SIMULATED HIGH-LEVEL WASTE-BASALT INTERACTION EXPERIMENTS
FIRST INTERIM PROGRESS REPORT

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SUMMARY

Reconnaissance experiments have shown that waste/basalt interactions are of real importance in understanding all aspects of total containment of radionuclides in a basalt repository. It has been shown that the reprocessed waste forms, calcine and glass, are relatively more reactive than the more crystalline waste forms, spent unprocessed fuel (SURF) and supercalcine. These experiments have established the direction of future research. The remainder of the program will be concerned with longer-duration and more-detailed experiments whose emphasis will be on understanding the mechanisms of reaction.

Long-duration and in-depth experiments are being initiated to establish kinetic relationships and get a better feel as to whether or not we are approaching equilibrium in our shorter-duration reconnaissance experiments. In some cases, especially at higher temperatures, it appears that we are approaching a steady-state wherein products are no longer changing. This, however, might be a metastable state. Experiments with cesium compounds thought to be present in SURF (Cs_2MoO_4), a simple cesium source (CsOH), labradorite, and ground water have shown that pollucite forms and, as a result, fixes 86 to 99 percent of the cesium (depending upon the amount of basalt present).

1.0 INTRODUCTION

In early February 1977, The Pennsylvania State University initiated a research program on the compatibility, especially at elevated pressures and temperatures, of nuclear waste and basalt. The objective of this effort was to provide insight and data needed to examine the feasibility of establishing a commercial nuclear waste repository in basalt formations. The first year of research resulted in the examination of waste/basalt interactions during the thermal period when solutions at elevated pressures and temperature conditions could potentially constitute a threat to the repository.

At present, the current research program is aimed at determining the detailed nature of waste/basalt interactions and to begin to understand their relevance to radionuclide release rates. Reconnaissance

experiments have been completed and utilized to define the needed long-term and detailed experiments now in progress.

The following material details the progress made to March 31, 1978 on reconnaissance experiments, waste/basalt interactions, and preliminary definition of waste criteria.

This report was edited by Drs. M. W. Grutzeck and R. A. Deju, Rockwell Hanford Operations.

2.0 PRELIMINARY EXPERIMENTS

2.1 RECONNAISSANCE EXPERIMENTS

For the purposes of this research program, we have defined "reconnaissance experiments" as those that will, within a relatively short time, indicate under what conditions either hydrothermal alteration of wastes or waste/basalt interactions would be likely to be significant. The particular set of experiments have the following characteristics:

- SPECIMENS: -200-mesh powder of waste, of basalt, or of an intimately mixed waste/basalt mixture; 50 percent by weight of "Hanford ground water" to solids added as the hydrothermal fluid;
- TEMPERATURES [nominal (actual)]: 100 (94); 200 (189); 300 (280); 400 (368)°C;
- PRESSURE: Approximately 300 bars;
- DURATION: 28-30 days;
- SIMULATED WASTES: SURF (early simulation); Battelle Pacific Northwest Laboratory (BNW) borosilicate glass #76-68; calcine PW-7a; and, supercalcine SPC-2;
- BASALTS: Hanford DDH-3 and U. S. Geological Survey (USGS) reference Columbia River Basalt BCR-1.

Characterization of the run products included examination under the binocular microscope, a routine X-ray diffractogram (XRD) and scanning electron microscope (SEM)/energy dispersive X-ray (EDX) examination of any specimens where interaction products were observed during optical examination. Clearly, characterization of these reconnaissance runs was not meant to be exhaustive, but only to indicate which specimens and conditions should be included in the more elaborate "long-duration" and "detailed" experiments to follow.

These reconnaissance runs have been completed, as is required by the program milestones. Run tables for experiments described in this report are given as Appendix A. Insights gained from the reconnaissance runs are as follows.

- As expected, the presence of excess water is important. In identical experiments with glass at 368°C, 1 with 50 percent by weight of water, 1 with only 2 percent, the former showed extensive bulk alteration by XRD, while the latter showed little or none.
- There is definite surface alteration of glass after the 189°C hydrothermal treatment and the bulk XRD also indicates a small amount of alteration to crystalline phases.
- Although bulk XRD gives no evidence of alteration of the glass after 1 month at 94°C, SEM examination (Figure 1) suggests that some may have occurred. We will look into this further.
- By bulk XRD, both supercalcline and SURF show no evidence of hydrothermal interaction. The SEM characterization of SURF does show crystallization of some of the more soluble fission product phases.
- The alteration of 76-68 glass at 280°C is shown to be quite extensive by XRD. The X-ray characterization will be discussed in the following section.
- There was no bulk hydrothermal alteration evident for either of the basalts in any reconnaissance experiments. Detailed XRD characterization of the original and hydrothermally treated basalts is described in Section 2.3.2.

The balance of this report and of the remainder of the program will be concerned with longer-duration and more-detailed experiments on glass, on certain of the fission product phases in SURF, and on the stability and behavior interaction products of these wastes and basalt. Most experiments will be performed at 200-300°C because these are both relevant repository temperatures and sufficiently high to study key waste/basalt interactions with reasonable experimental durations.

2.2 LONG-DURATION EXPERIMENTS

Simply defined, these are experiments lasting longer than 1 month. Considering that moderate (100-300°C) temperatures will prevail in the repository for at least decades, it is clear that some experimentation should be performed for quite long durations. In the near future, and in consultation with Rockwell Hanford Operations' personnel, a small matrix

FIGURE 1

SCANNING ELECTRON MICROSCOPE PHOTOMICROGRAPH OF 76-68 GLASS
AFTER HYDROTHERMAL TREATMENT AT 94°C/300 BARS FOR 28 DAYS
(150X)

Angular fragments of as-ground glass are evident, but the fine-grained material at the lower right may be an alteration product.

of specimens will be defined which can be treated hydrothermally for months to perhaps years in the 100-300°C temperature range. Meanwhile, we have continued runs with our existing matrix of 4 wastes and 2 basalts. Products from a 2-month (56-day) 280°C/300-bar run of this matrix are currently undergoing characterization by XRD (bulk and Gandolfi) and SEM/EDX. Again, this specimen consisted of -200-mesh 76-68 glass powder and 50 percent of its weight of Hanford ground water.

By bulk XRD, the extent of alteration of the glass to form the crystalline components of the product appeared to be about the same after 56 as after 28 days of treatment. Figure 2 gives portions of the XRDs of fresh 76-68 glass and the products of hydrothermal treatment for 28 and 56 days. It can be seen that the original 76-68 glass specimen was actually partially devitrified. Reflections of RuO_2 , one or more spinel-ferrite phases [e.g., $(\text{Ni,Fe})(\text{Fe,Cr})_2\text{O}_4$], a fluorite structure phase rich in CeO_2 and Pd metal have been identified. The fact that there are numerous weak reflections superimposed on the broad diffuse scattering maximum indicates that there are other, as yet unidentified, crystalline phases in this glass. After hydrothermal treatment, two prominent crystalline alteration products are observed. The more intense reflections are clearly typical of pyroxene (single chain silicate) X-ray patterns. The reflections cannot be attributed to any specific pyroxene mineral and they may actually be due to a composite of several moderately crystalline pyroxene phases. A number of pyroxene minerals have compositions that are consistent with the composition of the glass, for example:

- Acmite $\text{NaFeSi}_2\text{O}_6$;
- Hedenbergite $\text{CaFeSi}_2\text{O}_6$;
- Augite $(\text{Ca,Na})(\text{Mg,Fe},^{2+}\text{Fe},^{3+}\text{Ti,Al})\text{Si}_2\text{O}_6$.

The rather sharp and moderately intense reflections are those of wecksite, $(\text{Na,Cs})_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$. Reflections of RuO_2 and Pd remained after the treatments, but it was not possible to tell whether the spinels were present because their strong reflections are coincident with some of the pyroxene reflections. There are other weak, unidentified, reflections indicating that one or more additional crystalline alteration products were formed. The Gandolfi results on individual grains should help to identify these additional phases.

FIGURE 2

PORTIONS OF THE X-RAY DIFFRACTOGRAMS OF 76-68 GLASS BEFORE AND AFTER HYDROTHERMAL TREATMENT

It is interesting to compare the results of these 280°C treatments of powdered glass with the 300°C treatments of the glass spheroids described in Section 2.3.1 below. In the former, the water was Hanford ground water; while in the latter, it was deionized water. The amount of water was 50 percent of the solid weight in the former and a 10-fold excess in the latter. Yet, the 2 major crystalline reaction products were wecksite and a pyroxene. This, combined with the fact that the diffractograms in Figure 2 do not change much from 28 to 56 days, gives us encouragement that we may already be approaching an equilibrium reaction product assemblage for this particular set of temperature-pressure conditions.

Some SEM/EDX characterization has been performed on the product of the 56-day treatment. Figure 3 (A) is a low magnification photomicrograph that shows the heterogeneity of the reaction product. At the top of the figure are clusters of needle-like wecksite crystals. The light and dark components of the mosaic structure have similar EDX chemistry (Na, Ca, Fe, Si, and, possibly, Zr or P) and they may possibly be 2 pyroxene phases. Figure 3 (B) shows, under greater magnification, that the light component of the mosaic actually consists of a fibrous mat of crystals.

2.3 DETAILED STUDIES OF EQUILIBRIUM AND KINETICS

These are characterized by either larger specimens and solution volumes or by simpler combinations of waste and basalt components. The objectives of these experiments are to obtain more information on reactions identified in the reconnaissance experiments, to identify any solid phases formed, and to determine any species mobilized into the hydrothermal solution.

