

HYDROTHERMAL REACTIONS OF CLAY MINERALS AND SHALES WITH CESIUM PHASES FROM SPENT FUEL ELEMENTS

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Abstract—The immobilization of soluble Cs from spent fuel elements by ion exchange and direct chemical reaction with clay minerals or shales was investigated under hydrothermal conditions. Various clay minerals or shales were reacted with likely Cs sources and water at 300 bars pressure and 100°, 200°, and 300°C for 4, 2, and 1 months, respectively. Pollucite was the principal product, but CsAlSiO₄ was also observed, along with unreacted or hydrothermally altered aluminosilicates. From Cs concentrations of the product solutions partition of Cs between liquid and solids was found to vary depending on the Cs source, the clay or shale phase, temperature, and run duration. For example, illite-Cs₂MoO₄ interactions resulted in 19, 32, and 95% fixation of added Cs at 100°, 200°, and 300°C, respectively. Fixation of as much as 97% of the Cs in some solids was observed. In addition to Cs-aluminosilicates, Cs was fixed on cation-exchange sites by interlayer collapse in montmorillonite. Reactions with Cs₂MoO₄ also produced powellite because Ca was available in the reaction mixture. The U⁶⁺ from β-Cs₂U₂O₇ was reduced to form uraninite by sulfide- and/or organic-rich shales. (Cs,Na)₂(UO₂)(Si₂O₅)₃·4H₂O, an analog of weeksite, was produced in reactions with β-Cs₂U₂O₇. The reaction products pollucite and uraninite can immobilize much of the Cs and U from spent fuel elements because Cs in pollucite is extremely difficult to exchange and U in uraninite is insoluble.

Key Words—Cesium, Hydrothermal, Illite, Nuclear waste, Pollucite, Shale, Uranium.

INTRODUCTION

The research described here is part of a continuing program aimed at understanding the chemical reactions between nuclear waste materials and shale repositories in the presence of hot, pressurized ground water. This paper treats the immobilization of Cs released from spent fuel elements (SFE) by simulated hydrothermal fluids when this fission product interacts with clay minerals in the repository wall rock (McCarthy *et al.*, 1978; Komarneni and Roy, 1980).

Shale is one of the rock types considered suitable for nuclear waste repositories. To span the normal range of shale compositions, six different shales were examined in this study. Typical clay mineral components of shales were also reacted with Cs sources in order to understand the reactions of shales and their constituent phyllosilicate minerals with Cs. The Cs-containing phases actually present in SFE are not known with certainty but frequently cited possibilities are cesium uranates, Cs₂MoO₄, CsI, and Cs₂O (O'Hare and Hockstra, 1975; Osborne *et al.*, 1976). Cs₂O would instantly react with water to form CsOH. The compounds β-Cs₂U₂O₇, Cs₂MoO₄, CsI, and CsOH were chosen as representative examples for the present investigation.

The present experiments are applicable to repository behavior during the early thermal period (Cohen, 1977). The source of water in repositories could be trapped

water in the shales, infiltrating ground water, or an accidental flooding of the repository. The source of heat would be the decay heat of the waste, which would be less for SFE-type waste than for other wastes with higher loadings of fission products. The experiments reported here offer some guidance on the expected behavior of the waste material if the canister and Zircaloy cladding were breached and if water served as a reaction medium connecting the waste with the surrounding shale.

The present experiments used closed systems and provided data which are suitable for exploring the reactivity of solid-liquid systems and for establishing the direction of thermodynamic equilibrium. Water was present in excess so that all phase assemblages included a liquid phase whose composition was determined by the solubility of the various reactants and products. Analysis of the final solutions permitted an evaluation of partitioning of Cs between liquid and solids. Solution variables such as Eh and pH were fixed by the bulk composition and could not be varied independently. Another important consideration in the design of these experiments was the proportion of Cs to rock. The experiments were designed to study the reactions and not to model precisely a repository. Compared to the Cs:rock ratios used here, an actual repository would have a much greater proportion of shale.

Although these studies were directed towards spent fuel elements, many of the results are equally applicable to any nuclear waste form that could release Cs to solutions in a shale repository. The results are also ap-

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Table 1. Names, locations and/or sources and particle sizes of samples.

1. Kaolinite. Morro de Felipe deposits, Brazil. Yara Engineering Corporation, Georgia (courtesy G. W. Brindley). Pulverized.
2. Montmorillonite. Cheto, Arizona. SAZ-1. Source Clays Repository of the Clay Minerals Society. Pulverized.
3. Mica (green). Paços de Caldas, Brazil (courtesy G. W. Brindley). <105 μm .
4. Illite. Fithian, Illinois, Illinois Clay Products Company, Joliet, Illinois. <105 μm .
5. Chlorite. Anderson soapstone pit, Saline County, Arkansas (courtesy G. W. Brindley). <105 μm .
6. Shale. Salona Formation, Huntingdon County, Pennsylvania. <75 μm .
7. Shale. Antrim Formation, Alpena County, Michigan. <75 μm .
8. Shale. Brallier Formation, Huntingdon County, Pennsylvania. <75 μm .
9. Shale. Conasauga Formation, Oak Ridge Reservation, Tennessee. <75 μm .
10. Shale. Catskill Formation (oxidized and reduced types), Huntingdon County, Pennsylvania. <75 μm .

plicable to the design of reactive buffers or "overpacks" to be inserted around SFE assemblies or canisters in a nuclear waste repository.

EXPERIMENTAL

Materials

The clay minerals and shales used in the study are described in Table 1. The chemical and mineralogical composition of the six shales examined are listed in Table 2. Cs_2MoO_4 , CsI, and CsOH were obtained from a chemical supply house, and $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ was synthesized in the laboratory (Komarneni and Scheetz, 1981).

Methods

The clay minerals and shales were dry ground and sieved to obtain <105- μm and <75- μm fractions. X-ray diffraction (XRD) analysis of powders packed in glass cavities was carried out with a Philips diffractometer using $\text{CuK}\alpha$ radiation. Chemical analysis of the shales was performed by a lithium borate fusion technique (Medlin *et al.*, 1969).

