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**Hydrothermal Interactions Of
Cesium And Strontium Phases
From Spent Unreprocessed Fuel
With Basalt Phases And Basalts**

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Rockwell International

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PHASES FROM SPENT UNREPROCESSED FUEL WITH
BASALT PHASES AND BASALTS

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INTRODUCTION

This investigation is a segment of an extensive research program aimed at investigating the feasibility of long-term, subsurface storage of commercial nuclear waste. Specifically, it is anticipated that the waste will be housed in a repository mined from the basalt formations which lie beneath the Hanford Site. In the long range, research will be directed to evaluate the potential for release of radionuclides from the repository as a result of the interactions of heated groundwater, selected waste forms, and basalt rock. This will be accomplished by investigating those reactions which solubilize or precipitate possible radionuclide-containing phases under repository conditions. To date, the target waste forms are glass, supercalcline, and spent fuel. The purpose of this effort is to make a preliminary investigation into a portion of the Basalt-Spent Fuel Element-Water System. This is accomplished by assessing the hydrothermal reactivity of potentially hazardous phases contained by Spent Fuel Elements (SFE) and basalt.

The elements monitored during the present experiments were Cs and Sr. These two elements represent significant biohazards if released from a repository and are the major heat producing radionuclides present in commercial radioactive waste. We have reported the potential for Cs extraction from SFE by thermal waters in the range 200° to 300°C at 300 bars.^(1,2) These conditions represent present estimates of the maximum temperatures and pressure which might be encountered in a repository in basalt located 1,000 m below the surface. In these early experiments, Cs was extracted by hydrothermal leaching of an isolated (simulated) spent fuel element. In contrast, a cursory investigation in which SFE was in intimate contact with crushed basalt produced hydrothermal solutions which appeared to be devoid of Cs.⁽²⁾ The most direct explanation for these conflicting results is that in the later experiments Cs was bound by solid reaction products which resulted from the hydrothermal treatment of basalt. However, this was not satisfactorily verified even though

experience with other waste forms and geochemical predictions suggest that pollucite $[(\text{CsNa})\text{AlSi}_2\text{O}_6 \cdot n\text{H}_2\text{O}]$ would be a stable product and provide a ready host for Cs.^(3,4,5)²

One purpose of this investigation is to test this hypothesis. Toward this end, several Cs phases and/or solutions were reacted with either isolated basalt phases or bulk-rock basalt, and the resulting solids and solutions were analyzed. Another purpose of this study was to investigate the hydrothermal reactivity of SrZrO_3 , which is believed to be a probable host for Sr in SFE. While so far no evidence exists which indicates that Sr is present in a water soluble phase in SFE, detailed investigation of a potential hazard is warranted.

All experiments were conducted in sealed, noble metal capsules. Accordingly, they represent static (or stagnant) conditions in a flooded repository. Equilibrium values from such experiments are representative of maximum amounts of dissolved solute. Therefore, they can be used to generate the most conservative (i.e., pessimistic) models. In all experiments, care was taken to insure the presence of excess water ($P_{\text{H}_2\text{O}} = P_{\text{TOT}}$). Therefore, following experiment termination, the apparent solubility of a given element was measured by quantitatively analyzing the residual liquid using atomic absorption spectrophotometry. Only temperature, pressure, and water:solid and exchanging cation:Si ratios were controlled. Variables such as Eh and pH varied and were intrinsic to the bulk composition.

In perspective, the experiments were designed to cover a wide range in conditions and compositions. The purpose was specifically to investigate possible reactions which can occur between Sr/Cs phases and basalt. Therefore, although the experimental system necessarily reflects on radwaste storage in basalt, it is by no means intended as a scaled-down model of repository conditions. For example, an actual repository would have a much greater proportion of basalt:Cs or Sr in the hydrothermal reaction zone than is represented by these experiments.

EXPERIMENTAL PROCEDURES

MATERIALS

The two basalts used in this investigation are the U.S. Geological Survey's standard Basalt Columbia River-1 (BCR-1) and a section of core from Hanford Drill Hole DDH-3 (A2120/3320). The Columbia River basalt is composed of feldspar, augite, a small amount of ilmenite, and a significant, but varying amount of glass⁽⁶⁾ as the primary phases. In addition, the zeolite, heulandite, is present as a common secondary mineral phase in Columbia River basalts. In addition to the two basalts, both natural and synthetic samples of individual basalt phases were also used as reactants. This was done to provide more insight into the complex behavior of basalt-water-waste form interactions. The basalt phases which were used in this study include: (a) labradorite from St. John Lake, Quebec; (b) diopside (pyroxene) from the Duluth gabbro complex, Minnesota; (c) ilmenite from Baie St. Paul, Quebec; (d) heulandite from Teigarhorn, Berufjord, Iceland; and (e) synthetic basalt glass.

The synthetic basalt glass, whose bulk composition is similar to the glass phase described by Ames,⁽⁷⁾ was prepared to simulate the glassy component of the Columbia River basalt. Appropriate chemicals were mixed to get a composition of 58.3% SiO₂, 10.1% Al₂O₃, 2.5% Na₂O, 1.5% K₂O, 2.6% CaO, 12.8% FeO, 11.1% TiO₂, 0.9% P₂O₅, 0.1% SO₃, and 0.1% MnO, then melted in a platinum crucible and quenched in air.

