

HYDROTHERMAL REACTIONS OF STRONTIUM AND TRANSURANIC SIMULATOR ELEMENTS WITH CLAY MINERALS, ZEOLITES, AND SHALES

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Abstract—Reactions of Sr, La, and Nd (the latter two elements simulating Am and Cm) with potential backfill minerals for radioactive waste storage and with repository wall rocks, such as shale, were investigated under simulated repository conditions of 200° and 300°C for 12 weeks under a confining pressure of 30 MPa. The solid and solution reaction products were characterized to determine the nature and extent of reaction. Chlorite, illite, kaolinite, montmorillonite, mordenite, and clinoptilolite and four shales removed as much as 61.2 and 98.5% of the added SrCl₂ and Sr(OH)₂ from solution, respectively, by ion exchange and/or by forming new strontium compounds such as SrAl₂Si₂O₈, Sr₂MgSi₂O₇, SrCO₃ (strontianite), and SrAl₂Si₄O₁₂·2H₂O (Sr-wairakite). The formation of these sparingly soluble Sr phases by the reaction of the soluble Sr compounds with such backfill materials indicates that the backfill may serve as a barrier during the thermal period of the waste in the life of a repository. These same minerals and shales removed as much as 99.99% of the added La or Nd from solution at 300°C by forming new phases such as LaOHCO₃, NdOHCO₃, and possibly La or Nd oxides and hydroxides. Zeolites reacted with La and Nd to form smectite. Thus, if La and Nd truly simulate the reactivity of Am and Cm, properly designed backfills can serve as a barrier to the migration of transuranic elements of nuclear wastes.

Key Words—Chlorite, Clinoptilolite, Hydrothermal treatment, Illite, Lanthanum, Montmorillonite, Neodymium, Nuclear waste, Shale, Strontium, Zeolite.

INTRODUCTION

Chemical reactions between nuclear waste elements, such as Cs, Mo, and U, and potential backfill materials or wall rock under simulated repository conditions (McCarthy *et al.*, 1978) were reported by Komarneni and White (1981), Molecke *et al.* (1981), and Chapman *et al.* (1981). The identification of the reaction products of nuclear waste elements with such backfill materials or wall rock is important in determining the migration of elements from the repository site. Strontium is one of the most hazardous nuclear waste elements; it is released as Sr(OH)₂ from spent fuel elements (Komarneni, 1981), from proposed synroc² waste (Nesbitt *et al.*, 1981), and probably as a neutral salt from other waste forms. Among the transuranic waste elements, Am and Cm cause significant biohazard (Cohen, 1977) and are of concern in nuclear waste disposal. Because stable isotopes of Am and Cm do not exist and because Am and Cm are highly radioactive, trivalent rare earth elements are commonly used as chemical stand-ins for these nuclides in waste-fixation research (McCarthy and Davidson, 1975). Trivalent La and Nd were therefore used in the form of chlorides to simulate trivalent Am and Cm because of the similarity of their ionic radii (Pepin and Vance, 1981; Ringwood, 1982).

The objective of this paper is to determine the extent and nature of reaction of Sr, La, and Nd (the latter two elements simulating Am and Cm) with potential backfill materials, such as clay minerals and zeolites, and shale wall rock in repository environment. Decaying nuclear waste serves as a heat source, whereas infiltrating ground water and/or hydrated minerals serve as a water source in a nuclear waste repository. The hydrothermal experiments used here simulate the conditions and reactions expected during the early thermal period in a sealed, water-intruded repository after the waste canister has been breached. The results of these studies are relevant to any waste form and to any repository rock (with the exception of salt) where clay minerals and/or zeolites are used as a barrier to nuclide migration.

These experiments conducted in sealed noble metal capsules represent a closed-system in which the total mass is conserved and provide data for exploring solid-liquid reactivity. No attempt was made to control the Eh or pH which depended on the bulk composition of the reaction mixtures. High concentrations of Sr, La, and Nd were used in these experiments to produce enough reaction products for identification by X-ray powder diffraction. The product solutions were analyzed to determine the partitioning of waste elements between solid and solution phases.

