERALS AT 200°C AND 300 BARS FOR TWO MONTHS

Sample name and particle size	Weight of sample, mg	Weight of Cs added*, mg	% of added Cs fixed as a function of two different Cs sources	
			Cs_2MoO_4	CsOH
Basalts				
BCR-1, <75 μm	100	15.1	97.7	99.9
DDH-3, <75 μm	100	14.8	78.2	99.9
Basalt minerals				
Labradorite, <75 μm	100	14.8	99.7	98.5
Pyroxene, <75 μm	100	15.4	23.6	----
Glass (mineraloid), <75 μm	100	16.2	25.1	99.4

*The amount of Cs added was adjusted so as to utilize 25% of Si from basalts or basalt minerals in probable pollucite formation.

The above experiments clearly point out that if Cs were to be extracted from SURF by hydrothermal solutions at 200°C and 300 bars, the Cs would interact with the surrounding basalt to form pollucite. The formation of pollucite is a desirable outcome of waste-rock interactions because the Cs is tied up in pollucite formation.

STRONTIUM PHASE-BASALT INTERACTIONS

$SrZrO_3$, a potential component of SURF, was reacted with two reference basalts and five basalt mineral constituents plus a synthetic glass formulated to the composition of the mineraloid reported in Ames (1976). These mixtures were hydrothermally treated at 200°C and 300°C and 300 bars for 60 and 30 days respectively. Both sets of runs were completed and detailed bulk XRD and solution analyses were initiated.

X-ray diffraction studies of the two reference basalts from the 300°C hydorthermal treatment indicate that no detectable interactions have occurred. Solution analyses for Sr in the liquid phase have indicated that greater than 98% of the available strontium has been retained as $SrZrO_3$ or incorporated into basalt mineral phases or alteration products that are present below the limits of XRD detectability.

The basalt minerals labradorite, an ilmenite-magnetite mixture, a pyroxene and the synthetic basalt glass also showed no detectable interactions by bulk XRD. The solution analyses of these five experiments indicated that greater than 98% of the available Sr has been retained (Table VI).

The zeolite, heulandite, was shown to have undergone significant alteration and/or interaction with $SrZrO_3$. Heulandite was never found to coexist in stable equilibrium with any other phase and will transform under conditions of sufficient burial depths to other phases (Mumpton, 1977). After 28 days of hydrothermal treatment, the heulandite is x-ray amorphous when present alone or in the presence of $SrZrO_3$. In this reaction, the strontium zirconate also appears to be decomposing with only minor remnant diffraction peaks detectable in the bulk XRD patterns. Solution analyses of this run product suggest that greater than 98% of the available strontium is incorporated into the x-ray amorphous material or retained as the remnant $SrZrO_3$.

REPOSITORY SIMULATIONS -- CLOSED SYSTEM

The objectives of these experiments were to simulate the chemical environment in a repository containing breached canisters. Each run was composed of pieces of waste (SURF or glass 76-68) loosely wrapped in gold foil, surrounded by stainless steel (and zircaloy in the case of SURF) turnings which in turn are surrounded by a large excess of basalt fragments. A simulated

TABLE VI

STRONTIUM IN SOLUTION WITH TWO BASALTS PLUS BASALT MINERALS AFTER HYDROTHERMAL TREATMENT AT 300°C, 300 BARS FOR 30 DAYS

Sample	Amount of Sr added, mg	Sr remaining in solution, mg	Percentage of total available Sr in solution
$SrZrO_3$ + BCR-1	18.5	0.178	1.0
$SrZrO_3$ + DDH-3	20.1	0.150	0.7
$SrZrO_3$ + Labradorite	19.3	0.097	0.5
$SrZrO_3$ + pyroxene	20.5	0.079	0.4
$SrZrO_3$ + ilmenite	20.5	0.158	0.8
$SrZrO_3$ + syn. glass	19.3	0.137	0.7
$SrZrO_3$ + heulandite	19.7	0.044	0.2

Hanford groundwater formulation was added to these components (Ames, 1976) and the entire mixture sealed in gold capsules.

A complete set of repository simulation runs was not obtained due to capsule failures. For the successful simulation runs, optical description of alterations as well as chemical analyses of solutions are presented.

OPTICAL DESCRIPTION OF PRODUCTS

Tentative optical microscopic examinations are reported for the 30-day runs of basalt/SURF/Hanford groundwater at both 200°C and 300°C and one run at 300°C of basalt/glass/Hanford groundwater.