The exact Cs and Sr phases contained in SFE are not known with certainty. However, some frequently cited possibilities are Cs₂MoO₄, CsOH, Cs₂U₂O₇, and SrZrO₃.^(8,9) Both Cs₂MoO₄ and CsOH may be obtained in pure form from commercial vendors. However, Cs₂U₂O₇ and SrZrO₃ were synthesized by the investigators.

Cs₂U₂O₇ (β phase) was synthesized from nitrates using a 1:1 Cs:U ratio. CsNO₃ and UO₂(NO₃)₂·6H₂O were mixed and melted in platinum crucibles at 450°C. After one hour the temperature was raised to 600° to 620°C. To ensure complete degassing of NO_x, temperature was maintained for at

least three days. The crucible was then removed from the furnace and allowed to air cool. The result of the synthesis was a yellow-orange compound.

This was characterized by X-ray diffraction (XRD) only, and found to consist primarily of $\beta\text{-Cs}_2\text{U}_2\text{O}_7^{(10)}$ with a minor amount ($\sim 10\%$) of $\text{Cs}_4\text{U}_5\text{O}_{17}$. The well defined (sharp) X-ray reflections were taken as evidence for overall crystallinity.

SrZrO_3 was also synthesized from the nitrates. An aqueous solution containing stoichiometric amounts of Sr and Zr was boiled to dryness at 110°C . The resulting powder was fired at 800°C for six hours to complete denitration, then ground in an agate mortar, pelletized, and fired at $1,400^\circ\text{C}$ for 15 hours. The result was again characterized by XRD and verified as SrZrO_3 .

METHODS

The various basalt phases and basalts were dry ground to -200 mesh ($<75\ \mu\text{m}$). X-ray diffraction analysis of the various samples either packed in glass cavities or mounted on glass slides with collodion was carried out with either a Philips or Picker-Siemens diffractometer using $\text{Cu K}\alpha$ radiation.

All charges were reacted hydrothermally, using previously reported procedures.⁽¹¹⁾ A pressure of 300 bars was maintained over all samples, with two temperatures being investigated. Experiments conducted at 200°C lasted 56 days, while those at 300°C were terminated after 28 days. Prior to, or concurrent with the interaction experiments, each basalt phase, as well as the two basalts, was reacted with an equal weight of water. Conditions for these reference experiments were identical to those investigating Cs or Sr behavior.

The behavior of Cs phases was investigated in a stepwise fashion. The thermodynamic reactivity of a phase is a function of its active concentration or activity (a_i). Because hydrothermal reactions involve water as either a reagent or a flux, the aqueous solubility of species

is of considerable interest when interpreting the experimental results. It is well known that both CsOH and Cs_2MoO_4 are readily soluble in water. The room temperature solubility of these species may be appreciated by the following examples. It takes only 100 g of water to dissolve 300 g of CsOH or 200 g of Cs_2MoO_4 . These compounds are held by bonds which are largely ionic, and therefore dissociate readily. However, $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ has a much larger component of covalent bonding and was expected to be considerably less soluble. Therefore, the first step toward investigating Cs behavior was to gauge the hydrothermal solubility of $\text{Cs}_2\text{U}_2\text{O}_7$. These experiments utilized water to solid ratios of 10:1 and 1:2, and were conducted at 100°, 200°, and 300°C. Experiment duration varied with temperature. Experiments at 100°C lasted four months, those at 200°C lasted two months, and those at 300°C ran for one month.

In the next series of experiments, the hydrothermal stability of each Cs phase in the presence of each major basalt phase was investigated. Thus, CsOH , Cs_2MoO_4 , and $\text{Cs}_2\text{U}_2\text{O}_7$ were individually mixed with labradorite, diopside, and glass. The proportions of the solid mixtures were somewhat arbitrarily set at two different molar ratios of Si:Cs (8:1 and 2:1). This allows a range in the proportions of Cs phase:basalt phase to be investigated without overwhelming the amount of Cs present with copious amounts of basalt and thus obscuring potentially interesting results. The solid mixtures were then mixed with an equal weight of water to yield the experimental charge. In all, 18 samples were reacted in each complete set of experiments at each temperature. All experiments were contained in sealed gold capsules and subjected to conditions and procedures identical to those described earlier for $\text{Cs}_2\text{U}_2\text{O}_7$ solubility experiments.

In a final series of Cs stability experiments, each simulated waste was hydrothermally reacted with the two basalts (DDH-3 and BCR-1). Mixtures were prepared as for the previous experiments described above, and reacted using the same experimental conditions.

The tests performed on SrZrO_3 closely paralleled those performed on $\text{Cs}_2\text{U}_2\text{O}_7$. First, hydrothermal solubility was tested and then SrZrO_3 was reacted with each basalt or basalt phase. The SrZrO_3 :basalt component ratio was a 1:1 weight ratio as was the total solid:water ratio. Experiments were conducted at 200° and 300°C.