EXPERIMENTAL

Materials

The clay minerals, zeolites, and shales used in this research are listed in Table 1. The clay minerals and

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² An acronym for synthetic rock which is a titanate ceramic (Ringwood, 1982) waste form consisting of hollandite (BaAl₂Ti₆O₁₆), zirconolite (CaZrTi₂O₇), and perovskite (CaTiO₃).

Table 1. Names, locations, sources, and particle size of samples.

Chlorite. Anderson soapstone pit, Saline County, Arkansas (courtesy G. W. Brindley). <105 μm .
Illite. Fithian, Illinois, Illinois Clay Products Company, Joliet, Illinois. <105 μm .
Kaolinite. Morro de Felipe deposits, Brazil, Yara Engineering Corporation, Georgia (courtesy G. W. Brindley). Pulverized.
Montmorillonite. Cheto, Arizona, SAZ-1, Source Clays Repository, The Clay Minerals Society. Pulverized.
Clinoptilolite. Castle Creek, Idaho, Reference zeolite 27034, Minerals Research P.O. Box 591, Clarkson, New York 14430. <75 μm .
Mordenite. Union Pass, Arizona, Reference zeolite 27134, Minerals Research, P.O. Box 591, Clarkson, New York 14430. <75 μm .
Shale. Antrim Formation, Alpena County, Michigan. <75 μm .
Shale. Brallier Formation, Huntingdon County, Pennsylvania. <75 μm .
Shale. Conasauga Formation, Oak Ridge Reservation, Tennessee. <75 μm .
Shale. Salona Formation, Huntingdon County, Pennsylvania. <75 μm .

zeolites used here represent a variety of potential backfill materials. The four shales used in this study have distinctly different chemical and mineralogical compositions (Komarneni and White, 1981) and represent the range of shales considered to be potential repository rocks. The SrCl_2 , $\text{Sr}(\text{QH})_2$, LaCl_3 , and NdCl_3 compounds were obtained from a chemical supply company. These starting materials were characterized by X-ray

powder diffraction (XRD) analysis. Blank hydrothermal runs were made of these materials without the addition of Sr, La, or Nd. The results are summarized in Table 2.

Methods

All starting materials were gently dry ground and sieved to obtain <75- μm or <105- μm fractions. XRD analysis of air-dried samples deposited on glass slides as slurries was carried out with a Philips APD-3600 X-ray diffractometer using Ni-filtered, $\text{CuK}\alpha$ radiation. The chloride salts of Sr, La, and Nd were dissolved separately in deionized water to give concentrations of ~50,000 $\mu\text{g/ml}$ of the respective cations; their exact concentrations were later determined by atomic emission spectroscopy (AES). $\text{Sr}(\text{OH})_2$ is only slightly soluble in deionized water at room temperature (Seidell, 1965), and therefore, a solution of 50,000 $\mu\text{g/ml}$ of Sr could not be prepared from this Sr compound. A 100-mg portion of each sample was sealed with 200 μl of the above Sr, La, or Nd solutions in gold capsules by cold-weld sealing (Komarneni *et al.*, 1979) and hydrothermally treated at 200° and 300°C for 12 weeks under a confining pressure of 30 MPa. Reaction of $\text{Sr}(\text{OH})_2$ with each sample was accomplished by adding 30.3 mg of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and 200 μl of deionized water to 100 mg of sample in a gold capsule, sealing the capsule, and treating it by the hydrothermal technique described above. The capsules were weighed before and after hydrothermal treatment to check for their integrity. Four runs leaked out of a total of eighty runs; the leaked runs are indicated in the tables.

Table 2. X-ray powder diffraction analysis of the untreated and hydrothermally treated backfill materials without the addition of Sr, La, or Nd.

