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PHILLIPSITE IN Cs DECONTAMINATION AND IMMOBILIZATION

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Abstract—The Cs selectivity of several natural zeolitic tuffs and synthetic zeolites was measured. Phillipsite-rich tuffs from California and Nevada exchanged 13.5 and 23.7%, respectively, of the Cs present in simulated alkaline defense waste containing 0.00025 M CsCl in 5.5 M NaCl–NaOH solution from the Savannah River Plant, Aiken, South Carolina; whereas mordenite-rich tuffs from Arizona and Nevada exchanged less than 12.7%. The immobilization or fixation of Cs in phillipsite unlike other zeolites can be achieved by heating the zeolite at 600°C for 4 hr in air and collapsing the silicate (aluminate) tetrahedral rings around the Cs ions to produce a Cs-feldspar-type phase. Treatment of the Cs-exchanged phillipsite-rich tuff at 800° to 1000°C resulted in pollucite, $CsAlSi_2O_6$, which also "locks in" the Cs ions in its structure. The fixation of Cs exchanged in phillipsite can also be achieved by the formation of pollucite upon hydrothermal treatment at 300°C and 30 MPa pressure within 12 hr. These results suggest that phillipsite-rich tuffs are good candidates for Cs immobilization by heat treatment at low temperatures after they have been used as sorbents in waste decontamination.

Key Words—Cation exchange, Cesium, Cs-feldspar, Nuclear waste disposal, Phillipsite, Pollucite, Thermal treatment, Zeolite.

INTRODUCTION

The use of zeolites such as clinoptilolite in nuclear waste decontamination is a common practice (IAEA, 1972). Zeolites and zeolitic tuffs have also been used to decontaminate low- and intermediate-level liquid nuclear wastes (Mercer and Ames, 1978) and to separate ^{137}Cs from high-level radioactive defense wastes at Hanford, Washington (Nelson and Mercer, 1963; Brandt, 1970; Buckingham, 1970). Zeolitic ion exchangers, such as Ionsiv IE-95 (United States Nuclear Regulatory Commission, 1980) which consists of a mixture of natural chabazite and erionite from Bowie, Arizona and Ionsiv IE-96 (which consists of chabazite) + Linde A-51 (Hofstetter and Hitz, 1983) are currently used to clean up accident waste water at the Three Mile Island-Unit II reactor, Middletown, Pennsylvania. The *fixation* of radioactive Cs within these zeolites, however, has not received much attention although vitrification in glass or iron-enriched basalt has been investigated (Kelsey *et al.*, 1982). The effect of heat on vaporization and elution of ^{85}Sr and ^{137}Cs exchanged on zeolites was studied by Knoll (1963) but has not been optimized in any way. Cesium exchanged onto zeolites is expected to be removed slowly by leaching with ground water containing Ca^{2+}, Na^+, and K^+ by ion exchange if disposed of without any further processing.

Recently, Komarneni and Roy (1981, 1982) examined the thermal and hydrothermal treatment of zeolitic tuffs for the fixation of ion-exchanged Cs and Sr. These studies indicated that phillipsite is probably the best natural zeolite for exchange and fixation of Cs because of (1) its very high cation-exchange selectivity and capacity for Cs, and (2) the ease with which Cs can be immobilized by transforming the structure to a feldspar-type phase or to pollucite. The objective of the present study was to show in greater detail that ^{137}Cs exchanged by natural phillipsite-rich tuff can be easily immobilized by the formation of crystalline cesium aluminosilicates by heat treatment in air or under hydrothermal conditions.

EXPERIMENTAL

Materials

The source and/or location and particle size of the twelve natural zeolitic tuffs and four synthetic zeolite samples used in this study are given in Table 1. All of the zeolitic tuffs, except the phillipsite-rich tuff from California, the analcime-rich tuff from Arizona, and the Ionsiv IE-95 from Union Carbide Corporation, were supplied as <200 (<75 μm) or <600 (<25 μm) mesh powders (see Table 1). The phillipsite-rich tuff from California and the analcime-rich tuff from Arizona were supplied as 2 × 3 × 5″ hand specimens which were lightly ground in an agate mortar and pestle and screened to obtain <200 mesh powders. The Ionsiv IE-95 sample was supplied as ~1-mm aggregates and was used without any further treatment.