Each sample was sealed with each Cs phase along with 50% by weight of water in gold capsules (Komarneni *et al.*, 1979) and reacted hydrothermally at 300 bars pressure and 100°, 200°, and 300°C for 4, 2 and 1 months, respectively. The reaction periods were increased with a decrease in temperature so that enough reaction product would crystallize at lower temperatures to enable detection by XRD. Details of the hydrothermal experimentation were described by McCarthy *et al.* (1980). The reaction capsules were weighed before and after the hydrothermal runs to insure that the systems were closed. The amount of Cs added was adjusted to give high (8) and low (2) Si:Cs

ratios. Nominal chemical formulae were used to calculate the amount of Si in the clay minerals, and the actual chemical compositions (Table 2) were used to calculate the amount of Si in the shales.

At the completion of a hydrothermal run, the solid and solution phases from the capsules were separated as follows: the gold capsule was cut open in a long glass vial, and 20 ml of 0.1 N KCl was added. The glass vial was capped, and the contents were mixed in a shaker for about 15 min. The gold capsule free of sample was then removed from the vial with tweezers. The vials were centrifuged and a portion of the supernatant was collected in polyethylene bottles without disturbing the sediment. This procedure extracted the Cs present in solution and probably any Cs that was weakly adsorbed on the solids. The 0.1 N KCl served three purposes: (1) it brought easily exchangeable Cs, if any, into solution; (2) it helped to flocculate the sample during centrifugation, and (3) it removed the ionization interference during Cs analysis by atomic absorption (AA) spectrophotometry. The solid samples were then washed once with a water and acetone mixture and thrice with 95% acetone to remove the KCl. The solutions in the polyethylene bottles were analyzed for Cs by AA using a Perkin Elmer PE403 instrument.

RESULTS AND DISCUSSION

Interactions of Cs_2MoO_4 and CsOH with clays or shales

Clay-shale intercalations with Cs_2MoO_4 . The percentage of Cs remaining in solution decreased with an increase in temperature when Cs_2MoO_4 reacted with the clays and shales (Table 3). If the Cs had not reacted with clays or had not adsorbed strongly onto the clays, all of the Cs would have been present in the solutions because Cs_2MoO_4 is highly soluble (66.6 g/100 g at 18°C, Seidell, 1940). The reaction of Cs_2MoO_4 with clays or shales at high temperatures produced pollucite, $\text{CsAlSi}_2\text{O}_6$ (Table 3). Pollucite was not produced in any of the 100°C runs because of insufficient reaction as indicated by a high percentage of Cs remaining in solution (Table 3). Only for Ca-montmorillonite was a considerable percentage (~46%) of the added Cs retained at 100°C because of Cs exchange for Ca in the interlayers of the phyllosilicate. The evidence for this exchange was a decrease in $d(001)$ of the montmorillonite to ~12 Å and the formation of powellite, CaMoO_4 (Figure 1).

The reaction of Cs_2MoO_4 with clays or shales increased at 200°C and substantially increased at 300°C as indicated by the small percentages of Cs remaining in solution as well as by the formation of pollucite (Table 3). Pollucite was detected at 200°C with only a few of the clays but with all of the shales (Table 3). The oxidized Catskill shale was much more reactive with Cs than the reduced Catskill shale (Table 3), a difference that may be attributed to the smaller amount of Al in

Table 2. Chemical and mineralogical analyses of reference shales.

Constituent	Salona (carbonate- rich shale)	Antrim (sulfide- and organic-rich shale)	Brallier (clay-rich shale)	Conasauga (clay-rich shale)	Catskill (reduced shale)	Catskill (oxidized shale)
SiO ₂	47.0%	59.8%	56.7%	54.7%	77.6%	67.3%
Al ₂ O ₃	12.3	12.9	21.1	21.3	6.12	13.5
TiO ₂	0.51	0.75	0.91	0.91	0.50	0.88
Fe ₂ O ₃	1.66	3.27	5.27	4.15	2.00	4.01
FeO	0.57	2.87	2.79	4.59	5.17	2.63
MgO	1.95	1.44	1.80	2.25	1.80	1.74
CaO	15.0	0.47	0.02	0.52	3.13	0.67
MnO	0.04	0.03	0.045	0.060	0.16	0.07
SrO	—	—	0.011	0.017	0.005	—
BaO	—	—	0.069	0.078	0.020	—
Na ₂ O	0.72	0.63	0.36	0.74	1.01	1.11
K ₂ O	2.47	3.45	5.14	4.14	1.44	3.40
P ₂ O ₅	0.17	0.08	0.10	0.11	0.12	0.15
S	0.02	2.88	0.01	0.63	0.01	0.01
H ₂ O ⁻	1.84	1.25	0.92	0.96	0.09	0.64
H ₂ O ⁺	3.03	6.72	4.21	4.97	0.96	2.46
Cl	—	—	0.02	0.04	0.02	—
C	0.61	6.28	0.05	0.31	0.14	0.10
CO ₂	11.69	0.19	0.12	0.26	4.38	0.49
Less O ≡ S	0.01	1.26	—	0.31	—	0.00
Totals	100.47%	101.75%	99.64%	100.41%	99.68%	99.16%

Principal minerals in order of abundance as determined by XRD						
Calcite	Illite	Illite	Illite	Quartz	Quartz	Quartz
Quartz	Quartz	Quartz	Quartz	Illite	Illite	Illite
Illite	Pyrite	Kaolinite	Kaolinite	Feldspars	Feldspars	Feldspars
Feldspars	Feldspars	Chlorite	Feldspars	Calcite	Chlorite	

the latter (Table 2). Feldspars, illite, and kaolinite in the shales (Table 2) reacted with Cs₂MoO₄ to form pollucite. That plagioclase feldspars readily react with Cs₂MoO₄ to form pollucite and powellite (CaMoO₄) was demonstrated in other experiments on waste-rock interaction in basalt by McCarthy *et al.* (1979). Whenever Ca was present in the reaction mixture, Mo from Cs₂MoO₄ reacted with it to form powellite (Figure 1). At 300°C all of the clays except montmorillonite and all of the shales reacted to form large amounts of pollucite (Table 3) which suggests that this mineral is very stable under these hydrothermal conditions. Pollucite is a desirable product of the reaction of clays and shales with Cs because the Cs in pollucite is difficult to exchange up to 300°C (Komarneni *et al.*, 1978; Komarneni and White, 1981).