In both of the basalt/SURF/Hanford groundwater experiments, the basalt component, BCR-1, has shown extensive alteration of the pyroxene and glassy groundmass phases, exposing the large laths of feldspars. The 300°C capsule was pressurized with what appears to be an organic-like gaseous phase that was detected as a strong petroleum distillate odor. The experiment at the lower temperature, 200°C did not possess the gas overpressure nor the organic-like odor. In both cases, the gold foil bag containing the SURF was covered with a white crust coating the outer surface that was exposed to the basalt. No identification of the white crusty phase has yet been made. The SURF used in these experiments was prepared under reducing conditions to approximate the chemistry of spent unreprocssed fuel. It is a black powder that has an x-ray diffraction pattern with only the fluorite pattern of uraninite detectable (RHO-BWI-C-12). The observation of the reaction products in the 200°C experiment revealed that the SURF component of the system was black, apparently similar to the original starting material. However, the SURF component of the 300°C experiment possesses a chocolate brown coloration similar in appearance to UO_2 which is commercially available. This may reflect a change to a less oxidizing environment at the higher temperature.

The single interaction experiment with basalt/glass/Hanford groundwater at 300°C also yielded a pressurized capsule that possessed a sweet aromatic odor. There was an extensive development of a white to gray-green crust over the interior surface of the capsule. In addition, regions of white crystalline crusts, presumably alteration products of the basalt, were identified.

Detailed solid phase SEM and Gandolfi XRD analyses of the above runs are being continued. Additional repository simulation runs are presently being hydrothermally treated.

SOLUTION ANALYSIS

The repository simulation runs involving SURF/BCR-1/Hanford groundwater that

have been hydrothermally treated at 200°C and 300°C have been analyzed. Solution analyses of these runs indicate that the percentage of Cs, Rb, Sr and Ba remaining in solution decreased (Table VII) at 300°C compared to 200°C which indicates a greater interaction of these ions with the BCR-1 basalt minerals. The percentages of Cs and Rb remaining in both of these runs involving SURF is very small compared to SURF plus deionized water alone, wherein almost 100% of the Cs and Rb remained in solution at both of these temperatures. The above is further indication that Cs and Rb readily interacted with basalt resulting in their fixation at both 200°C and 300°C under these repository simulation experiments. This is a favorable result and will be further substantiated by XRD identification of new phase formation if possible.

The repository simulation run involving glass was completed at 300°C. Chemical analysis indicates that only 42% of the boron and 0.4% of the silicon were remaining in solution (Table VIII). The percentage of Cs remaining in solution was somewhat high at about 8% compared to the cesium released in the alteration of just glass alone. However, given enough time, the Cs might interact with the surrounding basalt as indicated by the repository simulation runs involving SURF. A complete set of repository simulation runs is now being hydrothermally treated.

WEEKSITE STABILITY IN A BASALT REPOSITORY ENVIRONMENT

The study of the stability of uranyl silicate phases was conducted as part of the investigation into the formation and stability of alteration products of candidate waste forms. The hydrothermal alteration of the glass waste form, PNL-76-68, has produced a crystalline phase that has been characterized as a hydrous uranyl silicate which possessed a structure similar to weeksite. Natural weeksite is a potassium silicate with the composition $(K,Na)_2(UO_2)_2Si_6O_{15}\cdot 4H_2O$; however, in this glass formulation there is no potassium present. Qualitative analyses for the weeksites formed from the glass alteration indicate a composition that most nearly approximates $(Na,Cs)_2(UO_2)Si_6O_{15}\cdot 4H_2O$.

The implication of the presence of this phase suggests that the condition of pH and Eh within these "closed" system experiments are such that the uranium is in equilibrium with the fluids as a hexavalent species. Uranium as well as the other transuranic elements of concern all possess higher solubilities in the more highly oxidized state. It is, for example, this solubility difference that allows the Purex process to separate uranium and plutonium by very subtle pH manipulations (Bebbington, 1976).

Actual repository conditions will represent an "open" system where leached ionic species can be transported away from the immediate canister vicinity and where the oxygen fugacity will be buffered by the ferrous/ferric ratio

TABLE VII

PERCENT OF TOTAL IN SURF OF VARIOUS EXTRACTED ELEMENTS REMAINING IN SOLUTION AFTER HYDROTHERMAL TREATMENT AT 200°C AND 300°C AND 300 BARS FOR 30 DAYS.