Methods

The mineralogical analysis (Table 1) of all the untreated samples was carried out by powder X-ray diffraction (XRD) using a Philips APD-3600 X-ray diffractometer with graphite monochromated CuKα ra-

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Table 1. Zeolitic tuffs and synthetic zeolites used in the investigation.

Name	Location/source	Reference zeolite	Particle size (μm)	Mineralogy by XRD
Phillipsite	Shoshone, California	25701[1]	<75	Phillipsite, trace clinoptilolite
Phillipsite	Pine Valley, Nevada	27154[1]	<75	Phillipsite, trace erionite
Mordenite	Union Pass, Arizona	27134[1]	<75	Mordenite
Mordenite	Lovelock, Nevada	27114[1]	<75	Mordenite, trace cristobalite
Clinoptilolite	Castle Creek, Idaho	27034[1]	<75	Clinoptilolite, quartz
Clinoptilolite	Hector, California	27124[1]	<75	Clinoptilolite, quartz, trace mordenite
Clinoptilolite	Mountain Green, Utah	27064[1]	<75	Clinoptilolite, cristobalite, quartz, trace mica
Erionite	Shoshone, California	27104[1]	<75	Erionite, feldspar, trace phillipsite
Erionite	Pine Valley, Nevada	27094	<75	Erionite, feldspar, quartz, cristobalite
Chabazite	Christmas, Arizona	27124	<75	Chabazite, quartz, trace mica
Chabazite	Bowie, Arizona	27114[1]	<75	Chabazite, erionite
Analcime	Wikieup, Arizona	25608[1]	<75	Analcime
Synthetic zeolite 3A	Alfa Products	87953[2]	<25	Zeolite A
Synthetic zeolite 4A	Alfa Products	87952[2]	<25	Zeolite A
Synthetic zeolite 5A	Alfa Products	87951[2]	<25	Zeolite A
Ionsiv	Union Carbide Corporation	IE-95[3]	~1000	Chabazite, erionite

[1] Minerals Research, P.O. Box 591, Clarkson, New York.
[2] Alfa Products, P.O. Box 299, 152 Andover Street, Danvers, Massachusetts.
[3] Union Carbide Corporation, Danbury, Connecticut.

diation. A total chemical analysis of the phillipsite-rich tuff from Nevada was performed using a lithium borate fusion technique (Medlin *et al.*, 1969) and spectrometric analysis (Table 2). The total cesium-exchange capacities of the two phillipsites were determined by washing the samples five times with 1 N CsCl, washing out the excess CsCl with 0.01 N CsCl (to prevent hydrolysis; a correction was made for 0.01 N CsCl which was determined by weighing) and by displacing the Cs from exchange sites with five washings of 1 N KCl solution. The solutions were analyzed for exchangeable Cs ions by atomic absorption (AA) using a Perkin Elmer PE 703 instrument with electrodeless discharge lamp.

Table 2. Chemical composition of phillipsite-rich tuffs from Nevada and California.

Oxide	Pine Valley, Nevada (27154)[1]	Shoshone, California[2]
SiO_2	52.3%	57.48%
Al_2O_3	15.0	14.29
TiO_2	0.17	0.10
Fe_2O_3	2.37	0.78
MgO	0.28	0.22
CaO	0.60	0.01
MnO	0.01	—
BaO	0.01	—
Na_2O	8.00	4.51
K_2O	2.71	6.55
P_2O_5	0.08	0.00
Loss on ignition	17.67	15.67
Total	99.20%	99.61%

[1] See Table 1. Analysis by lithium borate fusion technique (Medlin *et al.*, 1969) and spectrometric analysis.
[2] Analysis from Sheppard and Gude (1968). The phillipsite sample used in the present investigation is from the same general area as that analyzed by those authors.