The residual solid and liquid phases from all run capsules were saved for analysis. The capsules were opened into a glass vial. To enhance quantitative sample recovery, a 20 ml aliquot of 0.1N KCl was used to carefully wash adhered material from scissors used to open the capsule. Care was taken to avoid sample loss. The capsule was swirled in the vial to remove any trapped sample. When removed from the vial with tweezers, the capsules appeared free of all solid material. Vials containing the samples were centrifuged and portions of the supernatants were decanted into polyethylene bottles. The use of 0.1N KCl serves three purposes: (1) to bring any easily exchangeable Cs or Sr into solution; (2) to aid in the sedimentation of the sample during centrifugation; and (3) to suppress Cs ionization during cesium analysis by atomic absorption spectrophotometry. The solid samples were then washed once with water and acetone mixtures and three times with 95% acetone to remove the KCl and were then dried for XRD analysis. The solutions in the polyethylene bottles were analyzed for cesium and strontium by Atomic Absorption Spectrophotometry using a Perkin Elmer, PE403 instrument. X-ray diffraction analysis of the solid products was carried out as described above.

RESULTS AND DISCUSSION

REACTIONS WITH CESIUM PHASES

Hydrothermal Solubility of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ in Water

Experiments testing the solubility of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ employed two water:solid ratios--10:1 and 1:2. As might be expected, the mass amount of Cs dissolved is dependent on the solute-to-solvent proportions.

Analyses of residual liquids from experiments using a 10:1 water:solid ratio consistently indicate that approximately 33.5 wt% Cs dissolves and remains in solution (Table I). This value (g Cs in solution/g Cs in original solid) appears to be independent of the temperature and probably represents saturation, although it is unclear what conditions generated the observed value. Several possibilities are that: (1) Cs solubility in water is not a strong function of temperature over the range of interest (i.e., 33.5% is a value which holds for all temperatures investigated); (2) the experimental value is appropriate for some temperature between 30° and 100°C (at 300 bars pressure) and is produced during experiment termination; and (3) the solution values may be limited by a process other than simple saturation which is insensitive to changes in temperature over the range 100° to 300°C.

TABLE I. Analyses of Cesium Remaining in Solution upon Hydrothermal Treatment^a of β -Cs₂U₂O₇ at 100°C for 4 Months, 200°C for 2 Months, and 300°C for 1 Month.

Water to Solid Ratio	Percent of Cesium in Solution		
	100°C	200°C	300°C
10:1	34.5	33.2	33.5
1:2	11.0	8.9	6.5

^a300b pressure in all cases.

Analysis of residual solid material indicates that schoepite (UO₃·2H₂O) and perhaps another phase (as yet unidentified) are present in quantities sufficient to be easily detectable by X-ray. The presence of these phases lends credence to the last two arguments proposed above. Specifically, schoepite may be a quench phase implying that the unidentified phase (or perhaps even an amorphous phase) is Cs bearing. This would support the second argument above. Another possibility is that schoepite and Cs₂U₂O₇ are in equilibrium and that the Cs content of the solution is controlled to some extent by their interaction, which is relatively insensitive to temperature over the range 100° to 300°C. This would support the third argument.

Results of experiments using a 1:2 water to solid mixture are even more perplexing. Decreasing solubility with increasing temperature (in dissolutions which do not produce volatiles) is an infrequently observed phenomenon. However, the data show a decreasing trend and the possibility cannot be rejected out of hand. It is also possible that the results may be complicated by the inversion of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ to $\alpha\text{-Cs}_2\text{U}_2\text{O}_7$. If the two phases have significantly different hydrothermal solubilities (α being less soluble than β), then it is entirely possible that the apparent decrease in solubility with increasing temperature is really a measure of the extent of inversion. It is at least equally likely that the results have been clouded by complications arising from the very low liquid:solid ratio employed. For instance, extensive, well-crystallized schoepite is present in the residuum. If this phase is indeed stable, the water content of each experiment must decrease during the crystallization process. The extent of the decrease will be dependent on the amount of hydrate formed. So, with endothermic reaction, an apparent decrease will result. This argument can also be made, to a lesser extent, if schoepite is not an equilibrium phase.

While the exact interpretation of these results is presently unclear, several conclusions can be drawn from the study. First, it is apparent that $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ has an appreciable hydrothermal solubility and can therefore be expected to be a reactive phase when in contact with basalt. More importantly, the presence of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, whether quench or stable, implies that U^{6+} is present in solution. This is the mobile U species and not a particularly desirable result. While it is reasonable to assume that this is a direct result of the elevated oxygen pressure prevailing during the experiments, and may not occur under likely repository conditions (i.e., in the presence of basalt), it certainly bears mention.

The experiments also indicate areas for future investigation. The 10:1 experiments appeared to reach a plateau near 33.5 wt% Cs (relative) dissolved. If this concentration is a true saturation limit, then it will be a valuable input to thermodynamic models. In addition, the

stability of schoepite must be verified or disproven. The stability relations of this phase may lead to important implications concerning spent fuel elements in the basalt repository environment and identification of undesirable, soluble species.