	% of element in solution at different temperatures	
Element	200°C	300°C
Cs	4.9	0.8
Rb	2.2	ND
Sr	1.2	ND
Ba	1.3	0.8
Mo	0.7	3.1
Nd	ND*	ND
La	ND	ND
Zr	ND	ND

*ND = Not Detected

TABLE VIII

PERCENT OF TOTAL IN 76-68 GLASS OF VARIOUS EXTRACTED ELEMENTS REMAINING IN SOLUTION AFTER HYDROTHERMAL TREATMENT (REPOSITORY SIMULATION) AT 300°C AND 300 BARS FOR 30 DAYS.

Element	% of element in solution
B	42
Si	0.4
Mo	72
Cs	8.2
Rb	4.0
Sr	0.42
Ba	0.27
Ca	0.92
Ni	.34
Cr	ND*
Fe	0.03
La	0.1
Nd	0.1
Ti	ND
Zr	ND

*ND=not detected

in the basalt minerals. These conditions are very different from the "closed" hydrothermal experiments in which weeksite was formed. The fundamental differences in these two experiments may mean that weeksite will not exist in the buffered system.

An experiment has been designed and run in which actual weeksite crystals that had been formed in a glass alteration experiment were hydrothermally treated at 300°C and 300 bars for 28 days. Deionized water in a ratio of 30:1 to total solids was used along with a basalt in excess to weeksite by 60:1.

SOLID PHASE CHARACTERIZATION

The excess of basalt had efficiently buffered the oxygen fugacity to reduce the hexavalent uranyl silicate species to the less soluble tetravalent species. The solids remaining after the hydrothermal treatment were black in color but topotactically formed after the original weeksite crystals. The reduced phase has been identified by Gandolfi x-ray diffraction methods as being largely $UO_{2.25}$ with some minor unreduced weeksite still present. Conformation of the qualitative chemistry has been made with energy dispersive x-ray fluorescence. A comparison of Figs. 7 and 8 reveals the extent of alteration. Figure 7 is a typical cluster of crystals similar to those used in this experiment. Figure 8 is a small fragment of the total sample that was exposed to the basalt-buffered hydrothermal fluid. These lineations that are suggested in the photograph are remnants of the original subparallel weeksite crystals.

SOLUTION PHASE ANALYSES

Because of the size and morphology of the weeksite crystals used in this experiment, microprobe analysis for quantitative chemical composition was not possible. Therefore, the concentration of ionic species in solution will be presented as percentages of the total initial solid component and not referred to percentages leached from the solid into solution.

Analyses for Ti, Fe, Al and Ca did not detect the presence of these elemental species in solution. Cesium was detected and amounted to approximately 1% of the total weight of the original weeksite crystals while silicon represented approximately one-half of the total available silica in both the basalt and the weeksite crystals.

WEEKSITE STABILITY IN A BASALT ENVIRONMENT

The results of the present "closed" system study would indicate that in the presence of a large excess of basalt weeksite would not be stable with respect to the established oxygen fugacity of the basalt buffer. Generally, it has

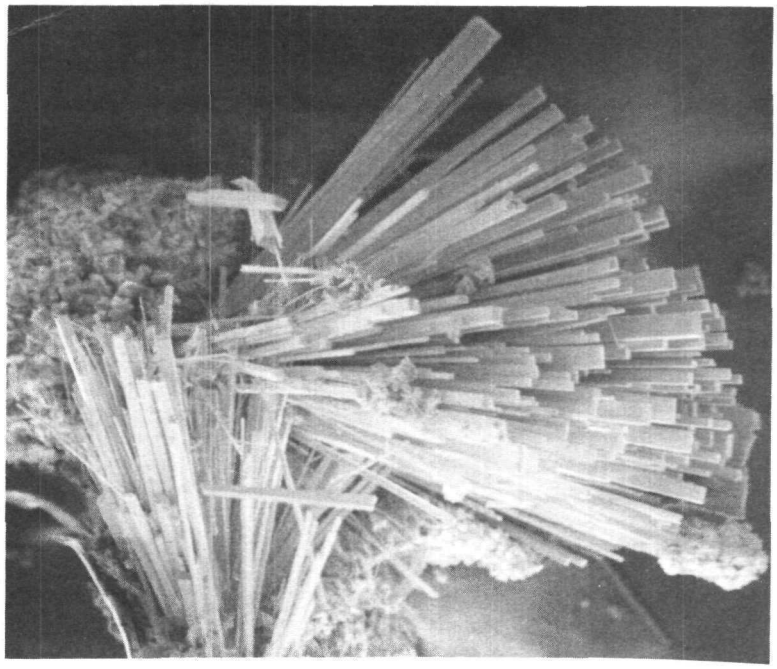

Figure 7. Typical weeksite crystals used in the basalt buffered experiment. (Magnification 150X.)