Sample ¹	Untreated	Mineralogical changes after hydrothermal treatment at	
		200°C/30 MPa/28 days	300°C/30 MPa/28 days
Chlorite	Chlorite	No obvious change	No obvious change
Illite	Illite, quartz, kaolinite	No obvious change	Illite better crystallized; no other obvious changes
Kaolinite	Kaolinite	No obvious change	No obvious change
Montmorillonite	Montmorillonite	No obvious change	No obvious change
Clinoptilolite	Clinoptilolite	No obvious change	No obvious change
Mordenite	Mordenite	No obvious change	No obvious change
Antrim shale	Illite, quartz, pyrite, feldspars	No obvious change	Illite better crystallized; pyrite decomposed; no other obvious changes
Brallier shale	Illite, quartz, kaolinite, chlorite	No obvious change	Illite better crystallized; no other obvious changes
Conasauga shale	Illite, quartz, kaolinite, feldspars, chlorite	No obvious change	Illite better crystallized; no other obvious changes
Salona shale	Calcite, quartz, illite, feldspars	Illite better crystallized; no other obvious changes	Illite better crystallized; no other obvious changes

¹ See Table 1 for descriptions and sources.

Table 3. Analyses of Sr remaining in solution and X-ray powder diffraction analysis of hydrothermal¹ products.

Sample	Weight of Sr added/100 mg sample (mg)	200°C		300°C	
		% Sr in solution ²	Mineralogical changes by XRD	% Sr in solution	Mineralogical changes by XRD
<i>SrCl₂ source</i>					
Chlorite	9.46	108.2	No obvious change	94.5	No obvious change
Illite	9.46	100.1	No obvious change	86.2	No obvious change
Kaolinite	9.46	52.7	No obvious change	79.6	No obvious change
Montmorillonite	9.46	74.4	No obvious change	70.2	15.5-Å spacing collapsed to 12.4 Å; quartz formed
Clinoptilolite	9.46	55.6	No obvious change	56.2	Cristobalite(?) formed
Mordenite	9.46	73.8	No obvious change	64.1	Cristobalite(?) formed ³
Antrim shale	9.46	96.3	No obvious change	43.8 ⁴	Feldspar disappeared; illite and chlorite better crystallized
Brallier shale	9.46	104.5	No obvious change	62.0	No obvious change
Conasauga shale	9.46	100.5	No obvious change	69.0	Feldspar disappeared; illite and chlorite better crystallized
Salona shale	9.46	38.8	Strontianite formed	35.8	Strontianite formed; illite and chlorite better crystallized
<i>Sr(OH)₂ source</i>					
Chlorite	10.0	35.7	Sr ₂ MgSi ₂ O ₇ formed	2.6	Sr ₂ MgSi ₂ O ₇ formed
Illite	10.0	3.6	SrAl ₂ Si ₂ O ₈ ⁵ formed	1.5	SrAl ₂ Si ₂ O ₈ formed
Kaolinite	10.0	3.6	SrAl ₂ Si ₂ O ₈ formed	1.2	SrAl ₂ Si ₂ O ₈ formed
Montmorillonite	10.0	2.2	SrAl ₂ Si ₂ O ₈ and Sr ₂ MgSi ₂ O ₇ (?) formed	1.1	SrAl ₂ Si ₂ O ₈ formed
Clinoptilolite	10.0	1.8	Sr-wairakite formed	4.2	Plagioclase, Sr-wairakite and SrAl ₂ Si ₂ O ₈ (?) formed
Mordenite	10.0	3.1	SrAl ₂ Si ₂ O ₈ formed	5.1	Sr paracelsian(?) formed
Antrim shale	10.0	4.6	Sr-wairakite(?) formed	3.9 ⁴	Illite and chlorite better crystallized; SrAl ₂ Si ₂ O ₈ formed
Brallier shale	10.0	2.1	SrAl ₂ Si ₂ O ₈ formed	1.1	Illite better crystallized; Sr paracelsian formed
Conasauga shale	10.0	1.6	SrAl ₂ Si ₂ O ₈ formed	1.8	SrAl ₂ Si ₂ O ₈ formed
Salona shale	10.0	2.5	Strontianite formed	1.5	Strontianite and SrAl ₂ Si ₂ O ₈ formed

¹ Hydrothermally treated at 200° and 300°C/30 MPa for 12 weeks.

² Greater than 100% indicates experimental error.

³ May have been present in starting material.

⁴ Indicates leaked runs.

⁵ Indicates Sr-anorthite.