2.3.1 Hydrothermal Treatment of Glass -- Closed Systems

Henceforth, we will differentiate between hydrothermal treatment in the sealed gold capsules (closed system) and in the flow-through vessel (open system) because of the potential of the latter to remove dissolved species well away from the interaction interface.

Figure 4 presents a conceptualized scheme for the observed alteration of BNW 76-68 glass samples that have been ground into approximately spherical form and treated hydrothermally with deionized water at 300°C, 300 bars for 7 days (Run 59) and for 14 days (Run 68). The interiors of both spheres

(A) PRODUCT OF 56 DAYS OF HYDROTHERMAL TREATMENT OF 76-68 GLASS AT 280°C

(B) DETAIL OF THE LIGHT GREY COMPONENT OF THE MOSAIC STRUCTURE IN THE LOWER HALF OF (A) (3,000 X)

FIGURE 3

FIGURE 4

SCHEMATIC REPRESENTATION OF THE ALTERATION FEATURES FOR 76-68 GLASS SPHERES IN HYDROTHERMAL RUNS 59 AND 68

have remained in what appears to be an unaltered condition. Although the depth of penetration of the fluid and the associated alteration of the glass vary between the two observed samples, the following statements are appropriate to both hydrothermal runs. A milky-white alteration zone appears adjacent to the inner unaltered glass.

The outermost multilayered alteration zone is a friable crust which, in some instances, exfoliates. Careful examination of this zone has shown that it is compositionally banded. In addition, growing on the exterior surface of both runs were millimeter-long lemon-yellow crystals which have been identified as the mineral-like phase, weeksite. Identified also on the sphere and on the inner surface of the gold ampul was another mineral-like phase, acmite.

We have been regularly utilizing the ETEX AUTO Electron Microprobe in the Mineral Constitution Laboratory for quantitative elemental characterization of the solid reaction products. Our objective is to combine analyses of the solids and solutions to obtain a mass balance interpretation of the hydrothermal alteration of 76-68 glass. With this in mind, we present a detailed description of the results obtained to date for two hydrothermal treatments of 76-68 glass.

Run 59 (300°C/300 Bars/7 Days)

The product from Run 59 has been sectioned and an electron backscatter image of the 3-millimeter (mm) diameter spheroid has been prepared (Figure 5). This specimen has been analyzed for concentrations of 14 elements along its major and minor axes in an effort to detect compositional differences resulting from the hydrothermal treatments. Table I presents these data. Unaltered Zone A represents the average of 4 analyses along the major elliptical axis and Unaltered Zone B represents the average of 3 analyses along the minor elliptical axis. Zones C and D are the averages from 3 analyses each in the altered zone.

Generally, the analysis of the 76-68 glass reported by BNW and that obtained on the Mineral Constitution Laboratory microprobe are in fair agreement. However, notable disagreement is found in the U oxide* and Na₂O analyses and more work is needed on these elements. It is also

*See footnote g in Table I.

FIGURE 5

ELECTRON BACKSCATTER IMAGE OF THE PRODUCT OF RUN 59
INDICATING THE LOCATION OF POINTS SAMPLED FOR MICROPROBE ANALYSIS (50X)

TABLE I

ELECTRON MICROPROBE ANALYSES OF 76-68 GLASS
BEFORE AND AFTER HYDROTHERMAL TREATMENT IN RUN 59

(Weight Percent)

OXIDE	ORIGINAL 76-68 SPECIMEN		TREATED 76-68 SPECIMEN			
	NOMINAL COMPOSITION ^a	MCL MICROPROBE ANALYSIS ^b	UNALTERED ZONES A ^c	ZONES B ^d	ALTERED ZONES C ^e	ZONES D ^f
CaO	2.02	1.98	1.92	1.88	2.04	2.04
Cs ₂ O	1.04	1.26	0.99	0.91	0.95	0.89
TiO ₂	3.01	3.17	2.87	2.89	2.88	2.96
CeO ₂	1.20	1.61	2.27	2.31	2.32	2.90
Nd ₂ O ₃	1.69	1.75	1.73	1.58	1.53	2.04
FeO	8.89	9.34	8.87	8.85	8.76	5.77
ZnO	5.03	4.83	5.43	5.48	5.29	5.22
SiO ₂	40.27	39.02	37.86	38.61	42.12	34.16
SrO	0.38	0.15	0.12	0.09	0.13	0.04
ZrO ₂	1.79	2.34	1.97	1.99	1.94	2.67
MoO ₃	2.31	2.39	2.27	2.42	0.24	0.82
UO ₂	4.46	7.19 ^g	5.49 ^g	5.24 ^g	5.77 ^g	4.25 ^g
K ₂ O	0.00	0.06	0.06	0.05	0.32	0.13
Na ₂ O	12.66	8.58	10.49	10.59	3.11	2.05
	<u>84.75%</u>	<u>83.67%</u>	<u>82.34%</u>	<u>82.89%</u>	<u>77.21%</u>	<u>66.12%</u>

^aModified from J. E. McElroy (Editor), Quarterly Progress Report, Battelle Pacific Northwest Laboratories, PNL-2264, Battelle Pacific Northwest Laboratories, Richland, Washington (November 1977).

^bAveraged from analyses of 5 randomly chosen points.

^cAveraged from analyses at points 1, 2, 3, 4, and 5 in Figure 5.

^dAveraged from analyses at points 6, 7, and 8 in Figure 5.

^eAveraged from analyses at points 9, 10, and 11 in Figure 5.

^fAveraged from analyses at points 12, 13, and 14 in Figure 5.

^gA suitable standard was not available for UO₂, so these values may be subject to a small systematic error.

possible that glass 76-68 has relatively large compositional inhomogeneities for certain elements. Another anomaly was the identification of a small amount of K_2O in the glass in the microprobe analysis, where none was included in the BNW composition. This element shows up repeatedly also in analyses of the altered zone, so we presume that it is actually present in the glass.

Zones C and D, taken from the obviously altered area of the glass, show several compositional variations from the original glass and the Unaltered Zone A. Both of these are located toward the interior of the specimen. One sees a marked depletion of Na and Mo in the altered zone. We have also analyzed the solution component of Run 59 for 10 elements. All but U were analyzed by atomic absorption spectrophotometry (AAS). In Table II, it is seen that Na, Mo, Cs, and Si are the chief elements extracted from the glass and, with the exception of Si, this observation is consistent with the depletion of these elements in the Altered Zone C.

TABLE II
CONCENTRATIONS OF SELECTED ELEMENTS (AS OXIDES)
IN THE SOLUTION COMPONENT OF RUN 59

OXIDE	CONCENTRATION (in mg)		PERCENT OF OXIDE EXTRACTED
	IN GLASS 76-68	IN THE SOLUTION OF RUN 59	
CaO	1.83	0.00	0.00
Cs ₂ O	0.94	0.02	2.13
ZnO	4.56	0.00	0.00
SiO ₂	36.49	1.45	3.97
SrO	0.35	0.00	0.00
MoO ₃	2.09	1.76	84.21
UO ₂	4.04	0.003	0.07
Na ₂ O	11.47	2.19	19.09
Rb ₂ O	0.12	0.00	0.00
NiO	0.18	0.01	5.56

Continued data analyses of the types just discussed should allow a reasonably complete mass balance description of the processes occurring during hydrothermal treatment of simulated waste glass.

Another mode of analysis on an electron microprobe gives striking visual representations of the type of chemical distribution data presented in Table I. The characteristic X-ray emission signal coming off of the surface of a specimen can be recorded as an "elemental map" and correlated to an electron image. In Figures 6 to 14, we have given the electron backscatter image and elemental maps for 2 representative areas of the hydrothermally treated glass in Run 59. Higher concentrations of an element give a greater density of dots. The following compositional trends, already discussed above, are readily visualized with these X-ray maps.

- U and Sr are enriched in the near-surface altered zones of specimen (see Figures 6, 10, and 11).
- Mo and Na are clearly depleted in the altered glass zones (Figures 13 and 14).
- Ca is generally homogeneously distributed, but also shows an enrichment in the near-surface alteration zones (Figure 12).
- Cs is homogeneously distributed (Figures 6, 7, and 9).

To complete the description of Run 59, we present photomicrographs of the 2 abundant crystalline products, weeksite (Figure 15) and acmite (Figure 16).

Run 68 (300°C/300 Bars/14 Days)

Quantitative elemental analyses on the solids by electron microprobe and on the solutions were also obtained for this run having twice the treatment time as 59. Some of the important observations were:

- The alteration zone is notably depleted in Cs, Nd, Sr, Zr, and Mo, compared to the original glass specimen; the Cs depletion in the altered area is about 82 percent and Mo is 100 percent;
- The following approximate percentages of elements originally in the glass were extracted into the solutions during the treatment:

Cs	9.3 percent;
Si	3.9 percent;
U	0.2 percent;
Mo	67.0 percent;
Na	61.0 percent;
Zn	0.2 percent;

- No Ca or Sr were detected in the solutions.