Cesium exchange by the zeolites was measured from three different solutions as follows: In one series, 25 ml of 0.04 M $NaNO_3$ solution containing 0.0002 M CsCl and 0.0001 M $SrCl_2$ was added to each 20-mg zeolite sample, and the mixtures were equilibrated by shaking in an end-over-end shaker for 24 hr at 25°C. In a second series, 15 ml of 4.0 M $NaNO_3$–1.5 M NaOH solution containing 0.00025 M CsCl and 1×10^{-6} M $SrCl_2$ with ^{137}Cs tracer was added to each 100-mg zeolite sample, and the mixtures were equilibrated for 18 hr without shaking at 25°C. Two replicates of each run were made. The composition of this solution simulates alkaline defense waste from the Savannah River plant (Ebra *et al.*, 1982). In a third series, 20 ml of 2 M NaCl solution containing 0.2 M CsCl was added to each 2-g zeolite sample, and the mixtures were equilibrated by shaking for 24 hr. This last experiment is similar to the cesium-exchange test that was suggested by Mercer and Ames (1978). The 18- or 24-hr equilibration used here may not represent a true exchange equilibrium but would suffice to give differences in Cs exchange selectivity among the various samples. After equilibration, the solid and solution phases were separated by centrifugation, and the Cs in solution was determined by either AA or by gamma counting using a scintillation method.

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Table 3. Cesium-exchange properties of natural zeolitic tuffs and synthetic zeolites.

Zeolite[1]	Cs exchange from 0.04 M $NaNO_3$ containing 0.0002 M Cs and 0.0001 M Sr		Cs exchange from 4.0 M $NaNO_3$–1.5 M NaOH containing 0.00025 M CsCl[2]		Cs exchange from 2 M NaCl containing 0.2 M CsCl[3]	
	(meq/100 g)	(% removal)	(meq/100 g)	(% removal)	(meq/100 g)	(% removal)
			Zeolitic tuffs			
Phillipsite, Shosone, California	19.5	78.0	0.506	13.5	109.2	54.8
Phillipsite, Pine Valley, Nevada	22.2	88.7	0.889	23.7	130.2	65.3
Mordenite, Union Pass, Arizona	20.6	82.2	0.394	10.5	64.2	32.2
Mordenite, Lovelock, Nevada	19.4	77.5	0.476	12.7	65.8	33.0
Clinoptilolite, Castle Creek, Idaho	—[4]	—	0.161	4.3	92.4	46.4
Clinoptilolite, Hector, California	19.5	78.0	0.326	8.7	—	—
Clinoptilolite, Mountain Green, Utah	—	—	0.323	8.6	78.3	39.3
Erionite, Shoshone, California	—	—	0.510	13.6	104.1	52.3
Erionite, Pine Valley, Nevada	22.5	89.9	0.671	17.9	127.0	63.8
Chabazite, Christmas, Arizona	20.5	82.0	0.559	14.9	116.1	58.3
Chabazite, Bowie, Arizona	21.6	86.1	0.518	13.8	136.2	68.4
Analcime, Wikieup, Arizona	—	—	—	—	5.5	1.4
			Synthetic zeolites			
Synthetic zeolite 3A	—	—	—	—	39.4	19.8
Synthetic zeolite 4A	—	—	ND[5]	ND[5]	39.0	19.6
Synthetic zeolite 5A	—	—	—	—	57.9	29.1
Ionsiv IE-95	21.3	85.1	—	—	112.0	56.2

[1] See Table 1.
[2] Simulated alkaline defense waste from the Savannah River Plant (Ebra *et al.*, 1982).
[3] Composition for Cs exchange test for zeolites as suggested by Mercer and Ames (1978).
[4] Not determined.
[5] ND = none detected.