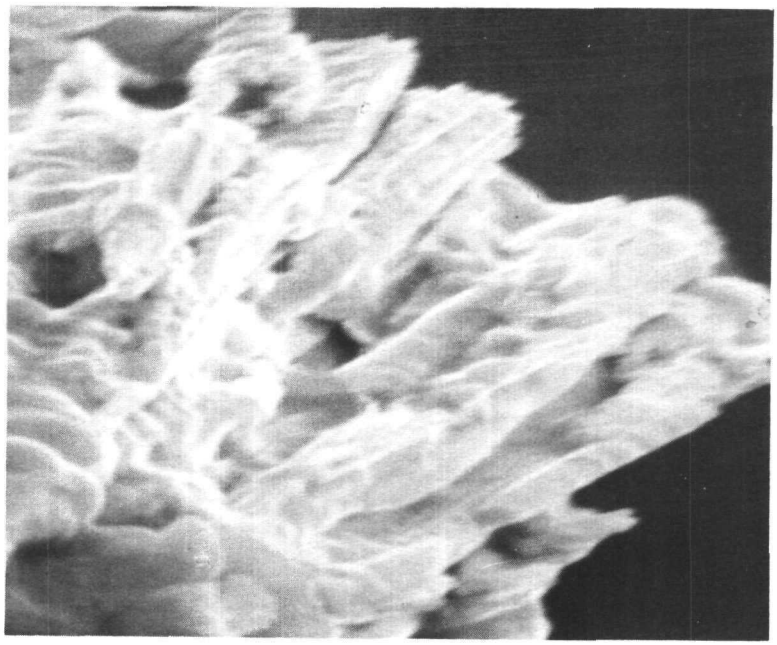

Figure 8. Remnant product after hydrothermal treatment of weeksite with excess basalt. (Magnification 1000X.)

been assumed that the conditions of Eh and pH in the vicinity of a repository would necessarily be "reducing" in the open system. Calculated Eh-pH diagrams similar to Langmuir (1978) or active-pH diagrams similar to Rai (1978) could readily be constructed if the pertinent data on the Eh, pH and concentrations of dissolved species of the Umtanum waters were known at the temperatures approaching the geothermal gradient; i.e. 40° to 70°C. All of these data are currently unavailable with the exception of a few references to pH measurements, perhaps in the range of 9.5 to 10.0 reported by Ames (1976).

RECONNAISSANCE EXPERIMENTS WITH LOW-PRESSURE FLOW-THROUGH APPARATUS

An equilibration study was completed. Deionized water was circulated past an equal mass of basalt at 40°C until solution concentrations reached a steady state in three to four weeks (Fig. 9). The concentrations at steady state are:

	Si	Na	Ca
ppm	14	2.4	4
$\frac{\text{millimoles}}{1000\ \text{g}}$	0.5	0.1	0.1
proportions in solution	5 :	1 :	1

In contrast, the proportions of these elements in the whole rock can be calculated for comparison from the analyses reported by Ames (1976):

	Si	Na	Ca
proportions in solid	5 :	1 :	2

All three concentrations and the pH, at approximately 7.5, are low compared to comparable groundwaters from Columbia River basalts. No attempt was made in this first practice run to provide the basalt with water which was already equilibrated with species other than CO_2 in air.

The next experiment will be to use as starting water deionized water saturated with respect to $CaCO_3$.