FIGURE 6

X-RAY IMAGES:

U	EBS
Sr	Cs

(160X)

FIGURE 7

X-RAY IMAGES:

U	EBS
Sr	Cs

(160X)

FIGURE 8

COMPOSITE EBS IMAGE OF FIGURES 6 AND 7 (160X)

FIGURE 9

Cs X-RAY MAP FOR FIGURE 8

FIGURE 10

U X-RAY MAP FOR FIGURE 8

FIGURE 11

Sr X-RAY MAP FOR FIGURE 8

FIGURE 12

Ca X-RAY MAP FOR FIGURE 8

FIGURE 13

Na X-RAY MAP FOR FIGURE 8

FIGURE 14

Mo X-RAY MAP FOR FIGURE 8

FIGURE 15

A CLUSTER OF WEEKSITE $[(\text{Na,Cs})_2(\text{UO}_2)_2\text{Si}_6\text{O}_{15} \cdot 4\text{H}_2\text{O}]$ CRYSTALS FORMED IN RUN 59 (150X)

FIGURE 16

CLUSTERS OF ACMITE $[\text{NaFeSi}_2\text{O}_6]$ CRYSTALS FORMED IN RUN 59 (700X)

X-ray maps of the altered and multilayered altered zones for 12 elements are shown in Figures 17 to 20. The dark arching areas in the electron back scatter images are either void spaces or cracks that have been filled with mounting plastic. From these maps, it is clear that U, Sr, Ca, and Fe have concentrated in the outer multilayered alteration zone, while Cs, Si, Ti, Zn, Nd, Ce, and Zr appear to be uniformly distributed throughout the altered glass zones. Sodium appears to be homogeneously distributed, except for a slight enrichment about one of the reniform concentrations of high atomic number atoms. Attempts to prepare an X-ray map for Mo confirmed that the quantitative microprobe analysis had indicated, namely, that all of the Mo, at least to the lower limits of detectability, has been extracted from the altered zones of the glass spheroid.

Further details of the outer multilayer alteration zone are revealed by the greater magnification X-ray maps in Figures 21 and 22. The enrichments of Ca, Fe, and Sr in these layers is vividly illustrated in Figure 21. The alkaline earths, Ca and Sr, appear to be in the same layer, while Fe is in another. Uranium in Figure 22 (A) appears enriched in 2 of the layers.

A third mode of data acquisition and display on a microprobe is to scan the beam across the region of interest and record the X-ray signal for elements of interest on a strip chart as a function of distance. Complex features such as the multilayered alteration zone are perhaps best studied by this operational mode. X-ray scans have been obtained for Si, U, Fe, Sr, and Ca in a traverse across the edge of the altered glass spheroid to a depth of 300 μm . The scans are collected in Figure 23. The dashed vertical lines mark the approximate positions of the multilayer zones. Arrows mark the positions of cracks at 89 and 133 μm in from the surface where the X-ray signal approaches zero. These cracks provide convenient distance markers for each scan. The overall structure of the concentration profiles for the 5 elements indicates that what we have called the multilayer alteration zone is about 34 μm thick at this area of the spheroid. A reniform growth was traversed at ~173 μm depth. It is sharply defined by the Ca, Sr, and U profiles, while Fe and Si show only a gradual concentration change in this vicinity. The scans for Ca and Sr confirm what we saw in the X-ray maps, namely that they concentrate in the same bands. The high concentration of Ca appears to coincide with the second

FIGURE 17

X-RAY MAPS:
(160X)

Sr	EBS
Cs	U

FIGURE 18

X-RAY MAPS:
(160X)

Na	EBS
Si	Fe

FIGURE 19

X-RAY MAPS:
(160X)

Zn	EBS
Ti	Ca

FIGURE 20

X-RAY MAPS:
(160X)

Zr	EBS
Ce	Nd

FIGURE 21

X-RAY MAPS OF NEAR-SURFACE ZONES
OF ALTERED GLASS FROM RUN 68

Sr	EBS
Fe	Ca

(A)

(B)

FIGURE 22

U X-RAY MAP (A) AND EBS IMAGE (B) OF FIGURE 21 (800X)

FIGURE 23
Si, U, Fe, Sr, AND Ca PROFILES
FOR THE OUTERMOST 300 μm OF THE
ALTERED GLASS SPHEROID IN RUN 68

most U-rich layer which, in turn, corresponds to a shoulder on the most Si-rich region at about 14 μm . This suggests the presence of a phase (crystalline or noncrystalline) rich in Ca, Sr, U, and Si.

We are continuing with interpretation of the data from all 3 operational modes of the electron microprobe and from the solution analysis and hope to have the overall picture of hydrothermal alteration of 76-68 glass at 300°C in the near future.

Finally, for completeness, we should note that crystalline weeksite and acmite phases were also identified among the solid products of this longer run. Most of the correlations between the 1- and the 2-week runs seem to support the observation made in Section 2.2 that we may be approaching an equilibrium reaction product assemblage for this particular set of temperature pressure conditions. Upcoming analyses of the products of 4- and 8-week hydrothermal treatments of 76-68 glass under the same conditions will answer this. We are currently performing similar product analyses on glass specimens treated identically, except that an equal weight of basalt (BCR-1) was also included in the capsule. This will be the next step in an increasingly complex sequence of experiments meant to culminate in the repository simulation runs described in Section 2.4.

2.3.2 Hydrothermal Treatment of Basalts -- Closed System

X-ray scans were made of the two basalts, BCR-1 and DDH-3, before and after hydrothermal treatment. The scans were on General Electric, Picker-Siemens, and Rigaku instruments; each has a diffracted-beam monochrometer, a scintillation detector, solid-state electronics, and strip chart recording. Peak positions and heights were compared with Powder Diffraction File (PDF) patterns for the minerals expected in the rock and with computer printouts of peak-positions generated by the Appleman Program. We looked for the presence or absence of minerals, for indications of composition, and for changes after hydrothermal treatment.

Basalts Before Hydrothermal Treatment

Components observed are labradorite, augite, and glass. Peaks at or near all strong peaks of labradorite and augite are present. A noisy broad maximum, consistent with the presence of glass, extends from 2 θ of about 15-35°; its maximum is at 22-24°.

Components not found are crystalline silica, ilmenite, and clays.

Detailed examination of the X-ray data shows differences between the peaks in the basalts tested and the lines in the patterns in the PDF for labradorite and augite. These are ascribed to the differences in composition between the labradorites and augites in the rocks tested and those in the PDF.

It would be instructive to characterize the kind of labradorite by, for instance, the difference in 2θ between the $\bar{1}\bar{3}1$ and 131 planes or the $\bar{2}41$ and $\bar{2}\bar{4}1$ peaks. In each of the regions of interest, strong augite peaks make such identification difficult. At 60 percent anorthite (PDF - 10-360), the $\bar{2}41$ - $\bar{2}\bar{4}1$ peaks are close together and obscured by an augite peak at $2\theta = 35.7^\circ$. In 38 percent anorthite (PDF - 10-359), they have separated enough to appear to either side of the augite peak. DDH-3, which contains labradorite of approximately 50 percent anorthite, lies somewhere in between; its scans show shoulders in the region anticipated by its composition, but it is difficult to measure peak positions well. On the other hand, the 131 line is clear in each case, but the $\bar{1}\bar{3}1$ is obscured throughout the composition range of interest by the 100 percent augite line. This line, in each case, is skewed toward the expected position of the labradorite $\bar{1}\bar{3}1$ line. An effort to resolve a shoulder was made on each of the instruments at our disposal, but without success.

It would be possible to pursue this method by using the Appleman Program, first to obtain all cell parameters from a few good lines, then to calculate the peak positions. The accuracy would always be reduced by the simultaneous presence of augite lines in the critical areas.

If it becomes necessary to follow changes in composition of this kind, it would be more productive to physically sort the basalt and X-ray the labradorite fraction separately.

Basalts After Hydrothermal Treatment

X-ray scans were made of basalts to which 50 percent water had been added prior to treatment at 300 bars for 30 days at nominal temperatures of 100, 200, 300, and 400°C. All peaks which were present in the basalt before hydrothermal treatment persist in the basalts after treatment. No new reflections are observed in the scans of these runs. In particular, no significant new peaks ascribable to clays or zeolites were found. There

are, however, several lines which just barely appear above the noise in the higher temperature runs. These will, of course, be watched in the longer-time runs and the flow-through experiments.

2.3.3 Low-Pressure Flow-Through Experiments

All of the necessary parts to proceed with the basalt reconnaissance run have been received and are presently being assembled. This apparatus has already been tested successfully with water alone at 40°C. The basalt sample sent by Dr. M. W. Grutzeck, Rockwell Hanford Operation, is being processed into selected size fractions so that it can be used in reconnaissance runs.

2.3.4 High-Pressure Flow-Through Experiments

All components of the apparatus have at last been received. The system is now being put together.

2.3.5 Hydrothermal Interactions of Phases from Spent Unreprocessed Fuel and Basalt

The reconnaissance runs (Section 2.1) indicated that the UO_2 component of SURF (~96.5 percent of typical SURF) has not yet shown major interactions with hydrothermal solutions. We do not intend to close the subject there and do plan more detailed evaluations of UO_2 - H_2O hydrothermal interactions in experiments similar to the 76-68 glass runs described in Section 2.3.1. Meanwhile, we have initiated detailed studies of the hydrothermal interaction behavior of two fission product components of SURF, Cs and Sr. We have consulted the (unfortunately sparse) literature of phase behavior in SURF to suggest in what phases the Cs and Sr may be present. These phases are either obtained or synthesized and then included with basalt or its mineral components in hydrothermal experiments.