To investigate the extent of Cs fixation by heat treatments, the phillipsite-rich tuffs from Nevada and California were loaded with 220 to 103 meq Cs/100 g and 196 to 117 meq Cs/100 g, respectively. The highest Cs loadings given above of the phillipsite-rich tuffs from Nevada and California correspond to 75 and 70% respectively of their expected total exchange capacities, the latter were calculated from the Al contents in Table 2. The different Cs loadings in the zeolitic tuffs were achieved by adding different amounts of CsCl in solution and equilibration by shaking for 24 hr. The extent of Cs loadings was determined after washing the samples free of excess salts and by repeatedly displacing the Cs with excess KCl and by determining the Cs using AA. The phillipsite-rich tuffs after the exchange of Cs from 0.04 M $NaNO_3$ (see above) were also heated in an attempt to fix the cesium. The Cs-loaded and Cs-exchanged phillipsite-rich tuffs were heated at various temperatures up to 1000°C in air for 4 hr, some were heated hydrothermally in gold capsules at 200° and 300°C for 12 hr under a confining pressure of 30 MPa. In the hydrothermal heating experiments, a solid to deionized water ratio of 1:5 was used. After the hydrothermal treatment, the gold capsules were checked for leaks by weighing. The gold capsules showing no weight changes and therefore assumed to have been free of leaks were opened with a scissors in a glass vial. Twenty milliliters of distilled water was added while washing the scissors, and the gold capsules were shaken to remove the sample from the gold capsule. The solid and solution phases were separated by centrifugation, and the solutions were analyzed for Cs by AA.

The solid samples after thermal and hydrothermal treatments were characterized by XRD and by scanning electron microscopy, the latter with an ISI DS-130 instrument.

RESULTS AND DISCUSSION

Exchange of Cs by zeolites

The results presented in Table 3 show that the natural phillipsite-rich tuffs exchanged the most Cs of the

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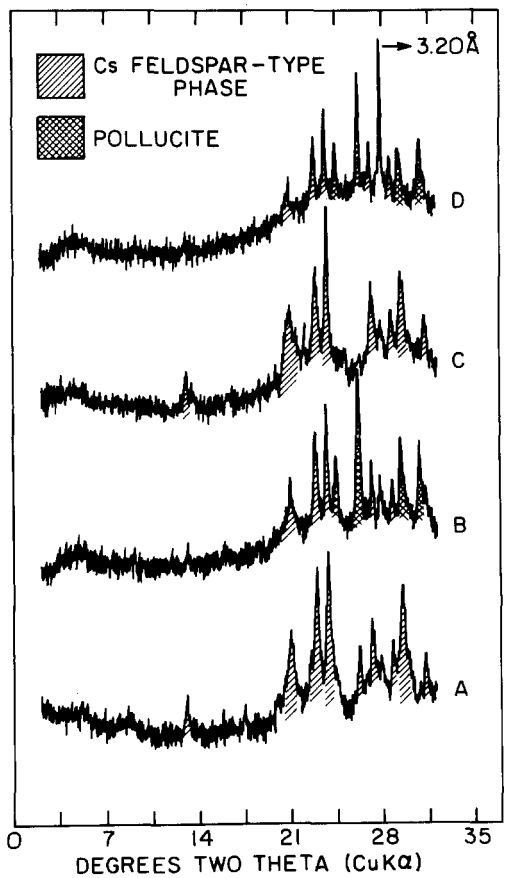


Figure 1. X-ray powder diffractograms of Cs-loaded phillipsite-rich tuffs heated in air. (A) Phillipsite-rich tuff from Shoshone, California, with a Cs-loading of 117 meq/100 g, heated at 600°C for 4 hr; (B) same as (A) but heated at 1000°C for 4 hr; (C) phillipsite-rich tuff from Pine Valley, Nevada, with a Cs-loading of 103 meq/100 g, heated at 600°C for 4 hr; (D) same as (C) but heated at 1000°C for 4 hr.