HIGH-PRESSURE FLOW-THROUGH APPARATUS

The analyses of the scoping studies and the more detailed experiments outlined in this report indicate that the control over the buffering capacity of the experimental system as it relates to a realistic "open" repository

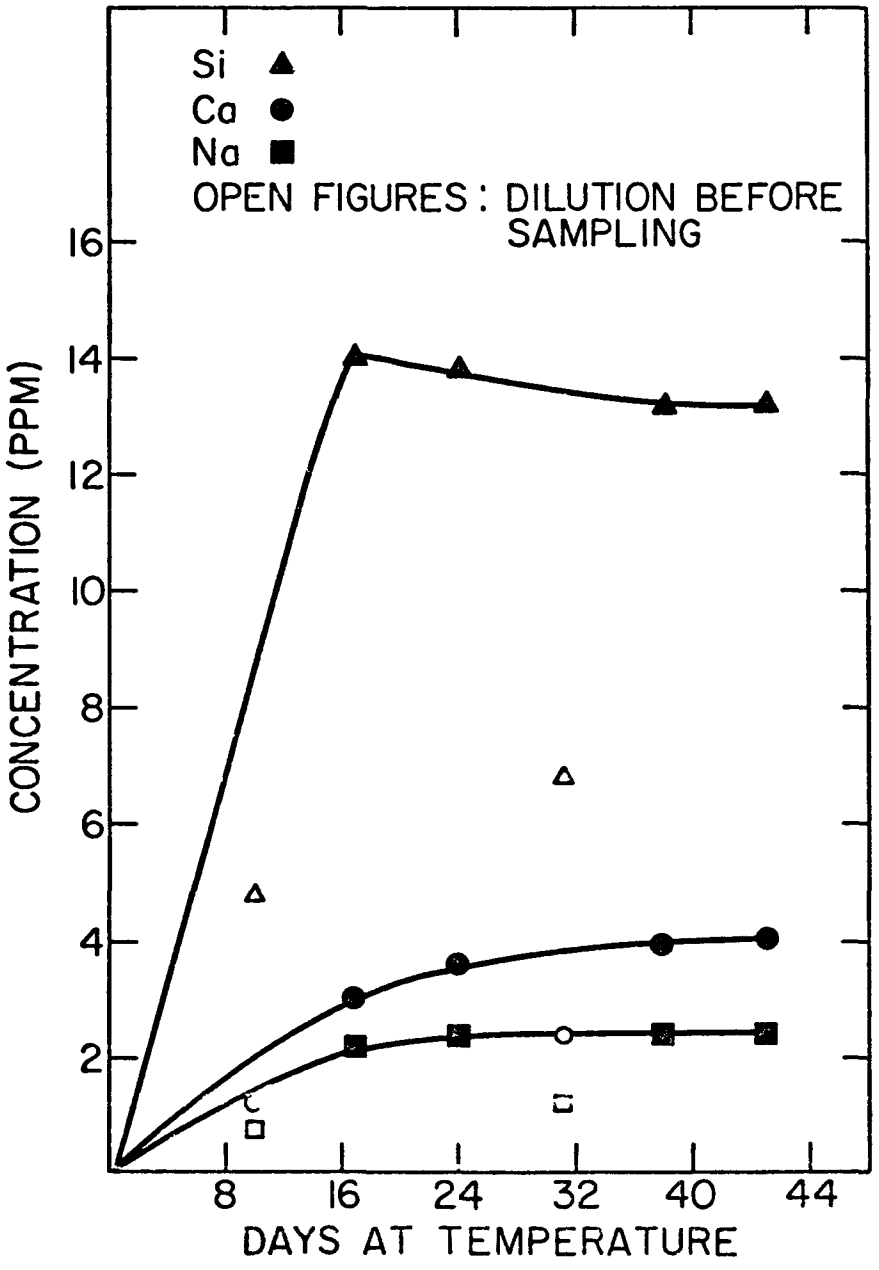

Figure 9. Concentration of dissolved elements in solution vs. time.

situation is an important factor for the prevention of mobilization of uranium and the transuranics. The flow-through high-pressure apparatus will serve as the ideal experimental system. This apparatus by its design allows for a high degree of flexibility for the design of experiments that can relate to specific repository problems.

The objective during the past year was to establish the high-pressure flow-through facility and to perform reconnaissance experiments with Hanford basalts as time permits. Most of the year was spent in assembling and testing, but at the time this report was prepared, the system was pressurized and operating at 40°C and 300 bars with a specimen of Umtanum Ridge basalt.