Cesium-Basalt Mineral Interactions

Labradorite; one of the major constituents of basalts, and 2 different cesium sources, Cs_2MoO_4 (a possible phase in SURF) and CsOH , were mixed with 50 percent by weight of water sealed into 5-mm gold capsules and reacted hydrothermally in an autoclave held at a nominal temperature of 200°C (actual temperature $\approx$ 189°C) and 300 bars pressure

for 10 and 60 days. The sample and solution from each gold capsule were quantitatively transferred to polyethylene centrifuge tubes by washing with 0.1N KCl. The tubes were centrifuged and the supernatant liquid transferred to volumetric flasks. The use of 0.1N KCl serves three purposes: (1) it brings an easily exchangeable cesium into solution; (2) it helps in the flocculation of the sample during centrifugation; and, (3) it removes the ionization interference during cesium analysis by AAS. The samples were then washed once with water and acetone mixtures and thrice with 95 percent acetone to remove the KCl and were then dried for X-ray diffraction analysis. The solutions in the volumetric flasks were analyzed for cesium by atomic absorption methods.

X-ray diffraction analysis (Table III; Figure 24) of various cesium source-labradorite interaction products revealed the formation of pollucite ($\text{CsAlSi}_2\text{O}_6$) after 10, as well as 60, days of hydrothermal treatment. There is virtually no difference between the 10- and 60-day runs, which indicates the ease with which the basalt mineral interacted with the various cesium sources to form pollucite. The cesium molybdate source reacted as fully as the cesium hydroxide source (Tables III and IV), which is another indication of the great stability of pollucite and ease of basalt mineral hydrothermal alteration in the presence of an active mineralizing species. When the cesium source is Cs_2MoO_4 , the molybdate also formed the scheelite structure phase, CaMoO_4 , by reacting with Ca in labradorite.

Analysis for cesium remaining in Solution (Table IV) indicated that at least 86 percent of the added cesium was fixed in any given experiment. Cesium was mainly fixed in the form of $\text{CsAlSi}_2\text{O}_6$, pollucite. However, in the case of CsOH-labradorite interaction, a small proportion of cesium was also fixed in another cesium aluminosilicate, CsAlSiO_4 .

These runs demonstrate that if Cs were to be extracted from SURF in the form of Cs_2MoO_4 by hydrothermal solutions at $\sim 200^\circ\text{C}$ and 300 bars, the Cs would interact with the massive amounts of labradorite in the surrounding basalt to form aluminosilicates. The relevant question then would be: how good are these aluminosilicate "source terms" at fixing radiocesium for the times necessary for decay to harmless levels? In other words, how stable are they in the long term (up to ~ 600 years) under relevant basalt repository conditions?

TABLE III

X-RAY DIFFRACTION ANALYSIS OF VARIOUS MIXTURES OF Cs PHASES AND LABRADORITE WHICH WERE HYDROTHERMALLY TREATED AT ~200°C AND 300 BARS FOR 10 AND 60 DAYS

NO.	SPECIMEN, PARTICLE SIZE AND DURATION OF HYDRO- THERMAL TREATMENT	PERCENT Si IN LABRA- DORITE EXPECTED TO BE INCORPORATED IN POLLUCITE FORMATION WHEN ALL THE ADDED Cs REACTS	POLLUCITE FORMATION BY XRD	LABRADORITE INTENSITY BY XRD	OTHER PEAKS BY XRD
<u>Basalt Mineral + Cs₂MoO₄ Mixtures</u>					
1.	Labradorite, <75 μm, 10 days	100	Very Strong	Slight	Scheelite (CaMoO ₄)
2.	Labradorite, <75 μm, 60 days	100	Very Strong	Trace	Scheelite (CaMoO ₄)
3.	Labradorite, <75 μm, 10 days	25	Very Strong	Slight	Scheelite (CaMoO ₄)
4.	Labradorite, <75 μm, 60 days	25	Very Strong	Moderate	Scheelite (CaMoO ₄)
<u>Basalt Mineral + CsOH Mixtures</u>					
5.	Labradorite, <75 μm, 10 days	100	Very Strong	Slight	CsAlSiO ₄
6.	Labradorite, <75 μm, 60 days	100	Very Strong	Slight	CsAlSiO ₄
7.	Labradorite, <75 μm, 10 days	25	Very Strong	Strong	None Detected
8.	Labradorite, <75 μm, 60 days	25	Very Strong	Strong	CsAlSiO ₄

FIGURE 24

PORTION OF X-RAY DIFFRACTOGRAMS SHOWING THE PRODUCTS OF HYDROTHERMAL INTERACTIONS OF Cs WITH LABRADORITE

TABLE IV

ATOMIC ABSORPTION ANALYSIS OF Cs REMAINING IN SOLUTION FROM VARIOUS MIXTURES OF Cs PHASES AND LABRADORITE WHICH WERE HYDROTHERMALLY TREATED AT ~200°C AND 300 BARS FOR 10 AND 60 DAYS

NO.	SPECIMEN, PARTICLE SIZE, AND DURATION OF HYDROTHERMAL TREATMENT	PERCENT Si IN LABRADORITE EXPECTED TO BE INCORPORATED IN POLLUCITE FORMATION WHEN ALL THE ADDED Cs REACTS	TOTAL WEIGHT OF THE LABRADORITE (mg)	TOTAL WEIGHT OF Cs ADDED (mg)	TOTAL WEIGHT OF Cs REMAINING IN SOLUTION (mg)	WEIGHT OF Cs FIXED	PERCENT Cs IN SOLUTION	PERCENT Cs FIXED
<u>Basalt Mineral + Cs₂MoO₄ Mixtures</u>								
1.	Labradorite, <75 μm, 10 days	100	100	59.07	8.25	50.82	14.0	86.0
2.	Labradorite, <75 μm, 60 days	100	100	59.07	8.19	50.88	13.9	86.1
3.	Labradorite, <75 μm, 10 days	25	200	29.53	0.09	29.44	0.3	99.7
4.	Labradorite, <75 μm, 60 days	25	200	29.53	0.08	29.45	0.3	99.7
<u>Basalt Mineral + CsOH Mixtures</u>								
5.	Labradorite, <75 μm, 10 days	100	100	59.13	7.15	51.98	12.1	87.9
6.	Labradorite, <75 μm, 60 days	100	100	59.13	7.77	51.36	13.1	86.9
7.	Labradorite, <75 μm, 10 days	25	200	29.61	0.40	29.21	1.4	98.6
8.	Labradorite, <75 μm, 60 days	25	200	29.61	0.43	29.18	1.5	98.5

Further experiments of this type are planned in the following areas:

- Repeat experiments with cesium uranates, another possible Cs phase in SURF;
- Perform similar experiments at 100 and 300°C;
- Repeat certain index experiments with other components of basalts (augites, glasses, etc.) and with one or more basalts.

In addition, we will continue to explore the stability and Cs release rates in pollucite and, to a lesser extent, CsAlSiO_4 , now that they have been confirmed as waste/basalt interaction products.

Hydrothermal Interactions of Phases from Spent Unreprocessed Fuel and Basalt

This set of experiments was designed to test for hydrothermal interactions between a Sr phase in SURF and the major mineral constituents of the Columbia River basalts. More specifically, this study has treated SrZrO_3 with a labradorite feldspar composition for 7 days at 300°C and 300 bars. Initial XRD examination of the exploratory runs indicates that no new crystalline phases have been formed. The cell constant for the pseudocubic SrZrO_3 cell has remained unchanged; however, there is some indication that the major reflections of the plagioclase phase may have experienced a small shift in location.

These above observations are, at this time, tentative and any further discussion will await the results of 30-day-duration hydrothermal treatments. It is anticipated that the solutions of these runs will be analyzed to aid in the identification of potential SrZrO_3 dissolution and/or chemical breakdown of the plagioclase phase.

2.4 REPOSITORY SIMULATIONS -- CLOSED SYSTEM

A class of runs has been initiated that has as its objective the simulation of the complete chemical environment around a repository containing breached canisters that is subjected to water intrusion during the thermal period. Monolithic pieces of waste (SURF or glass forms) are 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. Hydrothermal solutions can thereby contact each of the repository components and the potential for waste/basalt

interactions can be evaluated. All of the components of the simulation, including the solutions, will be characterized to the maximum extent possible.

2.4.1 Experimental Procedures

The combination of available gold tubing sizes, equipment considerations, and the sizes of specimens indicated the use of 1-cm-diameter gold capsules. This size of capsule permits the use of more than 3.5 g of reactants. These reactants are loaded into the capsule in the following weight ratios:

1 part of waste	8 parts of Basalt BCR-1
1 part of metal	6 parts of Hanford ground water.

A sealed capsule is illustrated in Figure 25. The total volume of each capsule is about 2.5 ml. The steam tables indicate a 75 percent fill at 300°C and 300 bars. Subtracting 0.8 ml of solids, this leaves 1.7 ml of free volume which permits 1.2 ml of fluid fill. A typical run will thus have the following components:

.200 mg of waste	1.6 mg of Basalt BCR-1
.200 mg of metals	1.2 ml of Hanford ground water.