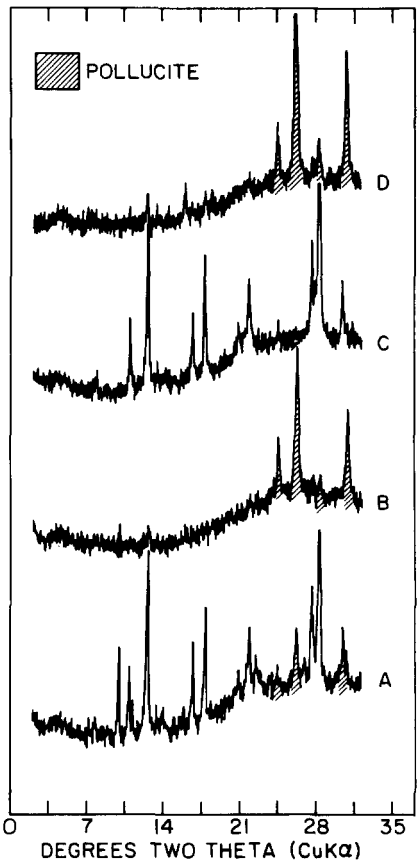


Figure 3. X-ray powder diffractograms of Cs-loaded phillipsite-rich tuffs heated hydrothermally at 300°C and 30 MPa. (A) Phillipsite-rich tuff from Shoshone, California, with a Cs-loading of 20 meq/100 g; (B) same as (A) but with a Cs-loading of 117 meq/100 g; (C) phillipsite-rich tuff from Pine Valley, Nevada, with a Cs-loading of 22 meq/100 g; (D) same as (C) but with a Cs-loading of 103 meq/100 g. Unshaded peaks = phillipsite.

samples tested from a variety of solutions. The phillipsite-rich tuff from California exchanged less Cs than the phillipsite-rich tuff from Nevada, a difference that may be attributed to at least two factors: (a) the former tuff has a lower Cs exchange capacity (263 meq/100 g) than the latter (292 meq/100 g) and (b) the untreated California tuff contains more K^+ than that from Nevada (Table 2). The K^+ in the untreated samples also competed for the exchange sites because batch-type experiments were used wherein all of the solution was in contact with the tuff during equilibration, unlike in column operations. K^+ is selectively exchanged over Na^+ by many zeolites (Ames, 1961), therefore, K^+ in zeolite competes more strongly with Cs^+ than does Na^+ (Ames, 1960, 1961, 1963). Because the phillipsite-rich tuff from California contained more K^+ in exchange sites than the phillipsite-rich tuff from Nevada (Table 2), the former was a poorer exchanger of Cs^+ than the latter under the experimental conditions used in this investigation.

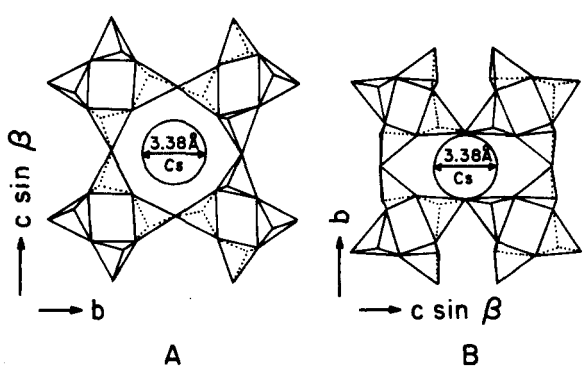


Figure 2. Schematic solid tetrahedra projections illustrating (A) phillipsite and (B) feldspar (after Breck, 1974).