After the hydrothermal treatment, the capsules were cooled to room temperature and the solid and solution reaction products separated as follows: one end of the gold capsule was cut open in a long glass vial, and 25 ml of deionized water was added. The glass vial was capped, and the contents were mixed in a shaker for about 15 min. The opened gold capsule free of sample was then removed from the vial with tweezers. The vials were then centrifuged, and a portion of the supernatant was collected in polyethylene bottles without disturbing the sediment. The solid samples were washed once with 95% acetone or ethanol to remove any soluble salts and dried in an oven at 40°C prior to XRD analysis. The

solutions in the polyethylene bottles were analyzed for Sr, La, Nd, Si, Al, Ca, Na, and K by AES using a computer-interfaced SpectraMetrics SpectraSpan III instrument. Some of the Na and K analyses were made by atomic absorption spectrophotometry (AAS) using a Perkin Elmer PE703 instrument.

The cation-exchange capacity (CEC) of the non-zeolite samples was determined by Ca²⁺-ion saturation (Dolcater *et al.*, 1968). The CEC values of the zeolites were determined by Cs⁺-ion saturation followed by washing the excess CsCl with 95% acetone, decomposition of sample (Buckley and Cranston, 1971), and determination of Cs by AAS.

Table 4. Cation-exchange capacities of samples and analyses of Sr, Na, K, and Ca in solution of mixtures¹ of Sr sources with samples.

Sample	Cation exchange capacity (meq/100 g)	200°C		300°C	
		Sr uptake (meq/100 g)	Na + K + Ca released (meq/100 g)	Sr uptake (meq/100 g)	Na + K + Ca released (meq/100 g)
		SrCl ₂ source (Sr(OH) ₂ source)			
Chlorite	0.8	ND ² (146.6)	0.8 (0.5)	11.8 (222.3)	1.5 (2.2)
Illite	25.5	ND (220.0)	3.8 (1.6)	29.7 (224.8)	15.0 (4.5)
Kaolinite	2.4	102.1 (220.0)	0.7 (0.3)	43.8 (225.5)	8.6 (2.6)
Montmorillonite	120.0	55.4 (223.0)	57.6 (0.9)	64.0 (225.7)	78.1 (7.1)
Clinoptilolite	159.0	95.8 (224.0)	7.1 (1.4)	94.2 (218.7)	168.2 (3.9)
Mordenite	135.0	56.7 (221.0)	47.2 (1.1)	77.2 (216.4)	114.5 (2.4)
Antrim Shale	—	7.9 (217.6)	5.3 (1.4)	120.8 (219.4)	21.3 (6.0)
Brallier shale	—	ND (223.4)	3.0 (1.2)	81.8 (225.7)	5.6 (4.0)
Conasauga shale	12.0	ND (224.6)	4.0 (1.2)	66.6 (224.0)	34.6 (5.0)
Salona shale	—	132.1 (222.5)	99.4 (3.2)	138.0 (224.8)	157.6 (12.5)

¹ Hydrothermally treated at 200° and 300°C/30 MPa for 12 weeks.

² ND = No uptake detected.

RESULTS AND DISCUSSION

Reactions with SrCl₂ at 200° and 300°C

Among the clay minerals examined, only kaolinite and montmorillonite reacted with Sr as indicated by the 52.7 and 74.4%, respectively, of added Sr remaining in solution after the reaction (Table 3). The reaction of Sr with kaolinite is clearly not an exchange phenomenon, because the CEC of kaolinite is too small to account for the total Sr uptake (Table 4). The Sr uptake by kaolinite

is therefore likely due to the formation of new Sr aluminosilicate phases. However, no such phases were detected by XRD (Table 3), suggesting that if such materials were formed, they are probably poorly crystalline. The reaction of Sr with montmorillonite seems to be one of ion exchange as indicated by the equivalent release of interlayer cations at both temperatures (Table 4). No Sr uptake was detected with chlorite and illite at 200°C, but 5.5 and 13.8% of the added Sr was taken up at 300°C. The Sr uptake at 300°C by these minerals

Table 5. Concentrations of Si and Al in the original capsule fluid from mixtures of Sr or La or Nd sources with samples.