The following are the procedures for preparing a repository simulation run:

1. With a razor, score and break tubes at 5-cm intervals;
2. Inspect tubes for visible flaws or pinholes;
3. Rinse and clean all tubes with acetone using pipe cleaner;
4. To anneal out strain from fabrication, bring all tubes to red heat and cool slowly;
5. With smooth-jawed vise or long-nose pliers, carefully flatten approximately 0.5 cm at the end of tube; care should be exercised here to ensure a sharp crease at edges without damaging the surface of tube;
6. Cold-seal as close to end of tube as possible, using the CHA Industries' crimper;
7. Place tube in the liquid nitrogen micro-welding apparatus (see Figure 26); liquid nitrogen cooling allows use of higher welder currents while enabling slower, more controlled welds (a fine, fairly smooth, shiny weld should be obtained); visual inspection under the scope should be made at various angles; filling the tube with acetone and brushing the weld over a tissue will also indicate pinholes; points to watch here -- sand electrode to a clean, fine point after each weld (the current should be high enough to produce a strong, steady arc -- the arc should not be held at ends of crimp, as they melt down rapidly); lightly scribe an identification number on surface of tube;

FIGURE 25

SCHEMATIC OF A REPOSITORY SIMULATION RUN CAPSULE

FIGURE 26

SCHEMATIC OF THE CAPSULE CLOSURE APPARATUS AND PROCEDURE

8. Weigh components in appropriate ratios and place in the capsule as indicated in Figure 25, adding fluid carefully before the final layer of basalt in order to restrict the fluid to lower end of tube for the final sealing process.

Clean the inside top of the tube with an acetone-soaked pipe cleaner and repeat steps 5-7 on the top end of tube. Care should be taken when welding to keep the tube temperature well below the boiling point of water, or visible pinholing and pitting will occur in weld due to vapor loss. The liquid nitrogen level should be checked frequently.

A simple check for seal integrity involves squeezing tubes between the fingers, slowly but firmly, while watching and listening for leakage. A more precise indication is provided through a thorough cleaning and weighing, followed by treatment in a vacuum oven at 110°C evacuated to ~1 torr. Any vapor escaping through pinholes will yield weight losses on the order of mgs upon reweighing.

After verification of closure, the capsules are loaded into a 300-500 ml autoclave as shown in Figure 27. With the configuration indicated in this figure and controlling temperature with the RFL Industries' Model 76K-1 Controller, the internal temperature accuracy should be $\pm 6^{\circ}\text{C}$ and the temperature variation during the run should not exceed $\pm 2^{\circ}\text{C}$. Pressure accuracy is ± 200 pounds per square inch (psi) (300 bars = 4,350 psi).

To put up a run, the vessel is pressurized to 4,400 psi, inspected for leakage, and then placed in a preheated furnace. Pressure increase is monitored and dropped back manually upon reaching 5,000 psi until stability is obtained. (An apparatus has been designed and parts have been ordered for a system that will provide automatic pressure bleeding at variable set points using contact-type pressure gauge, control box, and solenoid-operated pneumatic valve.) Pressure and temperature are monitored and recorded daily during runs. When the run is over, the furnace is shut down and the vessel is removed and cooled as rapidly as is feasible. The gold capsules are removed (some may be replaced for longer-duration runs), cleaned (a toothbrush is handy here), and reweighed to ensure seal integrity.

2.4.2 Practice Runs

The configurations and procedures just described are the result of lessons learned during practice runs. Some of the problems encountered and the solutions implemented include those listed below.

CUTAWAY OF FURNACE/VESSEL

FIGURE 27

SCHEMATIC OF AUTOCLAVE AND FURNACE ASSEMBLY

- Hard-to-find glass and SURF specimens among a mix of basalt, metal, and waste.
- Wrap waste loosely in gold foil and load capsules in a uniform sequence as in Figure 25.
- Mix-up on run numbers and conditions.
 - Adopt a completely descriptive run code (see below).
- Spacial relationships among waste, metal, and basalt are lost during opening and washing of products.
- Slit capsule down the side so as not to disturb the contents; load capsule in a uniform sequence as in Figure 25.

Chemical analyses have been obtained for 2 of the runs having 76-68 glass as the waste form. The amounts of some of the elements detected in the solution include those listed in Table V.

TABLE V

ELEMENTS DETECTED IN TWO RUNS WITH 76-68 GLASS AS THE WASTE FORM

	BR-1 ~200°C/300 Bars <u>14 Days</u>	(in μg)	BR-2 ~300°C/300 Bars <u>30 Days</u>
Na	504		538
Mo	110		170
Cs	5.0		10.0
Sr	0.0		0.0
Si	175		203
U	1.6		1.2

The weights of the glass specimens and the volumes of water added in each case were comparable, so the concentrations of elements detected in the solutions can be roughly compared. It is interesting to note that, in spite of a temperature 100°C greater and twice the treatment time, the concentrations in BR-2 are not that much greater than in BR-1. This is an indirect, and so far tenuous, indication that interactions with basalt may be helping to fix some of the species originally mobilized from the glass.

Figure 28 is an SEM photomicrograph of the surface of the glass specimen after the BR-1 treatment. The extent of an apparent reaction crust suggests that hydrothermal alteration is substantial, even in this relatively short time at 200°C/300 bars. These products are still being characterized.

The descriptive run code adopted recently is illustrated by an example: "BGH-330;" is a repository simulation run consisting of Basalt, Glass waste form, and Hanford ground water to be treated at 300°C for 30 days. Eight of these runs are now in progress:

BGH-330;	BSH-330;
BGH-390;	BSH-390;
BGH-230;	BSH-230;
BGH-290;	BSH-290.

Runs involving glass as the waste included 304 stainless steel turnings and those involving SURF include both the stainless steel and zircaloy.

FIGURE 28

SURFACE OF THE ALTERED 76-68 GLASS SPECIMEN IN RUN BR-1
(200°C/300 BARS/14 DAYS) (150X)

APPENDIX A

RUN TABLES FOR 100°C AND 300°C
RECONNAISSANCE EXPERIMENTS

RUN TABLE NO. 31

- ☐ DRY (Type A)
☐ HYDROTHERMAL - LOW WATER (Type C)
☒ HYDROTHERMAL - HIGH WATER (Type D)

TEMPERATURE: 100(94) °C
 DURATION: 30 Days
 PRESSURE: 4350 psi

Specimen	Code	Seal Maintained During Run?	Optical Microscope Observations	X-ray Observations
PH-7A/ BCR-1	58-A	yes	wet, loose powder (no apparent reaction). On drying, small euhedral colorless crystals were observed	no apparent change
BCR-1 76-68	58-B	yes	loose, wet, salt-pepper colored powder growth of small colorless equant grains on Au tube	no apparent change
SPC-2/ BCR-1	58-C	yes	loose, wet, light-gray powder. No apparent reaction	no observable change
BCR-1	58-D	leaked	loose, wet, gray powder, has spots in interior that are rust colored	
SURF/ BCR-1	58-E	yes	loose, wet, dark brown powder with colorless very small crystals (perhaps from liquid phase)	no apparent change
PH-7A/ DDH-3	58-F	yes	dark, wet, loose powder	no apparent change
76-68 DDH-3	58-G	yes	wet, loose, speckled powder, appears to be some segregation. Colorless euhedral crystals on inner Au surface	no apparent change
DDH-3/ SPC-2	58-H	leaked	loose, wet, gray powder	no observable change
DDH-3	58-I	leaked	loose, wet, gray powder	labradorite, augite, glass; new peak at $2\theta = 31.2$; $1/I_0 < 0.05$; scanned from $2\theta = 20$ to 40°
SURF/ DDH-3	58-J	yes	loose, wet, brown powder	no apparent change
PH-7a	58-K	yes	wet, dark, loose powder. No apparent reaction. Some buff-colored grains. (On drying, cluster reniform pale green crystals plus long colorless needle crystals.)	complex pattern
76-68	58-L	yes	wet, loose, speckled powder, appears to be some segregation (white grains next to gold tubing)	no apparent change

RUN TABLE NO. 32

☐ DRY (Type A)
☐ HYDROTHERMAL - LOW WATER (Type C)
☒ HYDROTHERMAL - HIGH WATER (Type D)

TEMPERATURE: 100 (94)°C

DURATION: 30 Days

PRESSURE: 4350 psi

Specimen	Code	Seal Maintained During Run?	Optical Microscope Observations	X-ray Observations
SPC-2	58-I	yes	loose, wet, violet-gray powder	no observable change
SURF	58-II	yes	loose, wet, brown powder, very fine	UO ₂ unaffected, some extra weak peaks
BCR-1/ 76-68/ SS-410	58-0	yes	wet, loose, salt-pepper colored powder. Apparently some growth of anhedral colorless bulbous grains	no apparent change
BCR-1/ 76-68/ SS-410	58-P	yes	dark, wet, 1-ose powder. Some colorless, perhaps euhedral grains	no apparent change

RUN TABLE NO. 33

- ☐ DRY (Type A)
☐ HYDROTHERMAL - LOW WATER (Type C)
☒ HYDROTHERMAL - HIGH WATER (Type D)