Fixation of Cs in phillipsites

Heat treatment. The two phillipsite-rich tuffs with 103 and 117 meq/100 g or higher Cs-loadings transformed

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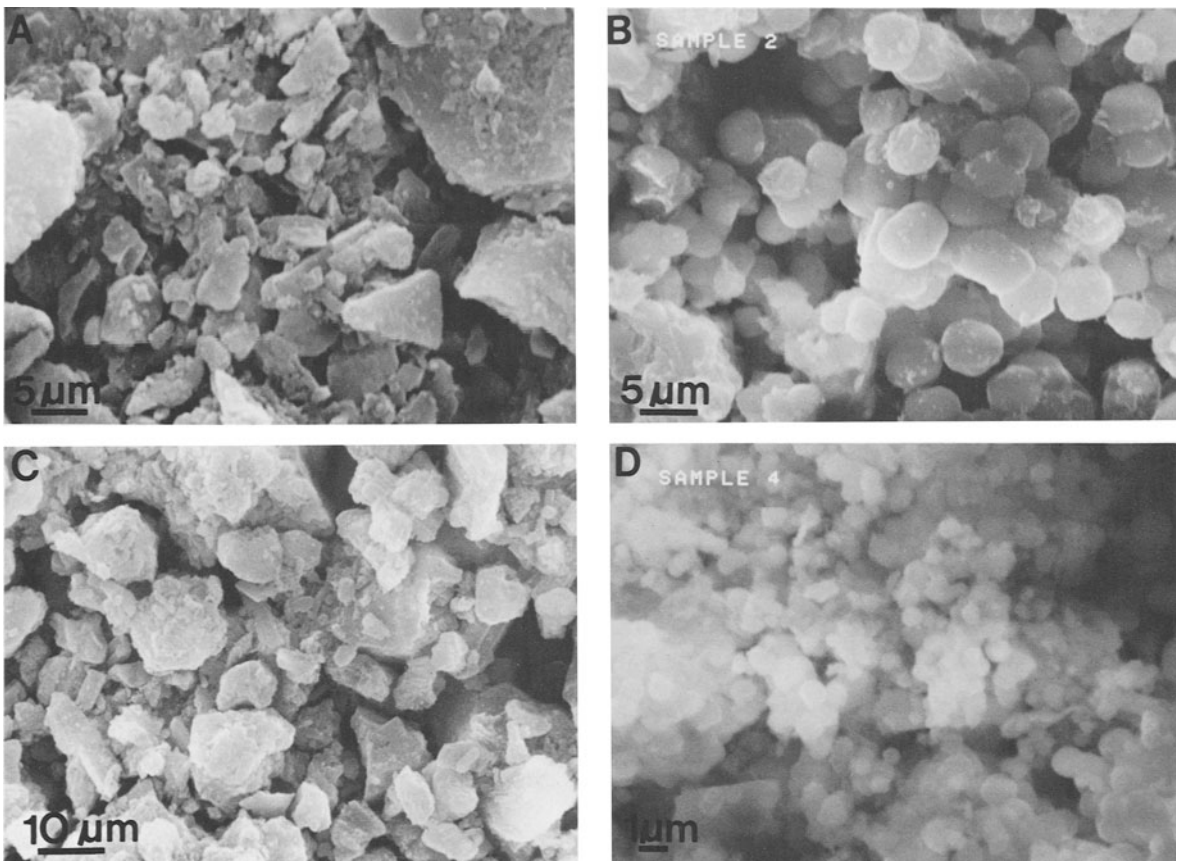


Figure 4. Scanning electron micrographs of untreated and hydrothermally altered phillipsite-rich tuffs. (A) Phillipsite-rich tuff from Shoshone, California; (B) same as (A) with a Cs-loading of 117 meq/100 g, showing pollucite formation at 300°C/30 MPa; (C) phillipsite-rich tuff from Pine Valley, Nevada; (D) same as (C) but with a Cs-loading of 103 meq/100 g showing pollucite formation at 300°C/30 MPa.