Basalt Phase or Basalt Interactions With $\beta\text{-Cs}_2\text{U}_2\text{O}_7$

The reactivity of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ with basalt and/or basalt components can be inferred from Table II. By far the most reactive phase is the feldspar, labradorite. At temperatures at or exceeding 200°C, labradorite effectively removes Cs from solution. In contrast, at 100°C there is ~40 relative wt% Cs in solution. This concentration is particularly noteworthy in light of the apparent 11% Cs observed in the experiments using $\text{Cs}_2\text{U}_2\text{O}_7$ and water only. The apparent increase in Cs solubility may result from a decrease in pH coincident with plagioclase dissolution (or reaction) and implies that $\text{Cs}_2\text{U}_2\text{O}_7$ solubility is sensitive to variations in solution pH. However, it appears that at elevated temperatures, labradorite can be considered a formidable barrier to aqueous migration of Cs^+ because it reacts to form pollucite and/or an unidentified phase (or phases) UP-3 (Tables III and IV; Figure 1). At low or moderate temperatures, labradorite enhances Cs mobility, perhaps because it contributes to a decrease in solution pH. Neither pollucite nor UP-3 are observed as products of the 100°C experiments.

At temperatures above 100°C, the least reactive of the basalt components tested was diopside. As with labradorite, the reactivity of diopside (indicated by the drop in Cs content of the solution) increases with temperature. An unidentified phase (UP-1) was detected by XRD. The reflections of this phase bear some resemblance to those of weeksite $[\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}]$. In fact, the pattern shown in Table V may represent more than a single phase. If the structure is indeed a Cs weeksite, and weeksite is an equilibrium phase, then a positive result (in terms of a basalt waste repository) has been produced by the hydrothermal reaction. This is an area for future investigation along with identification of UP-2 and UP-3. Less ambiguous and of certain value is the precipitation of UO_2 as the stable uranium-bearing phase in contact with basalt (Table VI).

TABLE II. X-ray Diffraction Data for the Products of Hydrothermal Treatment of β -Cs₂U₂O₇ at a Water to Solid Ratio of 10:1.

300°C/300b/30 days Products		200°C/300b/60 days Products		100°C/300b/120 days Products		Schoepite, UO ₃ ·2H ₂ O (PDF ³ 13-241)	
d	I	d	I	d	I	d	I
9.92	5						
7.36	90	7.37	60	7.39	90	7.35	100
				6.25	6		
				6.02	6		
4.51	8						
4.44	8	4.45	4	4.46	7	4.46	2
4.29	3	4.32	4	4.33	6		
3.69	100	3.70	100	3.67	90	3.66	50
3.53	15	3.58	15	3.57	25	3.62	2
		3.55	20	3.52	25	3.58	2
3.42	30	3.45	25	3.45	25	3.49	2
3.38	15	3.35	20	3.38	25		
		3.34	20	3.35	25		
						3.24	10
						3.21	4
3.19	70	3.20	60	3.19	100		
3.11	20	3.12	20	3.15	40	3.16	4
				3.13	40		
2.92	8			2.90	8		
2.85	8	2.87	4	2.87	8	2.81	2
		2.79	4	2.83	8		
				2.78	6		
2.55	8	2.58	5	2.56	10	2.57	4
2.51	20	2.52	13	2.52	20	2.53	2
2.46	20	2.47	8			2.45	10
		2.46	8				

TABLE III. X-ray Diffraction Data for the Products of Hydrothermal Treatment of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ at a Water to Solid Ratio of 1:2.

300°C/300b/30 days Products		200°C/300b/60 days Products		100°C/300b/120 days Products		$\alpha\text{-Cs}_2\text{U}_2\text{O}_7$		Schoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (PDF ³ 13-241)	
d	I	d	I	d	I	d	I	d	I
7.34	70	7.37	25	7.41	70			7.35	100
6.95	80	6.98	50	6.96	80	7.00	86		
6.16	4					6.19	--		
5.90	5								
4.41	7							4.46	2
4.10	15	4.09	10	4.10	15	4.10	--		
3.75	20	3.75	15	3.76	20	3.71	42		
3.69	100	3.69	100	3.70	100			3.66	50
3.48	100	3.49	100	3.49	100	3.50	40	3.49	2
3.34	70	3.34	50	3.34	80	3.34	100		
3.21	15	3.21	15	3.20	60			3.24 3.21	10 4
3.17	25	3.19	15						
3.14	45	3.14	30	3.14	55	3.15	65		
3.10	30	3.09	20	3.09	35	3.09	--		
2.82	8	2.81	3	2.82	8	2.82	--	2.81	2
2.69	6	2.70	5	2.70	6	2.70	--		
2.57	20	2.58	8	2.58	15	2.58	--	2.57	4
2.50	4	2.46	10	2.53	6	2.51	--		
2.40	8	2.40	5	2.41	8	2.40	--		
2.33	35	2.33	20	2.33	30	2.33	--		

TABLE IV. Analyses of Cesium Remaining in Solution^b
from Hydrothermally Treated^a Mixtures of Basalt Phases^b
or Basalts^b with Cesium Phases.