In Figure 2, compositions of experimental mixtures are plotted in the system Si–Cs–(Na + K). At a Si:Cs ratio of 8, the chemical compositions of various mixtures of shales and Cs phases fell in the compositional field of albite-quartz-pollucite. As expected from these compositions, pollucite was a dominant reaction product in almost all the runs at 300°C (Table 3). With a Si:Cs molar ratio of 2, the chemical composition of green

mica + Cs fell in the compositional field of nephelene-pollucite-CsAlSiO₄. Pollucite and CsAlSiO₄ were found as coproducts when green mica was treated with CsOH (Si:Cs = 2) as is discussed below. These results point out that the major control of pollucite formation is probably bulk composition and that the composition effect overwhelms any structural differences of the starting minerals involved.

Clay-shale interactions with CsOH. Highly soluble CsOH (75 g/100 g at 30°C, Seidell, 1940) reacted with all clays and shales as indicated by the small percentage of Cs remaining in solution (Table 3) as well as by the profuse formation of pollucite with all of the clays, except chlorite, and with all of the shales. Thus, Cs was fixed mainly as pollucite in all CsOH-clay or CsOH-shale reaction products except in the reaction between CsOH and green mica (Table 4). This reaction produced CsAlSiO₄ along with a small quantity of CsAlSi₂O₈ (Figure 1; Table 4), a result that may have been due to excess aluminum in the reaction mixture. The formation of Cs-aluminosilicates effectively fixed the released Cs. Recent data confirm that the Cs in pollucite and CsAlSiO₄ is not exchangeable at low temperatures (Komarneni *et al.*, 1978).

Table 3. Analyses of Cs remaining in solution and of pollucite formation from various mixtures¹ of clays or shales and Cs sources.

Sample	Weight of clay ² or shale ² + Cs phase (mg)	Weight of Cs added ³ (mg)	100°C		200°C		300°C	
			% Cs in solution	Pollucite formation by XRD	% Cs in solution	Pollucite formation by XRD	% Cs in solution	Pollucite formation by XRD
<i>Cs₂MoO₄ source</i>								
Kaolinite	120.8	12.9	89.7	ND ⁴	88.4	SI	15.9	SI
Montmorillonite	127.8	17.2	53.7	ND	55.6	ND	38.8	ND
Mica	120.5	12.5	92.1	ND	77.7	ND	42.5	St
Illite	128.6	17.8	81.3	ND	68.3	SI	4.7	V. St
Chlorite	114.4	9.0	97.3	ND	83.8	Tr	69.2	SI
Salona shale	120.9	13.0	89.1	ND	44.3	M	13.4	V. St
Antrim shale	126.6	16.6	93.5	ND	75.3	M	5.2	V. St
Brallier shale	125.2	15.7	92.3	ND	64.9	M	10.8	V. St
Conasauga shale	124.3	15.2	88.0	ND	17.9	V. St	5.0	V. St
Catskill shale, reduced	134.5	21.5	96.4	ND	71.0	St	46.2	V. St
Catskill shale, oxidized	129.9	18.7	86.1	ND	66.9	St	7.4	V. St
<i>CsI source</i>								
Kaolinite	125.2	12.9	—	—	—	—	92.9	ND
Montmorillonite	133.6	17.2	—	—	—	—	49.4	ND
Mica	124.5	12.5	—	—	—	—	81.5	ND
Illite	134.8	17.8	—	—	—	—	75.4	ND
Chlorite	117.6	9.0	—	—	—	—	81.8	SI
Salona shale	125.5	13.0	—	—	—	—	30.8	V. St
Antrim shale	132.4	16.6	—	—	—	—	69.4	St
Brallier shale	130.7	15.7	—	—	—	—	84.3	ND
Conasauga shale	129.7	15.2	—	—	85.0	ND	63.7	ND
Catskill shale, reduced	142.1	21.5	—	—	99.9	ND	66.6	St
Catskill shale, oxidized	136.5	18.7	—	—	—	—	48.9	V. St
<i>CsOH source</i>								
Kaolinite	114.6	12.9	—	—	5.4	St	—	—
Montmorillonite	119.6	17.2	—	—	3.4	V. St	—	—
Mica	114.5	12.5	—	—	19.7	Tr	—	—
Illite	120.1	17.8	—	—	4.8	St	—	—
Chlorite	110.1	9.0	—	—	73.0	ND	—	—
Salona shale	114.7	13.0	—	—	17.6	V. St	—	—
Antrim shale	118.7	16.6	—	—	18.9	V. St	—	—
Brallier shale	117.7	15.7	—	—	17.6	V. St	—	—
Conasauga shale	117.1	15.2	—	—	8.1	V. St	—	—
Catskill shale, reduced	124.3	21.5	—	—	26.4	V. St	—	—
Catskill shale, oxidized	121.1	18.7	—	—	22.4	V. St	—	—
<i>β-Cs₂U₂O₇ source</i>								
Kaolinite	141.4	12.9	37.9	ND	7.8	SI	9.0	Tr
Montmorillonite	155.3	17.2	29.3	ND	35.5	ND	25.4	ND
Mica	140.2	12.5	30.5	ND	19.8	ND	5.5	St
Illite	157.2	17.8	31.3	ND	31.2	M	2.0	V. St
Chlorite	128.9	9.0	35.1	ND	16.3	ND	7.4	Tr
Salona shale	141.9	13.0	19.5	ND	10.5	ND	4.3	St
Antrim shale	153.3	16.6	18.5	ND	24.9	ND	19.1	St
Brallier shale	150.5	15.7	20.5	ND	11.4	ND	5.8	St
Conasauga shale	148.7	15.2	35.2	ND	17.9	St	9.7	St
Catskill shale, reduced	169.1	21.5	20.9	ND	7.7	Tr	46.7	Tr
Catskill shale, oxidized	160.0	18.7	17.0	ND	7.9	ND	22.5	M

¹ Hydrothermally treated at 100°, 200° and 300°C/300 bars for 4, 2, and 1 months, respectively.