CIRCULATING SYSTEM

The high-pressure flow-through apparatus is shown in Figs. 10 and 11. Water is introduced into the circulating system from the reservoir through the pneumatic pump. This pump not only introduces the fluid but attains and maintains the pressure desired. The pump operates at a constant pressure ratio so that the pressure set on the air drive side determines the working pressure on the circulating system side. The system pressure is limited to 4800 psi by a spring-loaded pressure relief valve. Fluid is circulated in the system by a double-piston circulating pump. At each end of the pump, the branches from the two pistons are connected into the main circuit by a tee (not shown) so that the system volume, and therefore pressure, remains constant regardless of the position of the pistons. The rate of pumping is controlled by a motor speed control with a ten-turn potentiometer so that slow (0.18 - 4.5 ml/min) pumping rates may be reproducibly controlled.

Fluid is pumped from the inlet to the pressure vessel containing the previously inserted solid sample. Baffles in the vessel multiply the path length of the fluid past the rock by about 2.5X. The furnace for the pressure vessel has windings at top and bottom; each heater is adjusted by a variable transformer to deliver about 20% more wattage than needed, and the temperature is then set by a controller. Should one of the controllers burn out, the setting in the variable transformer will ensure that the temperature in the reaction vessel will not rise catastrophically. The fluid passing from the reaction vessel to the heat exchanger is maintained about 20°C hotter than that in the reaction vessel, in order to prevent precipitation in the capillary lines. Precipitation may occur in the heat exchanger where it will not impede flow and from whence it can be collected at the end of the run. A tee leads to the sampling system.

The sampling procedure is as follows:

- evacuate sample volume;

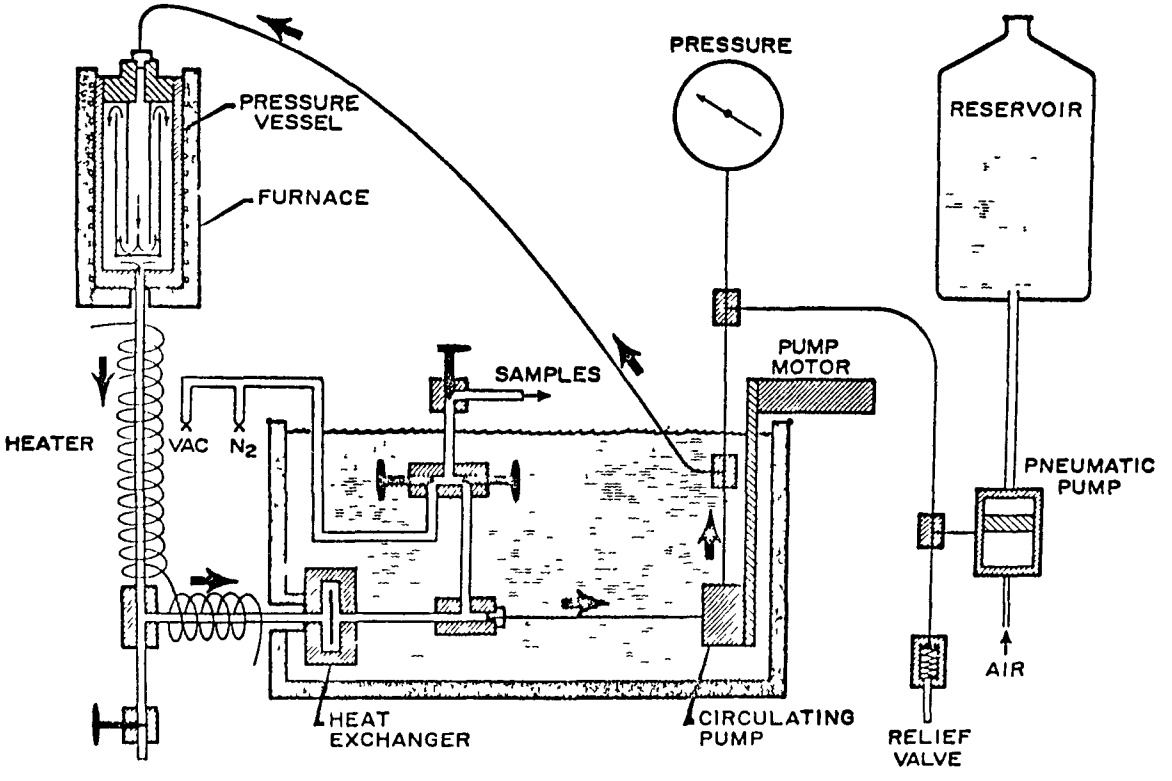

Figure 10. Schematic drawing of H. L. Barnes circulating hydrothermal system. (After Barnes, 1976.)