TEMPERATURE: 300(280) °C

DURATION: 28 Days

PRESSURE: 4300 psi

Specimen	Code	Seal Maintained During Run?	Optical Microscope Observations	X-ray Observations
BCR-1/ PW-7a	56-A	yes	wet, "cemented" powder covered with white crystals	extensive pollucite-analcime; other phases
BCR-1/ 76-68	56-B	yes	damp, loose powder. White crust with few white bulbous anhedral growths	evidence of interaction
BCR-1/ SPC-2	56-C	yes	damp, "cemented" powder. White scale on Au tube with several white crystals	no observable change
BCR-1	56-D	yes	very strong petroleum distillate odor. Pasty powder with small euhedral crystals on surface	labradorite, augite glass. New peak at $2\theta = 37.6$, $I/I_0 = 0.15$, not far above the noise; also new peak = 11° , $I/I_0 = 10$, just above noise
BCR-1/ SURF	56-E	yes	slightly "cemented" chocolate-brown powder. Wet. One black patch on surface	no apparent change
DDH-3/ PW-7a	56-F	yes	wet, "cemented" powder. Loose covering of white crystals on surface inside of Au tube noticeably discolored	extensive pollucite-analcime; other phases
DDH-3/ 76-68	56-G	yes	sweet petroleum odor. Wet, white scale next to Au tube. Large white bulbous anhedral growths	some evidence of interaction
DDH-3/ SPC-2	56-H	yes	pungent petroleum odor. "Cemented", wet powder. White crystals on surface	no observable change
DDH-3	56-I	yes	strong, aromatic, petroleum-distillate odor. Loose, wet, black and white spotted powder	labradorite, augite, glass; possible new peak near 11° , mainly hidden in noise
DDH-3 SURF	56-J	yes	loosely, "cemented" powder. Damp, chocolate-brown when dried surface appeared littered with anhedral crystals	No apparent change

RUN TABLE NO. 34

- ☐ DRY (Type A)
☐ HYDROTHERMAL - LOW WATER (Type C)
☒ HYDROTHERMAL - HIGH WATER (Type D)

TEMPERATURE: 300(280) °C

DURATION: 28 Days

PRESSURE: 4300 psi

Specimen	Code	Seal Maintained During Run?	Optical Microscope Observations	X-ray Observations
PH-7a	56-K	yes	wet, uniform, dark-green powder	complex pattern
76-68	56-L	yes	damp, pastey powder with numerous yellow-green crystals (looks like wecksite). White scale on inner surface of Au tube. Biaxial (+) parallel extinction $n > 1.542$.	
SPC-2	56-I	yes	slightly "cemented" gray powder. Het. Several areas of rust-color on Au-charge interface	no observable change
SURF	56-II	yes	loose, wet, chocolate-brown powder	
DDH-3/ 76-68/ SS-410	56-O	leaked	strong, petroleum-distillate odor. Damp powder with white scale and few anhedral white bulbous areas	
DDH-3/ Stain- less Steel 76-68/ SS-410	56-P	yes	loose, speckled powder. White skin with white anhedral bulbous growths	no apparent change

APPENDIX B

PREPARATION OF SIMULATED SPENT UNREPROCESSED FUEL

The SURF from light water reactors (LWR) consists of pellets of UO_2 plus a small amount of fission products clad in high-zirconium alloy (zircaloy) tubes. Because this contract calls for 80 percent of the experimentation to be related to SURF as the waste form, it has been necessary to prepare non-radioactive laboratory simulations of SURF. There is no established procedure or recipe for preparing SURF, so the procedures outlined below may well be the first aimed at obtaining a simulation of this waste form.

Data presented by Cohen* indicate that nuclear fuel from a LWR having a burn-up of 33,000 megawatt days per metric ton of uranium (MWd/MTU) will consist of approximately 3.5 weight percent fission products and 96.5 weight percent UO_2 (+ NpO_2 + PuO_2). Uranium dioxide will be used as a stand-in for the radioactive NpO_2 + PuO_2 in the SURF simulation. The major effort in preparing this SURF, therefore, is in synthesizing a fission product mix.

The number of elements in fission products includes more than one-third of the periodic table. In Table A-I are listed 21 elements or stand-ins that are present in the fission products at >0.2 weight percent. The actinides, Am and Cm, are, of course, produced by neutron capture, rather than fission, but they are included with Gd because of their crystal chemical similarity to this element. Note that radioactive Tc, gaseous Kr, and Xe and I are not included in this fission product mix.

The atomic concentrations of the elements in Table A-I come from the ORIGIN Code for a LWR fuel having a burn-up of 33,000 MWd/MTU. The third column in the table gives the recipe for obtaining these concentrations from a mixture of nitrates and oxides. The nitrates, nitrate solutions, and oxides are mixed vigorously with a large excess of water to give a homogeneous solution-suspension and were then dried as rapidly as possible on a stirrer-hotplate. The residue was further dried at 90°C and then slowly heated to 400°C in air to decompose most of the nitrates. These conditions were selected to minimize alkali and Ru volatilization. This product was ground thoroughly.

*B. L. Cohen, Rev. Mod. Physics, 49 (1), 1 (1977), and Sci. Am., 236 (6), 21 (1977).

TABLE B-1

SIMULATED SPENT UNREPROCESSED FUEL FISSION PRODUCTS^a

(Burn-up of 33,000 MWd/MTU)

ELEMENT	ATOMIC %	FORMULATION FOR A 100-MEq ^b BATCH		OXIDE	WT. % OXIDE
Zr	16.51	4.408g	ZrO(NO ₃) ₂ ·2H ₂ O	ZrO ₂	14.3
Mo	14.80	2.131g	MoO ₃	MoO ₃	14.9
Nd(Pm) ^c	11.37	4.980g	Nd(NO ₃) ₃ ·6H ₂ O	NdO _{1.5}	13.4
Ru	9.19	27.5 ml	10% Ru Nitrate Solution	RuO ₂	8.5
Cs	8.41	1.640g	CsNO ₃	CsO _{0.5}	8.3
Ce	7.94	3.454g	Ce(NO ₃) ₃ ·6H ₂ O	CeO ₂	9.5
Pd	4.98	5.3 ml	10% Pd Nitrate Solution	PdO	4.2
Sr	4.21	0.893g	Sr(NO ₃) ₂	SrO	3.1
Ba	4.21	1.099g	Ba(NO ₃) ₂	BaO	4.5
La	3.74	1.619g	La(NO ₃) ₃ ·6H ₂ O	LaO _{1.5}	4.3
Pr	3.58	1.564g	Pr(NO ₃) ₃ ·6H ₂ O	PrO _{1.5}	4.1
Sm	2.18	0.968g	Sm(NO ₃) ₃ ·6H ₂ O	SmO _{1.5}	2.6
Y	2.18	0.835g	Y(NO ₃) ₃ ·6H ₂ O	YO _{1.5}	1.7
Te	1.87	0.299g	TeO ₂	TeO ₂	2.1
Rh	1.56	1.61 ml	10% Rh Nitrate Solution	RhO _{1.5}	1.4
Rb	1.56	0.231g	RbNO ₃	RbO _{0.5}	1.0
GD(Eu,Am,Cm)	1.09	0.492g	Gd(NO ₃) ₃ ·6H ₂ O	GdO _{1.5}	1.4
Ag	0.31	0.050g	AgNO ₃	AgO _{0.5}	0.4
Cd	0.31	0.040g	CdO	CdO	0.3
					<u>100.0</u>

^aTc, I, Kr, and Xe are not included.^bMilliequivalent.^cElements in parentheses indicate that the preceding element is a stand-in.

The conditions in actual spent fuel would be highly reducing, as controlled by the initial stoichiometry of the UO_2 fuel. Thus, some fission products (FPs) would be present as metals rather than the oxides produced in the procedure up until this point. Therefore, an additional step was included that would provide reducing conditions where the appropriate oxides would be converted to metals. The oxidized product was placed on a Pt boat in a Vycor tube and fired at 600°C in flowing hydrogen for 4 hours. This treatment should have been sufficient to reduce the Ru, Pd, Te, Rh, and Ag oxides to metals and CeO_2 to Ce_2O_3 . No evidence of alkali volatilization was noted for this moderate temperature treatment.

The "reduced FP mix" was combined with UO_2 to give the 96.5 percent UO_2 .3.5 percent FP composition. In actual SURF, some of the FPs will have chemically reacted with UO_2 and with each other. Because the actual phase in which each FP species is combined can have a major influence on its dissolution behavior or reactivity, it was next necessary to treat the mixture at a high enough temperature to promote phase formation. This firing must be performed in a closed system to prevent the specimen from oxidizing. In the first attempt, pellets of the mixture were sealed into an evacuated silica vial and heated at $1,050^\circ\text{C}$ for 1 hour. After cooling, the silica glass showed extensive frosting due, almost surely, to alkali attack. In the next experiment, the temperature was lowered to $\sim 1,000^\circ\text{C}$ in order to reduce alkali volatilization and the pellets were sealed into more inert gold capsules. After the 1-hour firing, the interior of the gold capsule was clean and the pellets had a uniform black color. Thus, there was no sign of segregation of the more volatile constituents or of alloying of any of the metals with the gold.

The X-ray diffractograms of these simulated SURF products showed only the reflections of a well-crystallized fluorite structure phase with a unit cell slightly smaller than that of the original UO_2 . This decrease in unit cell size would be expected from the incorporation of rare earth and Zr oxides into solid solution with the UO_2 . The fact that none of the other FP constituents were observed by XRD was also expected. Altogether, these other constituents make up less than 2 weight percent of the simulated SURF batch and this amount is well below the level of detection of XRD, especially for such a highly absorptive matrix as UO_2 .

It is not maintained that this product is a perfect simulation of SURF. The pellets are not well sintered and the fission products are perhaps too homogeneously distributed. Ideally, the final firing should have been carried out so that the interior of the pellet was at 1,700-2,000°C and the exterior at ~600°C, as would be the case during actual fuel burn-up in a reactor. This would give the well-sintered, but cracked and compositionally zoned, structures typical of actual SURF. However, it is believed that this simulated SURF will be adequate to indicate the direction of equilibrium in any SURF/basalt hydrothermal interactions and, thus, it will be adequate to meet the objectives of the current contract.