² Weight of clay or shale is 100 mg in all cases.

³ Molar ratio of Si in clay or shale to Cs added in all cases is 8.

⁴ ND = None detected; Tr = Trace; SI = Slight; M = Moderate; St = Strong; V. St = Very strong.

Differences in reactivity of clay minerals with Cs₂MoO₄ and CsOH at 200°C. The difference between the reactivity of Cs₂MoO₄ and CsOH with clays and shales can be seen from the data in Table 3. Analyses for Cs re-

maining in solutions (Table 3) indicate that only a small percentage of the added Cs reacted with the clays or shales when Cs₂MoO₄ was the source, whereas >70% (<28% Cs remaining in solution) of the added Cs re-

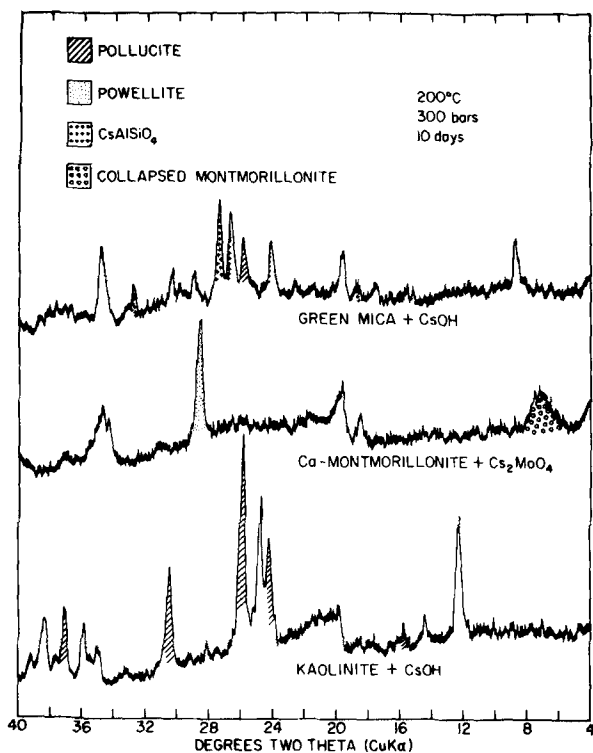


Figure 1. X-ray powder diffractograms of the hydrothermal reaction products of Cs phases and clays, depicting Cs-fixation mechanisms.

acted with the shales or clays (except chlorite) when CsOH was the source. That CsOH reacted readily with the clays or shales is not surprising because the high-pH CsOH solution decomposed the clay and formed Cs-aluminosilicates (Table 4).

Effect of time on reactivity. The cesium molybdate phase was slow in reacting with the various clay minerals even after 60 days. Analyses for Cs in solution and XRD analysis (Table 4) indicate a clear distinction between the 10- and 60-day runs with a greater amount of Cs immobilized (i.e., less Cs in solution) after 60 days of treatment. Pollucite was observed in all Cs₂MoO₄-clay reaction products (Si:Cs = 2) after the 60-day treatment, whereas pollucite was detected only in kaolinite and illite runs after 10 days of hydrothermal treatment. Some clays were consumed (Table 4) to form Cs-aluminosilicates, as evidenced by XRD.

Montmorillonite-Cs₂MoO₄ reactions resulted in slightly different reactions depending upon the duration of treatment. Irrespective of the Si:Cs ratio, the same amount (5.5 mg) of Cs was retained against displacement by KCl (Table 4) in the interlayers of montmorillonite after 10 days of treatment. After 60 days of treatment, however, pollucite was detected at a low Si:Cs ratio but not at a high Si:Cs ratio. The quantity of pollucite formed at the latter ratio was probably too small

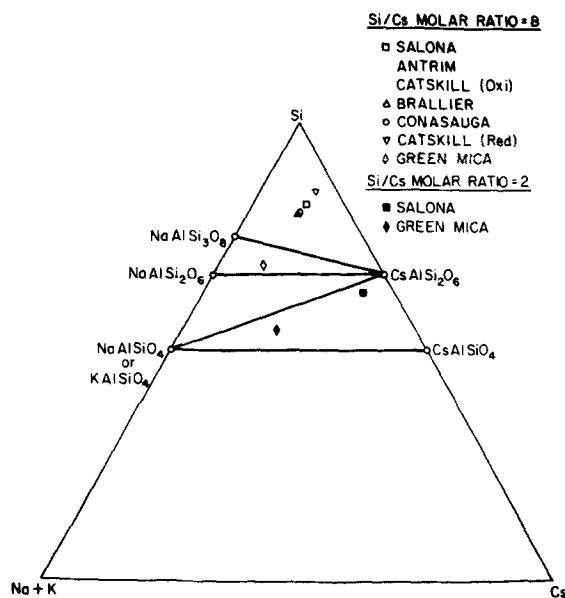


Figure 2. Compositions of experimental mixtures, plotted in system Si-Cs-(Na + K).

to be detected by XRD analysis (Table 4). Thus, montmorillonite with interlayer Cs seems to be a metastable phase, with pollucite forming with an increase in either treatment time or temperature.