Sample Name	Weight of Basalt Phase ^c or Basalt ^c + Cs Phase, mg	Weight of Cs Added, ^d mg	Percent of Cs in Solution		
			100°C	200°C	300°C
<u>Basalt phases or basalts + Cs₂MoO₄ mixtures</u>					
Labradorite	123.7	14.8	12.0	0.3	0.3
Diopside (pyroxene)	124.7	15.4	83.4	76.4	57.0
Glass (mineraloid)	125.9	16.2	84.4	74.9	0.6
BCR-1 basalt	124.2	15.1	72.4	2.3	0.4
DDH-3 basalt	123.7	14.8	84.6	21.8	0.5
<u>Basalt phases or basalts + CsOH mixtures</u>					
Labradorite	116.7	14.8	--	1.5	--
Glass (mineraloid)	118.2	16.2	--	0.6	--
BCR-1 basalt	117.0	15.1	--	0.1	--
DDH-3 basalt	116.7	14.8	--	0.1	--
<u>Basalt phases or basalts + β-Cs₂U₂O₇ mixtures</u>					
Labradorite	147.5	14.8	41.3	0.3	0.6
Diopside (pyroxene)	149.4	15.4	30.3	19.1	4.2
Glass (mineraloid)	151.9	16.2	26.8	10.4	1.6
BCR-1 basalt	148.6	15.1	21.0	11.5	2.8
DDH-3 basalt	147.6	14.8	16.0	10.0	3.8

^aAt 100°C for 4 months, 200°C for 2 months and 300°C for 1 month (300b pressure) in all cases).

^b<75 μ m particle size.

^cWeight of basalt phase or basalt is 100 mg in all cases.

^dMolar ratio of Si in basalt phase or basalt to Cs added in all cases is 8.

FIGURE 1. X-Ray Diffractograms of Hydrothermal Interaction Products of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ with Basalts and Basalt Phases.

TABLE V. X-Ray Diffraction Data for the Unidentified Phases (Refer to Table VI)
after Excluding Basalt Mineral and Pollucite Reflections.

UP-1		Weeksite (PDF 12-462)		UP-2		(Ca,Sr) ₂ U ₇ O ₂₃ · 10H ₂ O (PDF 13-150)		UP-3	
d	I	d	I	d	I	d	I	d	I
9.25	20							9.33	20
		8.98	90	6.86	50	6.82	60	6.83	30
7.11	80	7.11	100			6.06	20		
6.42	30					5.96	10		
5.90	30							5.86	90
		5.57	90	4.73	50				
5.42	20					4.55	20		
		4.83	30					4.14	40
		4.58	40	3.77	50				
		4.48	30	3.52	80	3.53	60		
4.33	50			3.46	100	3.47	80		
		3.84	40	3.38	60				
3.66	60			3.16	80	3.17	50		
3.54	100	3.55	70	3.14	80			3.13	100
3.53	90							3.12	100
3.50	70					3.11	100	3.11	80
3.35	40	3.34	40B					2.95	80
3.32	60	3.30	70					2.92	70
		3.20	50			2.79	30		
3.16	80					2.75	10	2.74	30
		2.99	40	2.69	70			2.70	30
2.90	60	2.91	60	2.67	40				
		2.80	30	2.57	20	2.58	10		
2.67	20								
		2.51	30						

TABLE VI. X-Ray Diffraction Analysis of
Hydrothermally Treated^a Mixtures^b of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$
with Basalt Phases^c or Basalts^c.

Sample and Temperature of Hydrothermal Treatment	Pollucite Formation by XRD	Other Phases by XRD
<u>Basalt phases or basalts + $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ mixtures, 100°C</u>		
Labradorite	ND ^d	$\text{UO}_3 \cdot 2\text{H}_2\text{O}$
Diopside (pyroxene)	ND	UP ^e -1
Glass (mineraloid)	ND	UP-2
BCR-1 basalt	ND	UP-3
DDH-3 basalt	Slight	UP-2
<u>Basalt phases or basalts + $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ mixtures, 200°C</u>		
Labradorite	Very Strong	UP-3
Diopside (pyroxene)	ND	UP-1
Glass (mineraloid)	Trace	UP-2
BCR-1 basalt	Trace	UO_2 ; UP-3
DDH-3 basalt	Slight	UO_2 ; UP-2
<u>Basalt phases or basalts + $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ mixtures, 300°C</u>		
Labradorite	Very Strong	UP-3; UO_2
Diopside (pyroxene)	Slight	$\text{UO}_3 \cdot 2\text{H}_2\text{O}$; UO_2
Glass (mineraloid)	Strong	UP-1
BCR-1 basalt	Very Strong	UO_2 ; UP-1
DDH-3 basalt	Very Strong	UO_2 ; UP-1

^aAt 100°C for 4 months, 200°C for 2 months, and 300°C for 1 month (300b pressure in all cases).

^bMolar ratio of Si in basalt phase or basalt to Cs added in all cases is 8.

^c<75 μm particle size.

^dND = None Detected.

^eUP = Unidentified Phases.