to Cs-feldspar-type phases at 600°C and to Cs-feldspar-type phase + pollucite at 1000°C (Figure 1), as was reported by Komarneni and Roy (1981). At lower Cs-loadings, feldspar-type phases formed at about 800°C. The formation of a feldspar-type phase can be attributed to the collapse of rings of silicate and aluminate tetrahedra around the Cs ions as shown in Figure 2 (Breck, 1974). Scanning electron microscopy (not shown) revealed no change in the morphology of the phillipsite upon its transformation to the feldspar-type phase. The structure of phillipsite thus traps or fixes Cs ions by collapse of the rings at a relatively low temperature of 500°–600°C. This feldspar-type phase transforms to pollucite, $CsAlSi_2O_6$, by heat treatment at a higher temperature of 800°–1000°C. Because pollucite is a better phase for ^{137}Cs immobilization than the feldspar-type phase (Komarneni and Roy, 1981), heat treatment to higher temperatures enhances the fixation of Cs in these phillipsite-rich tuffs. Other than phillipsites and heulandite, the commercially available natural zeolites do not undergo such structural collapse (Hoss and Roy, 1960; Breck, 1974; Komarneni and Roy, 1981) and, therefore, need very high temperatures of 1200°C (Mimura and Kanno, 1980; Forberg *et al.*, 1980) for the immobilization of Cs in crystalline phases. Heulandite, which was not investigated here, is also a potential zeolite for Cs fixation inasmuch as it undergoes structural collapse at >360°C (Mumpton, 1960). The collapse of the silicate rings of phillipsite around Cs ions at ~600°C during the formation of Cs-feldspar prior to the crystallization of pollucite around 800°–1000°C is expected to inhibit Cs volatilization which is a common problem with this element. Further studies are warranted to substantiate the above point.

Hydrothermal treatment. Hydrothermal treatment of the Cs-loaded phillipsite-rich tuffs at 200°C for 12 hr at 30 MPa pressure resulted in no detectable alteration, although at 300°C for 12 hr, pollucite formed (Figures 3 and 4). Thus, Cs-loaded phillipsite-rich tuffs can be transformed to pollucite under hydrothermal conditions at relatively low temperature. The pollucite par-

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Table 4. Percentage of Cs released and mineralogical changes upon hydrothermal treatment of phillipsite-rich tuffs at 300°C and 30 MPa pressure.

Tuff sample	Cs-loading (meq/100 g)	Cs released in capsule fluid (%)	Phases present (by X-ray powder diffraction)
Phillipsite, Shoshone, California	20	0.44	Phillipsite + pollucite
Phillipsite, Shoshone, California	117	0.37	Pollucite + trace phillipsite
Phillipsite, Pine Valley, Nevada	22	0.20	Phillipsite
Phillipsite, Pine Valley, Nevada	103	0.25	Pollucite + trace phillipsite

ticles were sphere-like (Figure 4) and showed no well-defined crystal faces within the short duration of the treatment. The transformation of the Cs-loaded phillipsite-rich tuffs to pollucite resulted in very little release of Cs into solution (Table 4). Cesium in phillipsite, unlike in other zeolites studied in this laboratory (Komarneni and Roy, 1981) can thus be easily immobilized as pollucite wbich has been found to be a resistant phase for ^{137}Cs immobilization (Komarneni and White, 1981; Komarneni and Roy, 1983), as has been previously suggested by Barrer (1978).

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Резюме—Измерялась Cs селективность нескольких природных цеолитовых туфов и синтетических туфов. Обогащенные филлипситом туфы из Калифорнии и Невады обменивали соответственно 13,5 и 23,7% Cs, присутствующега в 5,5 M NaCl–NaOH растворе, содержащем количество 0,00025 M CsCl, имитирующем щелочные отходы фабрики Савана Ривер в Аикен, Южная Каролина. В то же самое время обогащенные морденитом туфы из Аризоны и Невады обменивали менее 12.7%. Неподвижность или фиксация Cs в филлипсите в противоположность к другим цеолитом достигается путем обогрева цеолита при 600°C в течение 4 часов в воздухе и разрушения силикатных (алюминатных) тетраэдрических колец вокруг ионов Cs для образования фазы типа Cs-полевой шпат. Обработка Cs-обменного обогащенного филлипситом туфа при температуре от 800° до 1000°C приводила к образованию поллуцита, $CsAlSi_2O_6$, который также "закупоривал" ионы Cs в своей структуре. Фиксация обменного Cs в филлипсите могла также быть достигнута путем образования поллуцита в результате гидротермической обработки при температуре 300°C и давлении 30МПа в течение 12 часов. Эти результаты указывают на то, что обогащенные филлипситом туфы являются хорошим материалом для "нейтрализации" Cs путем термической обработки при низких температурах после того, как они использовались в качестве сорбентов при очищении отходов. [E.G.]