APPENDIX C

THE GANDOLFI X-RAY METHOD

Many of the reaction products formed in our stability experiments are minute crystals or crystal clusters which are intimately mixed with the reactants. It is usually possible to isolate a few clusters, but rarely is there enough material for a standard diffractometer sample. The use of the bulk sample in the diffractometer usually results in a complex pattern dominated by the reactants. Recognizing those product phases present in small quantities in these patterns is difficult at best.

For such minute samples, it is more effective to use camera methods. The Debye-Scherrer method has long been used for obtaining powder diffraction patterns and is capable of yielding patterns from samples smaller than 1 microgram. Quantities this small rarely have enough crystallites to yield a truly random pattern in the Debye-Scherrer Camera, and the patterns are often spotty and often not easy to utilize in search-match procedures on d-I data bases such as the Joint Committee on Powder Diffraction Standards Powder Diffraction File (JCPDS-PDF). The Gandolfi method is a modification of the Debye-Scherrer technique in which the sample is simultaneously rotated about 2 inclined axes, thus more effectively randomizing the sample orientation and yielding a more easily interpreted diffraction pattern.

The Gandolfi Camera consists of a pinhole collimator and beam stop, the sample rotation mechanism, and a cylindrical film cassette enclosed in a vacuum chamber. The camera center is the intersection of the X-ray beam and axis of the cylindrical film. The rotation mechanism is constructed, such that both rotation axes also intersect at this center. The sample is cemented to the tip of a very fine glass capillary and centered in the camera using an alignment telescope. Careful centering of the sample is necessary so that the crystal cluster traces out the smallest volume possible during rotation.

The samples are isolated and mounted using a long focal length binocular microscope. A fine glass capillary is chosen and broken under tension so that it yields a clean cross-fractured surface. This capillary material is either Pyrex or Lindeman glass. It is mounted in the detachable sample support which holds it in the camera. This assembly is then clamped in a

pin vise for easy manipulation under the microscope. Using a needle, a small drop of collodion in ether, nail polish, or Tacky Wax is placed on the exposed end of the capillary. The capillary is then touched to the isolated crystal cluster or fragment. A single crystal fragment may be used, or several fragments may be collected on the tip until a small ball of sample is formed. The assembly with the sample is then placed in the camera and centered.

The usual samples encountered in this study are crystal clusters around 100 μm in size. These samples rarely are difficult to mount. The large-diameter (114.6-mm) film cassette is used and evacuation of the camera to reduce air absorption X-rays is not necessary. Exposures around 12 hours usually yield good diffraction patterns. Samples as small as 10 μm may be used and, under special conditions, yield very usable diffraction patterns. The samples must be mounted on a very tiny capillary, preferably of Lindeman glass. For best results, a fairly rigid capillary is drawn out to a sharp point while holding it close to a heated platinum filament. A very small amount of cement is used. The small-diameter film cassette (57.3-mm) is usually employed, and the camera is evacuated during the exposure. Exposure times up to several hundred hours may be required.

Debye-Scherrer patterns usually suffer from poor resolution when compared with the capability of the powder diffractometer. The small samples which can be used in the Gandolfi Camera yield quite sharp diffraction lines and resolutions almost comparable to those of the diffractometer even with the small-diameter cassette. The use of a phase-pure sample, which is possible with the small size employed, usually makes identification of the resulting pattern fairly routine if the compound has a reference pattern in the PDF. The method has proved very effective in this project.

The Gandolfi method has some limitations which must be kept in mind when interpreting the diffraction patterns. Although it is quite effective at randomizing the sample orientation, it is not perfect. Occasionally, a diffraction line may be completely missed, especially when using single crystal samples of low symmetry. The small samples do require long exposures to reveal the strong lines, and weak lines may not be revealed. Regardless, the method is the best choice of all the available techniques.

APPENDIX D

HYDROTHERMAL RUN SOLUTIONS: PREPARATION AND ANALYSES

SEPARATION OF SOLID AND SOLUTION PHASES FROM THE RUN CAPSULES

The gold capsules were cut open at one end with a small stainless steel scissors in a plastic beaker. The inside, as well as outside, of the capsule was then gently washed with deionized water using a wash bottle. The capsule was then opened longitudinally, placed in the beaker for about 5 minutes to equilibrate, removed from the beaker, and washed again gently with a jet of water. The solid sample was then used for microscopic observation. The solution from the beaker was quantitatively transferred to a 25-ml volumetric flask, 186 mg of KCl were added to the solution 0.1N KCl and made up to volume. The use of 0.1N KCl serves two purposes: (1) it helps in the flocculation of the sample, if any, during centrifugation; and, (2) it removes the ionization interference during cesium analysis by AAS. The solution was then centrifuged in polycarbonate tubes at 2,500 rpm so as to sediment any fine particles in the solution. The solution was then pipetted out from the polycarbonate tubes into polyethylene bottles. A drop of toluene was added to the solution to prevent any bugs from growing. Various elements in the solution were then analyzed using the appropriate techniques.

CHEMICAL ANALYSIS

All the elements, except uranium, were analyzed by AAS using a Perkin-Elmer PE 403 instrument. Table D-I lists the various chemicals used for standards, sensitivities, detection limits, and linearity for different elements.

TABLE D-1

ELEMENTS DETERMINED BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

<u>ELEMENT</u>	<u>STANDARD</u>	<u>DETECTION LIMIT μg/ml</u>	<u>SENSITIVITY μg/ml FOR 1% ABSORPTION</u>	<u>LINEAR UP TO μg/ml</u>
Cs	CsCl	0.05	0.2	15
Sr	Sr(NO ₃) ₂	0.01	0.15	5
Rb	RbCl	0.005	0.05	5
Na	NaCl	0.002	0.015	1
Ca	CaCO ₃	0.001	0.07	7
Zn	Zn Metal	0.002	0.018	1
Ni	Ni Metal	0.01	0.1	5
Si	Na ₂ SiO ₃ ·9H ₂ O	0.08	2.0	150
Mo	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	0.03	0.6	60

Uranium was determined by a fluorometric method* using a Jarrell-Ash JA-2600 Fluorometer. The standard U solution was prepared using UO₂(NO₃)₂·6H₂O. The above method is useful in determining U concentrations in the range of 5 ppb to 50 ppm.

*A. Y. Smith and J. J. Lynch, "Uranium in Soil, Stream Sediment and Water," Geological Survey of Canada Paper 69-40 (1970).

APPENDIX E

DESCRIPTION OF THE ETEX MICROPROBE (MODEL AUTOPROBE)

The application of the electron microprobe to areas of study in the fields of metallurgy, ceramics, and the geosciences has a history spanning almost two decades. Therefore, no description of the basic theories and design of the microprobe will be presented. The reader is referred to perhaps the best currently available source for pertinent information concerning the electron microprobe, Electron Microprobe Analysis, S.J.B. Reed (1975).

INSTRUMENT DESCRIPTION

The ETEX AUTOPROBE which is available in the Mineral Constitution Laboratory at The Pennsylvania State University is equipped with a dedicated INTERDATA Computer with a memory capacity of 64K and two floppy discs for storage. The dedicated computational system is the major improvement over the more traditional electron microprobes. In its X-ray wavelength dispersive mode, the AUTOPROBE can be programmed and standardized by means of 3 computer-controlled variable spectrometers for quantitative analysis at 14 elements per analysis in 2 to 3 hours, with individual analyses requiring 2 to 5 minutes. This rapid data processing and turnover time is contrasted to the traditional systems which required perhaps 1 day to standardize and collect data and then an additional day to format the data and process it through a centralized computational system. The ability to evaluate the quality of an analysis in 5 minutes and to make the proper corrections has enabled this system to yield analyses that sum to 99 percent of the total solids. This feature was used in the analysis presented in Table I.

The 3 variable spectrometers are equipped with the standard array of crystals that allow the analysis of elements from carbon through uranium. With the proper spectrometer window, the AUTOPROBE has the capability for boron analysis.

Almost instantaneous X-ray energy spectra are available with a KEVEX 5100C X-Ray Energy Spectrometer. This KEVEX system is equipped with its own computer which will allow storage of 2 data sets, typically

covering the energy range from 0 to 18 KeV, for display and/or comparison on a cathod ray tube. Specific X-ray energy spectra for individual elements can be superimposed upon the display on the cathod ray tube to aid in the identification of the specimen spectra. This feature has been particularly useful in identifying the rare earth elements, Zn, Zr, Sr, and Mo. The detection level for the system is stated typically at 1 weight percent. In a limited number of metal systems, the KEVEX unit can be used to obtain quantitative analyses that sum to the 98 percent of total solids.

The AUTOPROBE is also equipped with a rastering capability for the electron beam which will allow the formation of images in a scanning mode; i.e., it can function as a normal SEM. The resolution on this particular instrument is approximately 200Å. Additionally, electron backscatter imaging and specimen current imaging capabilities are available (see, for example, Figure 8).

To supplement the quantitative data with visual representations of the elemental distributions within samples, X-ray maps for individual elements can be obtained and stored, as can any of the signals displayed on the cathod ray tube on the ETEX VISTASCAN. The VISTASCAN is a storage device which enables 4 different cathod ray tube images to be stored and displayed individually or as 1 set of 4 images (as in Figure 6). Finally, as a supplemental visual aid in interpreting elemental distribution, X-ray line scanning is possible. This technique employs a single spectrometer and auxiliary motor drives that are attached to the x and y specimen stage positioners. The sampling electron beam can be positioned and the motor drive and strip-chart recorder manually initiated, thus tracing out concentrations as a function of distance across a sample. Figure 23 is an example of this data acquisition mode.