The reactivity of the basalts and glass with $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ is comparable (see Table VI). The close correspondence of these phases may be significant. Although the data are sparse, it can be speculated that either: (1) the glass present in the bulk basalt acts to control reaction with the solution; or (2) the major control on these reactions is bulk composition and that the composition effect overwhelms any contribution of crystal structure.

Basalt Phase or Basalt Interactions with CsOH

The basalt phases or basalts readily reacted with CsOH at 200°C. This inference arises from the very low percentage of Cs remaining in solution (Table IV) as well as strong pollucite formation (Figure 1; Table V). In the case of the labradorite-CsOH reaction, a small amount of CsAlSiO_4 was also formed (Table VII). These experiments indicate that Cs^+ , as might form in CsOH solution, is very reactive in a basalt environment.

Basalt Phase or Basalt Interactions with Cs_2MoO_4

Like CsOH, Cs_2MoO_4 is a highly soluble compound which dissociates readily in water. It is not surprising that it reacts very readily with labradorite to form pollucite, powellite (CaMoO_4), and UP-2 (see Table VIII). However, we have difficulty explaining the Cs_2MoO_4 data shown in Table IV. They are presented here for the sake of completeness, but are considered suspect by the authors. Of particular concern is the drastic difference at 200°C in the reactivity of two very similar basalts and the precipitous rise in reactivity for most components between the temperatures of 200° and 300°C. In conclusion, from elementary chemical considerations Cs_2MoO_4 is expected to behave similarly to CsOH provided solution pH is not a significant variable, and the stability of powellite is somewhat uncertain.

Effect of Changing the Silicate:Cs Ratio on Reactivity

Data obtained at 200°C from experiments in which labradorite and either CsOH or Cs_2MoO_4 were reacted are compared in Figure 2 and Table IX. These data were singled out for illustration because they dramatically

TABLE VII. X-Ray Diffraction Analysis of Mixtures^a of Cs Phases with Basalt Phases^b or Basalts^b which were Hydrothermally Treated^c.

Sample and Temperature of Treatment	Pollucite Formation by XRD	Other Phases by XRD
<u>Basalt phase or basalt + Cs₂MoO₄ mixtures, 100°C</u>		
Labradorite	Strong	Moderate powellite
Diopside (pyroxene)	Slight	Slight powellite
Glass (mineraloid)	ND ^d	ND
BCR-1 basalt	Slight	Slight powellite
DDH-3 basalt	ND	Trace powellite
<u>Basalt phase or basalt + Cs₂MoO₄ mixtures, 200°C</u>		
Labradorite	Very Strong	Strong powellite
Diopside (pyroxene)	Slight	Slight powellite
Glass (mineraloid)	ND	ND
BCR-1 basalt	Very Strong	Moderate powellite
DDH-3 basalt	Moderate	Trace powellite
<u>Basalt phase or basalt + Cs₂MoO₄ mixtures, 300°C</u>		
Labradorite	Very Strong	Strong powellite
Diopside (pyroxene)	Slight	Moderate powellite
Glass (mineraloid)	Very Strong	Moderate powellite
BCR-1 basalt	Very Strong	Strong powellite
DDH-3 basalt	Very Strong	Strong powellite

^aMolar ratio of Si in basalt phase or basalt to Cs added in all cases is 8.

^b<75 μ m particle size.

^cAt 100°C for 4 months, 200°C for 2 months and 300°C for 1 month (300b pressure in all cases).

^dND = None Detected.

TABLE VIII. X-Ray Diffraction Analysis of Mixtures of Cesium Phases and Labradorite^a Hydrothermally Treated at 200°C/300b.

Sample Name and Duration of Hydrothermal Treatment	Molar Ratio of Si in Labradorite to Cs added	Pollucite Formation by XRD	Other Phases by XRD
<u>Labradorite + Cs₂MoO₄ mixtures</u>			
10 days	2	Very Strong	Strong powellite
10 days	8	Very Strong	Moderate powellite
60 days	2	Very Strong	Strong powellite
60 days	8	Very Strong	Moderate powellite
<u>Labradorite + CsOH mixtures</u>			
10 days	2	Very Strong	Moderate CsAlSiO ₄
10 days	8	Very Strong	ND ^b
60 days	2	Very Strong	Moderate CsAlSiO ₄
60 days	8	Very Strong	Slight CsAlSiO ₄

^a<75 μ m particle size.

^bND = None Detected.

FIGURE 2. X-Ray Diffractograms of Hydrothermal Interaction Products of Two Cs Phases with the Basalt Mineral Labradorite.

TABLE IX. Analyses of Cesium Remaining in Solution from Mixtures of Cesium Phases and Labradorite^a Hydrothermally Treated at 200°C/300b for Different Periods.

Sample Name + Cs Phase	Molar Ratio of Si in Labradorite to Cs Added	Weight of Labradorite ^b + Cs Phase mg	Weight of Cs Added, mg	Percent of Cs in Solution	
				10 days	60 days
Labradorite + Cs ₂ MoO ₄	2	194.6	59.1	14.0	13.9
Labradorite + Cs ₂ MoO ₄	8	123.7	14.8	0.3	0.3
Labradorite + CsOH	2	166.7	59.1	12.1	13.1
Labradorite + CsOH	8	116.7	14.8	1.4	1.5

^a<75 μ m particle size.