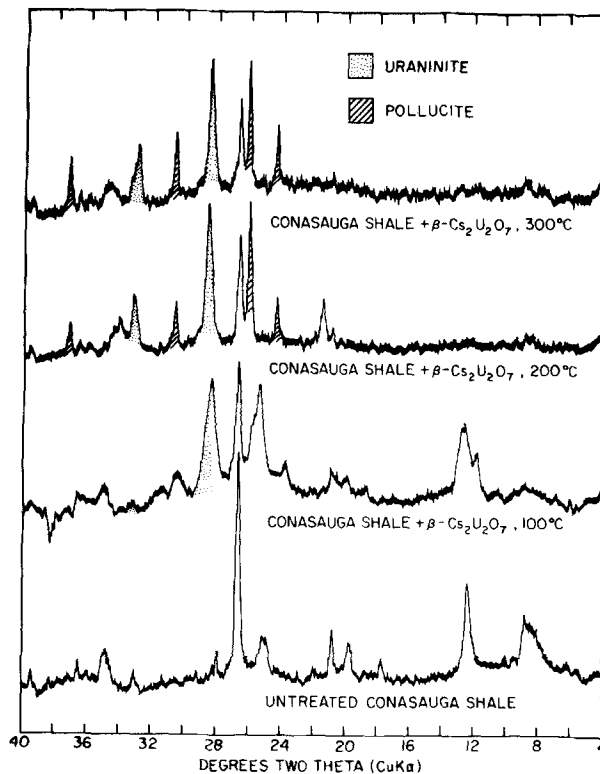


Figure 3. X-ray powder diffractograms of hydrothermal reaction products of β -Cs₂U₂O₇ and Conasauga shale.

Table 4. Analyses of Cs remaining in solution and XRD analysis of various mixtures¹ of Cs phases with clays.

Sample	Molar ratio of Si in clay to Cs added	Weight of Cs added (mg)	% Cs in solution	Pollucite formation by XRD	Changes in clay by XRD	Other phases by XRD
<i>Clay² + Cs₂MoO₄ mixtures heated for 10 days</i>						
Kaolinite	2	51.6	97.9	Slight	No obvious change	ND ³
Kaolinite	8	12.9	93.8	Slight	No obvious change	ND
Montmorillonite	2	69.6	92.1	ND	15.5 Å collapsed to ~12 Å	Powellite
Montmorillonite	8	17.4	68.7	ND	15.5 Å collapsed to ~12 Å	Powellite
Mica	2	51.2	86.9	ND	No obvious change	ND
Mica	8	12.8	85.2	ND	No obvious change	ND
Illite	2	71.2	91.3	Moderate	Better crystallized	ND
Illite	8	17.8	84.8	ND	Better crystallized	ND
<i>Clay + Cs₂MoO₄ mixtures heated for 60 days</i>						
Kaolinite	2	51.6	75.2	Moderate	Some clay consumed	ND
Kaolinite	8	12.9	88.4	Slight	No obvious change	ND
Montmorillonite	2	69.6	71.1	Moderate	Most clay consumed	Powellite
Montmorillonite	8	17.4	55.6	ND	15.5 Å collapsed to ~12 Å	Powellite
Mica	2	51.2	92.7	Slight	No obvious change	ND
Mica	8	12.8	77.7	ND	No obvious change	ND
Illite	2	71.2	85.1	Moderate	Better crystallized	ND
Illite	8	17.8	68.3	Slight	Better crystallized	ND
<i>Clay + CsOH mixtures heated for 10 days</i>						
Kaolinite	2	51.6	2.1	Very strong	Totally consumed	Boehmite
Kaolinite	8	12.9	7.8	Strong	Some clay consumed	Boehmite
Montmorillonite	2	69.6	28.3	Very strong	Totally consumed	ND
Montmorillonite	8	17.4	14.7	Strong	15.5 Å collapsed to ~12 Å	ND
Mica	2	51.2	6.4	Moderate	Totally consumed	Strong CsAlSiO ₄
Mica	8	12.8	28.0	Slight	Some clay consumed	Moderate CsAlSiO ₄
Illite	2	71.2	14.4	Strong	Totally consumed	Slight CsAlSiO ₄
Illite	8	17.8	8.1	Strong	Better crystallized	ND
<i>Clay + CsOH mixtures heated for 60 days</i>						
Kaolinite	2	51.6	1.9	Very strong	Totally consumed	Boehmite
Kaolinite	8	12.9	5.4	Strong	Most clay consumed	Boehmite
Montmorillonite	2	69.6	29.4	Very strong	Totally consumed	ND
Montmorillonite	8	17.4	3.4	Very strong	15.5 Å collapsed to ~12 Å	ND
Mica	2	51.2	4.3	Slight	Totally consumed	Very strong CsAlSiO ₄
Mica	8	12.8	19.7	Trace	Some clay consumed	Moderate CsAlSiO ₄
Illite	2	71.2	11.8	Very strong	Totally consumed	Slight CsAlSiO ₄
Illite	8	17.8	4.8	Strong	Most clay consumed	ND

¹ = Hydrothermally treated at 200°C and 300 bars pressure.

² Weight of clay is 100 mg in all cases.

³ ND = None detected.

Analyses for Cs remaining in solution and XRD analyses of various CsOH-clay reaction products (Table 4) revealed no significant differences between the 10- and 60-day runs which indicates that the reaction was essentially complete after 10 days. Thus, the reactivity of Cs₂MoO₄ appeared to be time dependent but that of CsOH did not under these experimental durations.

Effect of Si:Cs molar ratio on reactivity. Pollucite was detected in almost all of the runs at both Si:Cs ratios

(Table 4). The quantity of pollucite produced in some of the Cs-clay reactions at a Si:Cs ratio of 8 may have been too small to be detected by XRD (Table 4) because the amount of Cs available for pollucite formation is lower than with a Si:Cs ratio of 2. However, the percentage of added Cs incorporated in the solids was higher at the higher Si:Cs ratio than at the lower ratio (Table 4). This is a very significant result because the rock:waste ratio would be large under natural conditions, i.e., Si:Cs ratios would be large.