Sample	SrCl ₂ source		Sr(OH) ₂ source		LaCl ₃ source		NdCl ₃ source	
	Si (μg/ml)	Al (μg/ml)	Si (μg/ml)	Al (μg/ml)	Si (μg/ml)	Al (μg/ml)	Si (μg/ml)	Al (μg/ml)
200°C runs								
Chlorite	30	0.9	28	2100	36	<0.13	46	12
Illite	28	2.4	730	100	31	<0.13	52	37
Kaolinite	25	3.9	59	16.5	90	18	64	130
Montmorillonite	73	2.4	310	16.0	170	<0.13	150	27
Clinoptilolite	38	0.8	870	9.0	77	<0.13	88	16
Mordenite	30	5.2	580	13.0	59	<0.13	57	36
Antrim shale	34	3.7	370	13.5	56	<0.13	66	38
Brallier shale	23	2.8	500	51	8	<0.13	19	39
Conasauga shale	31	3.5	420	65	25	<0.13	19	34
Salona shale	49	9.2	690	170	28	<0.13	55	13
300°C runs								
Chlorite	26	<0.13	76	<0.13	30	<0.13	47	<0.13
Illite	31	<0.13	1690	725	125	<0.25	58	<0.13
Kaolinite	75	22	150	90	14	34	45	57
Montmorillonite	51	<0.13	310	29	44	<0.13	45	<0.13
Clinoptilolite	8	<0.13	450	3	47	<0.13	57	<0.13
Mordenite	9	<0.13	710	5	46	<0.13	47	<0.13
Antrim shale	38	13	375	39	125	<0.25	140	<0.4
Brallier shale	29	<0.13	1150	310	2	<0.13	22	1
Conasauga shale	75	20	540	170	14	<0.13	15	<0.13
Salona shale	100	17	440	130	38	<0.25	100	<0.25

¹ Hydrothermally treated at 200° and 300°C/30 MPa for 12 weeks.

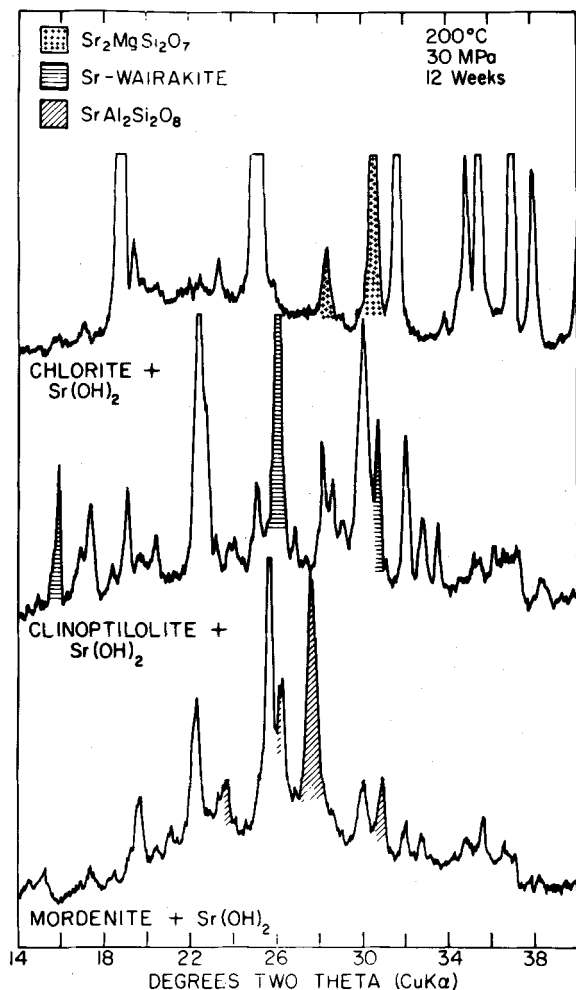


Figure 1. Portions of X-ray powder diffractograms of reaction products of minerals with $\text{Sr}(\text{OH})_2$ source.

was not by ion exchange alone because the Sr uptakes exceeded their CECs (Table 4). Formation of new strontium phases may account for some of the Sr uptake. The zeolites removed from 26.2 to 44.4% of the added Sr from solution (Table 3). Ion exchange alone cannot account for Sr reaction with zeolites because Sr uptake of some of the runs exceeded the amounts of cations released to solution (Table 4). New phases may have formed, but none were detected, except cristobalite (Table 3). Cristobalite was not detected in the untreated zeolites and did not form upon hydrothermal treatment without the addition of Sr at 200° and 300°C (Table 2). Shales, with the exception of the Salona sample, did not take up much Sr at 200°C but removed as much as 38% of the added Sr out of solution at 300°C (Table 3). The carbonate-rich Salona shale (Komarneni and White, 1981) was very reactive with Sr by the formation of SrCO_3 (strontianite) at 200° and 300°C. No SrSO_4 (celestite) was detected in the reaction products