^bWeight of labradorite is 100 mg in all cases.

illustrate the potential for increased reaction when the bulk rock:waste form ratio is large. By increasing the bulk rock to waste form proportions, in effect one has increased the exchanging cation:Cs ratio. From Le Chatelier's principle, it is easy to see that this drives the reaction toward incorporation of Cs in a stable product. In fact, for reactions with labradorite, which admittedly has a high proportion of exchangeable cation per mole, a four-fold increase in the relative amount of plagioclase yields an order of magnitude increase in the amount of Cs stabilized. Given the very large rock:Cs ratio anticipated in a repository, these results are significant when estimating the capacity of basalt to retain Cs in the near field repository environment.

REACTIONS OF SrZrO_3 WITH WATER

When dissolution of SrZrO_3 in an equal weight of water was attempted over the temperature range 200° to 500°C at 300 bars, it became obvious that the phase was quite stable. Over the entire range of temperature there is an apparent decrease in the amount of Sr in solution, but the variation is on the order of 0.8% which is not statistically significant (Table X). In fact, the bulk of the difference (0.6%) occurs between 300° and 400°C. It is likely that this can be explained by analytical error or impurities or unreacted reagent in the starting materials. No solid phases other than SrZrO_3 were present in quantities sufficient to be detected by XRD.

TABLE X. Strontium Remaining in Solution upon Hydrothermal Treatment of SrZrO_3 as a Function of Temperature at 300 Bars and 28³ Days of Treatment.

Temperature (°C)	Weight of SrZrO_3 , mg	Initial Weight of Sr in Solid, mg	Weight of Sr in Solution mg	% Sr in Solution
200	100.0	38.6	0.95	2.5
300	100.0	38.6	0.92	2.4
400	100.0	38.6	0.74	1.8
500	100.0	38.6	0.66	1.7

Interactions of Basalt Phases or Basalts With SrZrO_3

The hydrothermal interaction of basalts or basalt phases with SrZrO_3 decreased the fraction of Sr remaining in solution (Table XI) relative to when SrZrO_3 was reacted with water alone (see Table X). This decrease in Sr concentration becomes even more significant when the water to SrZrO_3 ratios are taken into consideration. The water to SrZrO_3 ratio was 1:1 when SrZrO_3 was treated with water alone. However, this ratio increases by an unspecified amount when mixtures of basalt phase or basalt with SrZrO_3 are prepared. This change results from the fact that the solid mixtures are only partly composed of SrZrO_3 with the remainder being basalt or basalt phase. Thus, when the mixtures are prepared, and a total water:solid ratio of 1:1 is employed, there is a net increase in the water: SrZrO_3 proportions. With a higher water to SrZrO_3 ratio, more Sr should be present in solution under equilibrium conditions. This increase is not observed following experiments containing the mixtures which suggests that there is some kind of interaction between basalt phases and SrZrO_3 . The exact mechanism of reaction is unclear because the reaction products indicated no new phases by XRD (Table XII).

Basalt or Labradorite Interactions with SrZrO_3

The results of the Sr analyses in solution resulting from SrZrO_3 -basalt interactions show virtually no variation in reactivity between the two basalt samples at either temperature. Solution analysis for Sr in the labradorite mixture at 200°C indicates slightly more Sr than the corresponding basalt- SrZrO_3 mixtures. However, the amount of Sr in solution dropped from 1.0 percent at 200°C to 0.5 percent at 300°C. This correlation, in which the amount of Sr in solution decreases with increasing temperature is probably indicative of usual endothermic reaction. Characterization of the reaction products by XRD, however, showed no perceptible changes in the phases (Table XII).

TABLE XI. SrZrO_3 Interactions with Basalt or Basalt Phases under Hydrothermal^a
Conditions at 200°C for 2 Months and 300°C for 1 Month.

Sample	Weight of Basalt or Basalt Phase + SrZrO_3	Weight of Sr Added, mg	Weight of Sr in Solution, mg	% Sr in Solution
<u>Basalt or basalt phases + SrZrO_3 mixtures at 200°C</u>				
BCR-1	111.8	21.6	0.18	0.9
DDH-3	92.2	17.8	0.12	0.7
Labradorite	102.0	19.7	0.21	1.0
Diopside	95.8	18.5	0.23	1.2
Ilmenite	95.8	18.5	0.16	0.9
Heulandite	97.9	18.9	0.20	1.1
<u>Basalt or basalt phases + SrZrO_3 mixtures at 300°C</u>				
BCR-1	95.8	18.5	0.18	1.0
DDH-3	104.1	20.1	0.15	0.7
Labradorite	99.9	19.3	0.10	0.5
Diopside	106.1	20.5	0.08	0.4
Ilmenite	106.1	20.5	0.16	0.8
Synthetic glass	99.9	19.3	0.14	0.7
Heulandite	102.0	19.7	0.04	0.2

^a300b pressure in both cases.