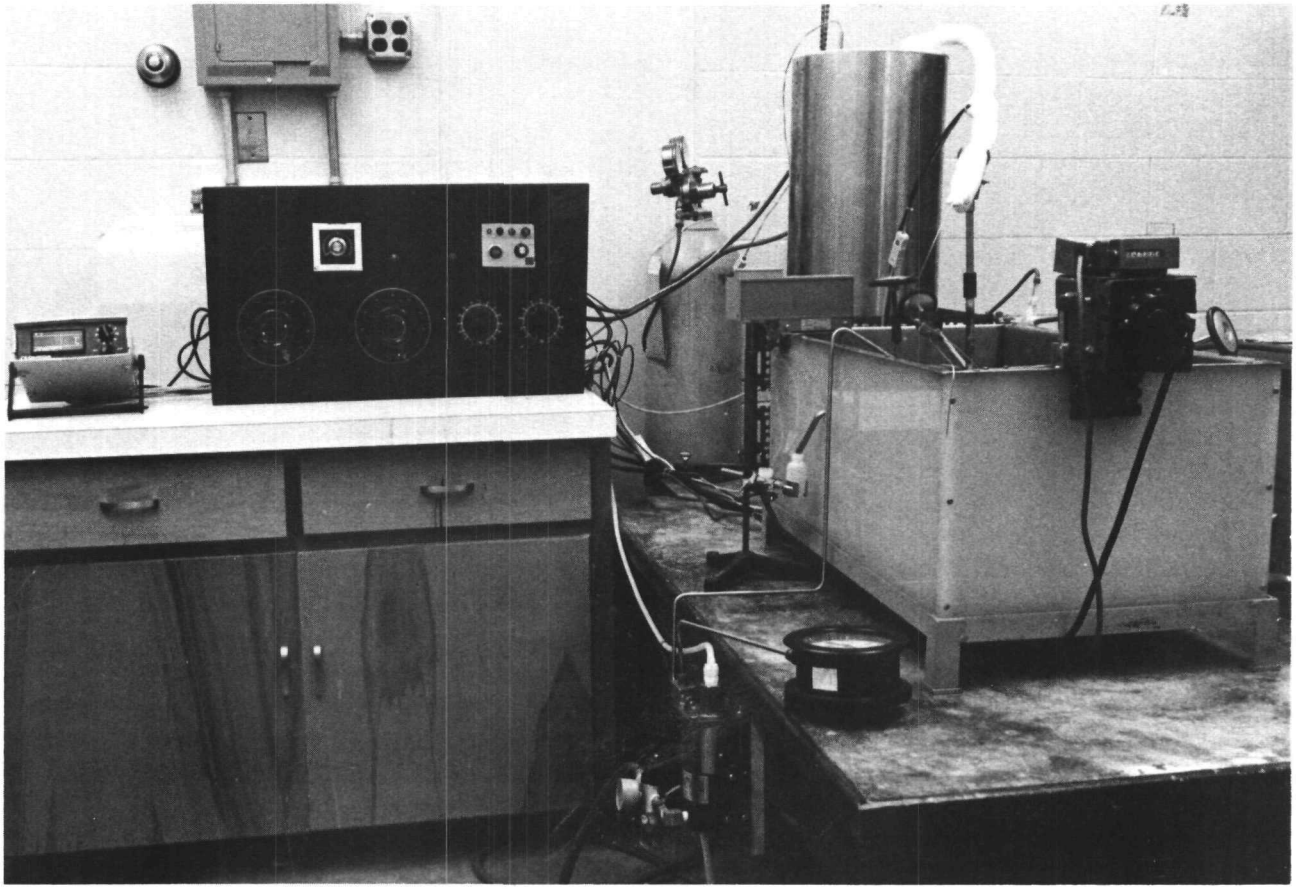

Figure 11. Photograph of the high-pressire hydrothermal flow-through apparatus.

- isolate sample volume from vacuum pump and open it to the system;
- isolate sample volume from the system and open it to a pre-weighed sample container;
- sweep the sample out of the sample volume with a low pressure (<20psig).

The volume of the sample is approximately 5 cc.

Samples of fluid will be taken at gradually increasing intervals during the run; at the end after disassembling the system, the solids in the reaction vessel and any solids in the heat exchanger will be studied.

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