Table 5. X-ray diffraction analysis of various mixtures of β -Cs₂U₂O₇ with clays or shales.¹

Sample	Mineralogical changes by XRD ²	New phases other than pollucite by XRD ²
100°C		
Kaolinite	No obvious change	UP-1; UO ₃ ·~2H ₂ O
Montmorillonite	None detected, masked?	UP-2; UO ₃ ·~2H ₂ O
Mica	No obvious change	UP-1; UO ₃ ·~2H ₂ O
Illite	Better crystallized	UP-1; UO ₃ ·~2H ₂ O
Chlorite	No obvious change	UP-1; UO ₃ ·~2H ₂ O
Salona shale	No obvious change	UP-1; UO ₃ ·~2H ₂ O
Antrim shale	No obvious change	UP-1; UO ₂ ; UO ₃ ·~2H ₂ O
Brallier shale	No obvious change	UP-1; UO ₃ ·~2H ₂ O
Conasauga shale	No obvious change	UP-1; UO ₃ ·~2H ₂ O; UO ₂
Catskill shale, reduced	No obvious change	UP-1; UO ₂
Catskill shale, oxidized	No obvious change	UP-1; UO ₂
200°C		
Kaolinite	No obvious change	UP-1; UO ₂
Montmorillonite	15.5 Å collapsed to ~12 Å	UP-1; UO ₂
Mica	No obvious change	UP-1; UO ₂
Illite	Some clay consumed	UP-1; UO ₂
Chlorite	No obvious change	UP-1; UO ₃ ·~2H ₂ O
Salona shale	No obvious change	UP-1; UO ₂
Antrim shale	No obvious change	UP-1; UO ₂
Brallier shale	Illite decreased	UP-1
Conasauga shale	F and K disappeared; Illite decreased	UO ₂
Catskill shale, reduced	No obvious change	UP-1; UO ₂
Catskill shale, oxidized	Illite decreased	UP-1; UO ₂
300°C		
Kaolinite	Most clay consumed	UO ₃ ·~2H ₂ O
Montmorillonite	15.5 Å collapsed to ~12 Å	UP-3
Mica	Some clay consumed	UP-4
Illite	Totally consumed	UO ₂
Chlorite	No obvious change	UP-1; UO ₃ ·~2H ₂ O
Salona shale	Illite decreased	UP-3; UO ₂
Antrim shale	Illite decreased	UO ₂
Brallier shale	Illite decreased	UP-3; UO ₂
Conasauga shale	Illite and K decreased	UO ₂
Catskill shale, reduced	Illite decreased	UP-5; UO ₂
Catskill shale, oxidized	Illite decreased	UP-5; UO ₂

¹ Hydrothermally treated at 100°, 200° and 300°C/300 bars for 4, 2, and 1 months respectively. Molar ratio of Si in clay or shale to Cs added in all cases is 8.

² UP = Unidentified phase; F = Feldspars; K = Kaolinite.

Clay-shale interactions with CsI

CsI is highly soluble (46.1 g/100 g at 25°C, Seidell, 1940). This phase did not react with clays or shales as readily as Cs₂MoO₄ or CsOH at both 200° and 300°C, as indicated by the larger percentage of added Cs remaining in solution (Table 3). At 200°C, no pollucite was detected in the reaction products from two shales by XRD analysis, but at 300°C pollucite was detected in the products of the chlorite and four of the six shales (Table 3). In reactions with montmorillonite, Cs from CsI was fixed mainly in the interlayers as indicated by a decrease in the *d*(001) spacing from 15.5 Å to ~12 Å. Cs from CsI seems to have reacted readily with feldspars of shales to produce pollucite (Table 3), but not with illite, as indicated by the percentage of Cs remain-

ing in solution in the illite and green mica reactions (Table 3).

Clay-shale interactions with β -Cs₂U₂O₇

The reaction of β -Cs₂U₂O₇ with clays or shales was affected by the somewhat lower solubility of this Cs phase (Komarneni, 1981) which is much less than that of Cs₂MoO₄ and CsOH. The Cs in solution after these reactions was determined by the solubility of unreacted β -Cs₂U₂O₇ as well as by the extent of Cs-clay or Cs-shale reactions. Pollucite was not detected in the 100°C reaction products with any of the clays or shales but was detected with some of the clays or shales at 200°C and with all of the clays except montmorillonite and with all the shales at 300°C (Table 3). As expected, the

Table 6. X-ray diffraction data¹ for unidentified phases listed in Table 5.

UP-1		Weeksite (PDF 12-462) ²		UP-5		UP-2		(Ca,Sr) ₂ U ₇ O ₂₃ ·10H ₂ O (PDF 13-150)		UP-3		UP-4	
<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
—	—	8.98	90	8.94	80	6.82	70	6.82	60	6.65	30	6.43	100
7.11	70	7.11	100	7.10	50	—	—	6.06	20	—	—	6.31	35
6.44	30	—	—	6.41	25	5.98	8	5.96	10	5.92	40	6.10	10
—	—	—	—	5.86	20	—	—	—	—	5.86	50	5.60	10
5.48	15	5.57	90	5.55	40	5.43	5	—	—	—	—	5.57	10
4.75	15	4.83	30	—	—	4.77	9	—	—	—	—	4.48	20
—	—	4.58	40	4.55	40	—	—	4.55	20	—	—	4.13	15
—	—	4.48	30	—	—	—	—	—	—	4.29	30	3.32	25
4.33	40	—	—	—	—	—	—	—	—	4.20	60	3.22	70
—	—	3.84	40	3.84	40	—	—	—	—	3.61	50	3.06	20
3.66	50	—	—	—	—	—	—	—	—	3.59	50	3.05	20
3.55	80	—	—	—	—	—	—	3.53	60	3.54	70	2.58	15
3.53	100	3.55	70	3.54	60	3.47	70	3.47	80	—	—	2.56	25
3.49	70	—	—	3.50	50	3.42	60	—	—	—	—	—	—
—	—	3.34	40B	—	—	—	—	—	—	3.30	60	—	—
—	—	3.30	70	—	—	3.17	20	3.17	50	—	—	—	—
3.21	25	3.20	50	3.19	90	3.10	100	3.11	100	3.13	100	—	—
3.16	50	—	—	3.18	90	2.96	9	—	—	—	—	—	—
3.15	40	—	—	—	—	2.92	9	—	—	2.92	40	—	—
3.09	20	—	—	—	—	2.76	8	2.79	30	—	—	—	—
2.95	70	2.99	40	2.98	50	—	—	2.75	10	—	—	—	—
2.93	60	2.91	60	2.92	100	—	—	—	—	2.67	35	—	—
—	—	2.80	30	—	—	—	—	—	—	2.60	30	—	—
—	—	—	—	2.69	10	2.57	8	2.58	10	2.58	35	—	—
2.51	20	2.51	30	—	—	2.44	30	2.41	10	2.42	40	—	—
—	—	2.41	40	2.40	20	2.28	25	2.28	20	—	—	—	—
2.37	10	2.37	50	2.37	15	—	—	—	—	—	—	—	—