TABLE XII. X-Ray Diffraction Characterization of
Reaction Products Resultant from Hydrothermal
Treatment of Basalts or Basalt Phases.

Sample	XRD Observations
<u>Treatment at 200°C/300b for 56 days</u>	
BCR-1	No perceptible change
BCR-1 + SrZrO_3	No perceptible change
DDH-3	No perceptible change
DDH-3 + SrZrO_3	No perceptible change
Labradorite	No perceptible change
Labradorite + SrZrO_3	Labradorite slightly decreased
Diopside	No perceptible change
Diopside + SrZrO_3	No perceptible change
Ilmenite	No perceptible change
Ilmenite + SrZrO_3	No perceptible change
Synthetic glass	Partially devitrified (unidentified pattern)
Heulandite + SrZrO_3	No perceptible change
<u>Treatment 300°C/300b for 28 days</u>	
BCR-1	No perceptible change
BCR-1 + SrZrO_3	No perceptible change
DDH-3	No perceptible change
DDH-3 + SrZrO_3	No perceptible change
Labradorite	No perceptible change
Labradorite + SrZrO_3	No perceptible change
Diopside	Poorly crystalline, large amorphous background
Diopside + SrZrO_3	Pyroxene phase is better crystallized; SrZrO_3 diminished in intensity
Ilmenite	No perceptible change
Ilmenite + SrZrO_3	No perceptible change
Synthetic glass	Amorphous background with two peaks at 25.6° and $32.6^\circ 2\theta$
Synthetic glass + SrZrO_3	SrZrO_3 slightly better crystallized
Heulandite	Large amorphous background, unidentifiable peaks at 26.2 , 27.5 and $27.9^\circ 2\theta$
Heulandite + SrZrO_3	Large amorphous background, SrZrO_3 greatly decreased

Additional tests were conducted to investigate reactions between individual phases and SrZrO_3 . These phases included diopside, ilmenite, heulandite, and synthetic glass. Because of the extremely low hydrothermal solubility of SrZrO_3 very little could be elucidated from these results. The results are tabulated and presented without discussion. It seems quite safe to say that SrZrO_3 is a phase which is very resistant to hydrothermal alteration and/or dissolution and will probably remain unreacted and in place for the life of the repository.

SUMMARY AND CONCLUSIONS

This investigation has determined that some Cs compounds likely to be stable components of spent fuel (i.e., CsOH , Cs_2MoO_4 , $\text{Cs}_2\text{U}_2\text{O}_7$) have significant hydrothermal solubilities. However, these solubilities are greatly decreased in the presence of basalt and/or basalt minerals. The decrease in the amount of Cs in solution results from reactions which form pollucite and/or CsAlSiO_4 , with the production of pollucite exceeding that of CsAlSiO_4 .

Dissolution of $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ implies solubilizing a uranium species to an undetermined extent. The production of schoepite ($\text{UO}_3 \cdot 3\text{H}_2\text{O}$) during some experiments containing basalt phases, indicates a tendency to oxidize U^{4+} to U^{6+} . However, when diopside (nominally $\text{CaMgSi}_2\text{O}_6$) and $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ were hydrothermally reacted, at 300°C both UO_2 and $\text{UO}_3 \cdot 3\text{H}_2\text{O}$ were produced. This may suggest that either the equilibrium conditions for oxidation of U^{4+} to U^{6+} was approached or that the stability fields of both species were intersected during the run. In either case, the experiment shows that UO_2 is a stable phase at 300°C under comparatively oxidizing conditions. The fact that no $\text{UO}_3 \cdot 3\text{H}_2\text{O}$ is observed in results from experiments containing bulk basalt supports the hypothesis that iron components of the rock reduce available oxygen to the point that oxidation of U^{4+} is restricted. The extent of oxidation and dissolution of uranium remains to be tested.

Results of experiments on SrZrO_3 show it to be an unreactive phase. Interpretations of the hydrothermal phase relations of SrZrO_3 in the presence of basalt are obscured by its low solubility. In contrast to the results obtained from experiments on Cs compounds, no phases other than the reactants were detected following either SrZrO_3 -water or SrZrO_3 -water-basalt experiments. Given the extreme insolubility of ZrO_2 in distilled water, and the detectable amounts of Sr in solution, it seems likely that some unobserved phase (possibly ZrO_2) may have been present following SrZrO_3 -water experiments. This may also have occurred during the SrZrO_3 -water-basalt tests, which showed less dissolved Sr than the SrZrO_3 -water tests. Because of the small amount of Sr in solution, it is also possible that Sr may have been incorporated by the reactants.

Finally, it can be stated that there are several observable controls on the potential for a biohazard produced by the dissolution of the Cs/Sr phases investigated. As with most hydrothermal reactions, after temperature, the most important parameter is the water:solid ratio. Of less, but still significant importance are the exchangeable cation:Cs (and probably Sr) ratio and oxygen fugacity. It is recognized that additional parameters, such as pH, are also potentially important to these reactions. However, the effects of pH as with other interesting relations identified in this manuscript are left for subsequent investigation.

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