Resümee—Es wurde die Cs-Selektivität von verschiedenen natürlichen Zeolith-Tuffen und synthetischen Zeolithen gemessen. Phillipsit-reiche Tuffe von Kalifornien und Nevada tauschten 13,5 bzw. 23,7% des in simuliertem alkalischem Abfall vorhandenen Cs aus, der 0,00025 m CsCl in einer 5,5 m NaCl-NaOH-Lösung von der Savannah River Plant, Aiken, South Carolina, enthielt. Mordenit-reiche Tuffe von Arizona und Nevada tauschen dagegen weniger als 12,7% aus. Die Immobilisierung oder Fixierung von Cs in Phillipsit kann anders als bei anderen Zeolithen durch Erhitzen des Zeolithes auf 600°C in Luft für 4 Stunden erreicht werden, wodurch die Silikat- (Aluminat-) Tetraederringe um das Cs-Ion kollabieren und eine feldspatartige Cs-Phase entsteht. Eine Behandlung der Cs-ausgetauschten Phillipsit-reichen Tuffe bei 800°–100°C führt zur Bildung von Pollucit $CsAlSi_2O_6$, der ebenfalls die Cs-Ionen in seiner Struktur "einsperrt." Die fixierung von durch Phillipsit ausgetauschtem Cs kann auch durch die Bildung von Pollucit aufgrund hydrothermaler Behandlung bei 300°C und 30 MPa Druck über 12 Stunden erreicht werden. Diese Ergebnisse deuten darauf hin, daß Phillipsit-reiche Tuffe gute Anwärter für die Cs-Immobilisierung durch Behandlung bei niedrigen Temperaturen sind, nachdem sie als Sorbenten bei der Abfalldekontamination verwendet wurden. [U.W.]

Résumé—On a mesuré la sélectivité Cs de plusieurs tuffs zéolitiques naturels et de zéolites synthétiques. Des tuffs riches en phillipsite de Californie et du Nevada ont échangé 13,5 et 23,7% respectivement du Cs présent dans un déchet de défense alkalin simulé contenant 0,00025 M CsCl dans une solution 5,5 M NaCl-NaOH provenant du Savannah River Plant, Aiken, Caroline du Sud; tandis que des tuffs riches en mordénite d'Arizona et du Nevada ont echangé moins que 12,7%. L'immobilisation ou la fixation de Cs dans la phillipsite, dissimilairement aux autres zéolites, peuvent être atteintes par échauffement de la zéolite à 600°C pendant 4 heures à l'air et en fermant les anneaux silicates (aluminate) tetraédriques autour des ions Cs pour produire une phase du type Cs-feldspar. Le traitement du tuff riche en phillipsite échangé au Cs de 800° à 1000°C a resulté en de la pollucite, $CsAlSi_2O_6$, qui enferme aussi les ions Cs dans sa structure. La fixation de Cs échangé dans la phillipsite peut aussi être atteinte par la formation de pollucite lors du traitement hydrothermique à 300°C et 30 MPa de pression endéans 12 heures. Ces résultats suggèrent que les tuffs riches en phillipsite sont de bons candidats pour l'immobilisation de Cs par traitement à la chaleur à de basses températures après qu'ils aient été employés comme solvants dans la décontamination de déchets. [D.J.]

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