¹ Clay, shale, and pollucite reflections are excluded.

² UP = Unidentified phases; PDF = Powder diffraction file.

reaction rate increased with temperature (Table 3). The extraction of Cs into solution from β -Cs₂U₂O₇ in the presence of clays resulted in the formation of schoepite, UO₃·~2H₂O, in most samples and uraninite, UO₂, in some samples (Table 5). The formation of uraninite requires a reducing environment to bring the uranium to the tetravalent state from the hexavalent state in β -Cs₂U₂O₇. Uraninite was formed most readily when β -Cs₂U₂O₇ was reacted with a reducing type shale, such as the Conasauga shale (Figure 3) and the Antrim shale (Table 5), both of which contain organic matter and/or sulfides (Table 2). Divalent iron in the sample can also reduce U⁶⁺ in β -Cs₂U₂O₇, but large amounts of FeO are needed to reduce all of the uranium added. For example, the Catskill (reduced) shale required about 5 times more FeO than is present in the shale (Table 1) in order to reduce all the uranium added to it. Uraninite is a desirable product of U–shale reactions because the U in uraninite is insoluble. The reduction of U⁶⁺ to U⁴⁺ by reducing-type shales has similar implications to the solubility of Pu and other transuranic elements under repository conditions.

The d-spacings and intensities of the unidentified phases listed in Table 5 are listed in Table 6. Some re-

flexions of unidentified phase UP-1 and especially UP-5 match those of weeksite, K₂(UO₂)₂(Si₂O₅)₃·4H₂O, and the Cs- and Na-analogs of this phase may have been produced. Most of the reflections of UP-2 and UP-3 match those of calcium strontium uranium oxide hydrate, (Ca,Sr)₂U₇O₂₃·10H₂O (Table 6), a not unreasonable product because Ca-montmorillonite and Salona shale (calcite-rich) reacted with β -Cs₂U₂O₇ to produce UP-2 and/or UP-3 (Table 5). UP-4 has not been identified; and spacings and intensities are listed in Table 6.

Mechanism of Cs fixation

XRD characterization of the products of Cs-clay and Cs-shale reactions showed that pollucite formed from all clays or shales irrespective of the nature of the added Cs phase (Table 3). For example, illite, the most abundant clay mineral in shales, readily reacted with three of the added Cs phases used in this study to form pollucite under hydrothermal conditions. In pollucite Cs is in 12-fold coordination with oxygen (Newnham, 1967) and is not exchangeable (Barrer, 1950). Cs from pollucite is very difficult to exchange in salt solutions up to 300°C (Komarneni *et al.*, 1978; Komarneni and

White, 1981). The fixation of Cs was also achieved by the formation of CsAlSiO_4 in some of the Cs-clay reactions (Table 4; Figure 1). Cs from CsAlSiO_4 is also nonexchangeable at 25°C in salt solutions (Komarneni *et al.*, 1978). Cs was also fixed in the interlayers of montmorillonite by ion exchange (Figure 1). Cs-montmorillonite seems to be a metastable phase and may eventually recrystallize to form pollucite. Thus, Cs is fixed in Cs-aluminosilicate minerals as well as in the interlayers of montmorillonite as shown in Figure 1.

SUMMARY

Cs from CsOH, CsI, Cs_2MoO_4 , and $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ reacted with all the clays and shales to form Cs-aluminosilicate minerals such as pollucite and CsAlSiO_4 . Cs was also fixed in the interlayers of montmorillonite. The formation of insoluble pollucite dominated all of the reactions leading to the immobilization of much of the Cs. Mo from Cs_2MoO_4 reacted directly with Ca from the shales and clays to form powellite, CaMoO_4 . The insoluble alkaline earth molybdates seem to be common end products for molybdenum from nuclear waste. They have been observed in many other reaction products. Uranium from $\beta\text{-Cs}_2\text{U}_2\text{O}_7$ followed two pathways depending on the redox conditions of the shale. If the shale contained reducing phases, such as sulfides or organic material, a portion of the uranium formed insoluble uraninite, UO_2 . Under more oxidizing conditions, the Cs compound released hexavalent uranium and yielded a schoepite-type compound ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$). The reaction product of U^{6+} with the clay minerals is thought to be an analog of wecksite with the probable formula $(\text{Cs,Na})_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5) \cdot 4\text{H}_2\text{O}$. Thus, aluminosilicate minerals in a repository wall rock can have beneficial effects on the immobilization of Cs, Mo, and U waste elements. The direct chemical reaction of Cs to form pollucite, aided by the presence of water and heat, provides a useful barrier to Cs migration from the immediate vicinity of a breached, spent fuel element canister.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy through subcontract E512-3400 with the Office of Nuclear Waste Isolation, Battelle. Sincere appreciation is expressed to Dr. G. J. McCarthy for helpful suggestions, and to Catherine A. Smith for assistance in carrying out the XRD analysis.