DESCRIPTION OF SAMPLE PREPARATION FOR THE MICROPROBE

The sample preparation that has been employed for use with this instrument is identical to that used with the SEM as described in RHO-BWI-C-2 (unclassified) May 1978, G. J. McCarthy and B. E. Scheetz, "High-Level Waste/Basalt Interactions, Annual Progress Report for the Period February 1, 1977 to September 30, 1977." Samples for quantitative analyses are mounted in a cold mounting plastic and polished to 0.3 µm diamond paste finish. The samples are subsequently coated with an evaporated layer of carbon that typically does not exceed 450Å in thickness.

APPENDIX F

UPDATE ON SOME PROCEDURES IN HYDROTHERMAL EXPERIMENTATION

AUTOCCLAVE TEMPERATURE CALIBRATION

Figure 26 shows one of our standard autoclaves with a high-pressure feed-through for an internal thermocouple. For reasons of safety and convenience, routine procedure does not include the use of this special cap and feed-through. Therefore, it is necessary to calibrate the internal temperature against the temperature measured externally at the level of the run capsules. After experiencing several months of delays in obtaining the appropriate fittings and feed-through, these calibration procedures were finally completed during this last quarter. We also used this opportunity to try out a number of heater and insulation packing configurations in order to minimize the longitudinal, as well as the transverse, thermal gradient. It should also be noted that the presence of three "run baskets" containing the usual total of 48 gold capsules was simulated in the autoclaves because their presence or absence would affect the internal convection behavior of the hydrothermal fluids.

In Figure F-1, we present the results of the autoclave calibrations for two different configurations of high-temperature felt-type (Fiberfrax) insulation. The dashed curve is the relation of the drop in internal temperature as a function of the externally measured temperature with no extra insulation around the autoclave, except for that provided by the furnace enclosure. The solid curve is for insulation packed around the top half of the autoclave. We now use the latter configuration because of the obviously smaller temperature difference. The temperature variation from the top to the bottom of an assemblage of run capsules was $\pm 2^{\circ}\text{C}$. Combining this with the precision of the controller and the thermocouple read-out, we estimate that the temperature reported for any given run has an accuracy of $\pm 6^{\circ}\text{C}$.

STANDARD OPERATING PROCEDURES

The following are our current standard operating procedures for hydrothermal experiments.

FIGURE F-1

TEMPERATURE CALIBRATION FOR A STANDARD AUTOCLAVE IN THE FURNACE WITH AND WITHOUT EXTRA INSULATION
 (ΔT = DROP IN INTERNAL TEMPERATURE COMPARED TO EXTERNALLY MEASURED TEMPERATURE)

Preparation of Gold Tubes for Hydrothermal Runs

Cutting

1. Cut tubing to appropriate length with a razor blade using one smooth stroke. Bend tubing carefully to separate.

Annealing and Cleaning

2. Rinse well with distilled water.
3. Place tube in a crucible and put in a pot furnace pre-set at 700°C. Anneal for two hours.

Initial Sealing

4. Crimp one end of the tube with CHA Pinch OFF Device.

Labeling

5. Using a scribe, mark tube with appropriate run and sample number.

Filling

6. Weigh tube and fill with the appropriate amount of sample. Weigh tube with the sample, subtract tube weight and record net weight of the sample.
7. Clean the upper interior edge of tube with a pipe cleaner wetted with acetone. Add appropriate amount of water with syringe.

Final Sealing

8. Crimp top of filled tube with CHA Pinch OFF Device.

Testing Seal

9. Weigh piece of weighing paper, weigh tube on weighing paper and calculate net weight of sealed tube.
10. Place tube in vacuum-heating unit, set temperature at #3 (90-95°C) and evacuate. Remove after one hour.
11. Reweigh the tube using the same procedure as before (Step 9).
12. If there is a change of 1% or greater in the weight of the sealed tube, repeat the vacuum heating procedure (Steps 15 and 16) and see if the weight loss continues (an indication of a weighing error). Replace leaky tubes.

Preparing Tubes for Placement in Bridgman Hydrothermal Vessel

13. Place tubes in steel net and tie with platinum, chromel or alumel wire.

Small Cold Seal Vessels

1. Obtain clean cold seal vessel, 3/8" nipple (w/2 collars and gland), reducer, 1/4" nipple (w/2 glands and 2 collars).
2. Preheat furnace to desired temperature.
3. Place sample in cold seal vessel.
4. Fill vessel w/distilled water.
5. Place 3/8" nipple through cap nut, slip gland over 3/8" nipple and screw collars on both ends leaving 2 threads exposed on each cone. Screw on reducer. Slip both glands on 1/4" nipple screw a collar on each end leaving 2 threads exposed on the cones. Screw nipple to reducer.
6. Lubricate vessel threads with "Never Seez" (Never Seez (R) Compound Corp., Bradview, IL 60155) and screw cap nut assembly to cold seal vessel.
7. Using two adjustable crescent wrenches tighten cap nut snugly. Tighten various glands and reducer proceeding from the cap nut to the top of the apparatus.
8. Attach assembled vessel to the valve of an appropriate station and tighten. Attach readout thermocouple to vessel.
9. Place shielding around vessel. Open valve. Pressurize vessel using the intensifier. Close valve. Check for leaks. Bleed pressure. Close valve and remove shielding.
10. Place vessel in furnace. Pressurize to desired psi. Bleed pressure as necessary to maintain approximate pressure desired.
11. When temperature has stabilized, pressurize if necessary with the intensifier.
12. When the run is completed turn the controller off, remove the furnace, and allow the vessel to air cool.

Large Cold Seal Vessels

1. Obtain clean cold seal vessel, plunger (w/collar and gland), reducer, and 1/4" nipple (w/2 glands and 2 collars).
2. Preheat furnace to desired temperature.
3. Place sample in cold seal vessel.
4. Fill vessel w/distilled water.
5. Place plunger in cap nut, slip gland over plunger and screw collar on the plunger leaving 2 threads exposed on cone. Screw on reducer. Slip both glands on 1/4" nipple, screw one collar on each end leaving 2 threads exposed on the cones. Screw nipple to reducer. Lubricate vessel threads with "Never Seez" and screw cap nut assembly to cold seal vessel.
6. Place assembled vessel in a large vise using adapter.
7. Tighten cap nut snugly. Tighten various glands and reducer proceeding from the cap nut to the top of the apparatus.
8. Attach assembled vessel to the valve of an appropriate station and tighten. Attach readout thermocouple to the vessel.
9. Place shielding around vessel. Open valve. Pressurize vessel using the intensifier. Close valve. Check for leaks. Bleed pressure. Close valve and remove shielding.
10. Place vessel in furnace. Pressurize to desired psi. Bleed pressure as necessary to maintain approximate pressure desired.
11. When temperature has stabilized, pressurize if necessary with the intensifier.
12. When the run is completed turn the controller off, remove the furnace, and allow the vessel to air cool.

Bridgman Autoclaves

Assembly Technique

1. Clean inside of vessel and rinse well. Polish seal and any area of the apparatus touching the seal.
2. Place samples in vessel and fill with deionized water.
3. Place seal ring on plunger, screw plunger on to main nut, place thrust washer on top followed by lock nut. Very lightly coat threads of main nut with graphite lubricant.
4. Place vessel in vise. Screw this apparatus into body of vessel.
5. Tighten the main nut by inserting a rod into the holes of the main nut and turning. Very lightly coat threads of all set screws with graphite lubricant.
6. Tighten all set screws 'finger tight.'
7. Using a torque wrench tighten one set screw to 20 foot pounds. Then tighten the opposing set screw to 20 foot pounds. Continue until all set screws have been tightened to 20 foot pounds, using this 'criss-cross star pattern.'
8. Repeat Step 12, tightening all set screws to 40 foot pounds.
9. Attach tested pressure gauge-rupture disc apparatus to top of plunger. With a wrench, tighten gland on rigid tubing securely to plunger.

Heating and Pressurizing Procedure

1. Place entire vessel inside shielding. Using the intensifier, pressurize to desired psi. Close valve and check for leaks. Bleed pressure and close valve.
2. Using two lengths of wire attach two chromel-alumel thermocouples to exterior of vessel in sample range.
3. Place entire vessel in pre-heated furnace with the rupture disc facing the wall. Be sure control thermocouple is in furnace. Seal top of furnace with Fiberfrax insulation.
4. Attach one thermocouple to the digital temperature readout and one to the chart temperature readout.
5. Pressurize to desired psi. Bleed pressure as necessary to maintain approximate pressure desired. When temperature has stabilized, pressurize if necessary with the intensifier.

6. Monitor run temperature and pressure daily.
7. To terminate run: (a) turn off controller; (b) very carefully lift vessel out of furnace and allow to air cool.

Dissassembly Technique

1. Check bleed valve to be sure there is no pressure remaining in vessel.
2. Place vessel tightly in vise.
3. Loosen a set screw to 20 foot pounds. Then, loosen the opposing set screw to 20 foot pounds. Continue until all set screws have been loosened to 20 foot pounds, using criss-cross star pattern.
4. Repeat Step 3, removing all set screws. Remove pressure gauge-rupture disc assembly.
5. Loosen main nut and remove. Remove samples.

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