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(Received 12 January 1981; accepted 3 March 1981)

Резюме—Путём обмена ионов в прямой химической реакции с глинистыми минералами или сланцевыми глинами исследовалась иммобилизация растворимого Cs из затраченных элементов топлива в гидротермальных условиях. Разные глинистые минералы или сланцевые глины реагировали с источниками Cs и водой при давлении 300 бар и температуре 100°, 200°, и 300°C в течение 4, 2, и 1 месяцев соответственно. Поллцит являлся главным продуктом, но наблюдалось также присутствие CsAlSiO₄ вместе с непрореагировавшими или гидротермально изменёнными алюмосиликатами. На основе концентрации Cs в растворах продукта получено разделение Cs между жидкими и твёрдыми растворами. Это зависело от источника Cs, глинистой или сланцевой фазы, температуры и времени реакции. Взаимодействие иллита с Cs₂MoO₄, например, фиксировало 19, 32, и 95% добавленного Cs соответственно при температурах 100°, 200°, и 300°C. В некоторых твёрдых телах наблюдалась фиксация 97% Cs. Кроме образования Cs-алюмосиликатов, Cs был также зафиксирован в катионообменных местах путём сплюснения слоев в монтмориллоните. В результате присутствия Ca в смеси, реакции с Cs₂MoO₄ приводила также к образованию повеллита. U⁶⁺ из β-Cs₂U₂O₇ формировал уранинит с помощью сульфида и/или органически богатых сланцевых глин. (Cs,Na)₂(UO₂)(Si₂O₅)₃·4H₂O, аналог уиксита, был образован в реакции с β-Cs₂U₂O₇. Продукты реакции поллцит и уранинит могут привести к иммобилизации большого количества Cs и U из затраченных элементов топлива, потому что очень трудно обменять Cs в поллците, а U в уранините нерастворим. [E.C.]

Resümee—Es wurde die Bindung von löslichem Cs aus verbrauchten Brennelementen durch Ionenaustausch und durch direkte chemische Reaktion mittels Tonmineralen und Schiefer-tonen unter hydrothermalen Bedingungen untersucht. Verschiedene Tonminerale oder Schiefer-tonen wurden mit möglichen Cs-Quellen bei einem Druck von 300 Bar und Temperaturen von 100°, 200°, und 300°C für 4, 2, und 1 Monat zur Reaktion gebracht. Das vorherrschende Produkt war Pollucit. Es wurde aber auch CsAlSiO₄ zusammen mit unveränderten oder hydrothermal veränderten Aluminosilikaten beobachtet. Aus der Cs-Konzentration der erzeugten Lösungen ergab sich, daß die Cs-Verteilung zwischen der Flüssigphase und den Festphasen sehr stark von der Cs-Quelle abhängt sowie vom Tonmineral oder vom Tonschiefer, von der Temperatur und der Reaktionszeit. Die Illit-Cs₂MoO₄-Wechselwirkungen ergaben z.B. bei 100°, 200°, und 300°C die Bindung von 19, 32, bzw. 95% des zugegebenen Cs. Es wurde die Fixierung von bis zu 97% Cs in einigen Festsubstanzen beobachtet. Zusätzlich zu Cs-Aluminosilikaten wurde Cs an Kationenaustauschplätzen durch das Zusammenbrechen der Zwischenschicht in Montmorillonit fixiert. Die Reaktionen mit Cs₂MoO₄ ergaben auch Powellit, da Ca in den Reaktionsmischungen zur Verfügung stand. Das U⁶⁺ aus β-Cs₂U₂O₇ wurde durch Tonschiefer, die reich an Sulfiden und/oder organischen Substanzen waren, reduziert und bildete Uraninit. (Cs,Na)₂(UO₂)(Si₂O₅)₃·4H₂O, ein Analog von Weeksit, wurde bei den Reaktionen mit β-Cs₂U₂O₇ gebildet. Die Reaktionsprodukte Pollucit und Uraninit können einen Großteil des Cs and U aus verbrauchten Brennelementen fixieren, da das Cs in Pollucit sehr schwer auszutauschen und das U in Uraninit unlöslich ist. [U.W.]

Résumé—On a investigué sous des conditions hydrothermales l'immobilisation par échange d'ions et par réaction chimique directe avec des minéraux argileux ou des shales de Cs soluble d'éléments de fuel brûlé. On a fait réagir des minéraux argileux variés ou des shales avec des sources probables de Cs et de l'eau à 300 bars de pression et 100°, 200°, et 300°C pendant 4, 2, et 1 mois, respectivement. La pollucite était le produit principal, mais CsAlSiO₄ a aussi été observé, ainsi que des aluminosilicates qui n'avaient pas réagi, ou altérés hydrothermalement. A partir de concentrations de Cs de solutions produites, la partition de Cs entre liquide et solide a varié de en fonction de la source de Cs, et de la phase argileuse ou de shale, de la température, et de la durée de l'expérience. Les interactions illite-Cs₂MoO₄, par exemple, ont résulté en la fixation de 19, 32, et 95% de Cs ajouté à 100°, 200°, 300°C, respectivement. On a observé jusqu'à 97% de fixation de Cs dans certains solides. En plus des aluminosilicates-Cs, Cs a été fixé sur des sites à échange de cations par effondrement interfeuille dans la montmorillonite. Des réactions avec Cs₂MoO₄ ont aussi produit de la powellite parce que Ca était disponible dans le mélange. L'U⁶⁺ de β-Cs₂U₂O₇ était réduit par des shales riches en sulfide ou en matière organique pour former de l'uraninite. (Cs,Na)₂(UO₂)(Si₂O₅)₃·4H₂O analogue au weeksite, a été produit dans des réactions avec β-Cs₂U₂O₇. Les produits de réaction pollucite et uraninite peuvent immobiliser beaucoup du Cs et de l'U des éléments de fuel brûlé parce que le Cs dans la pollucite est extrêmement difficile à échanger, et l'U dans l'uraninite est insoluble. [D.J.]