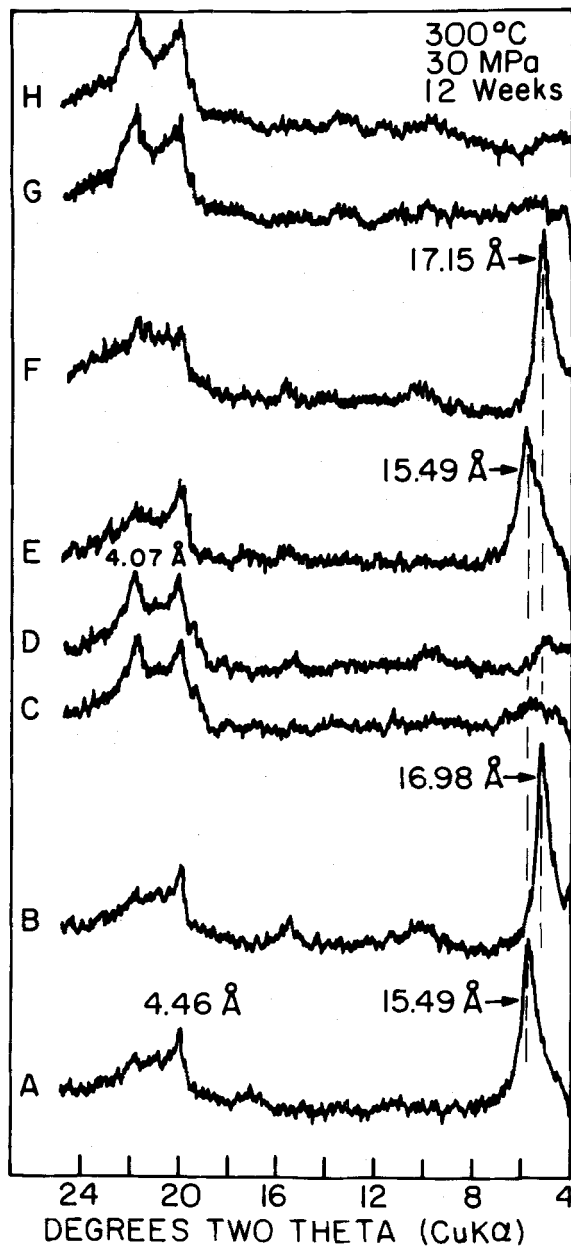


Figure 2. Portions of X-ray powder diffractograms of reaction products of clinoptilolite and mordenite with La and Nd sources: A. Clinoptilolite + LaCl_3 ; B. Same as A but exposed to ethylene glycol; C. Mordenite + LaCl_3 ; D. Same as C but exposed to ethylene glycol; E. Clinoptilolite + NdCl_3 ; F. Same as E but exposed to ethylene glycol; G. Mordenite + NdCl_3 ; H. Same as G but exposed to ethylene glycol.

because the materials used here contained little or no sulfate. These results show that the uptake of Sr was strongly influenced by the mineralogy, chemistry, and temperature of reaction. The reaction time used here is an instant compared to the thermal period (~200 years) in the life of a repository (Cohen, 1977); hence, further

Table 6. Analyses of La and Nd remaining in solution and X-ray powder diffraction analysis of mixtures¹ of La or Nd sources with samples.

Sample	Weight of La or Nd added/100 mg sample (mg)	200°C		300°C	
		% La or Nd in solution	Mineralogical changes by XRD	% La or Nd in solution	Mineralogical changes by XRD
<i>LaCl₃ source</i>					
Chlorite	9.73	47.7	No obvious change	5.9	New peaks at 2.63 Å, 3.10 Å
Illite	9.73	64.8	No obvious change	23.1	Illite better crystallized; new peaks at 3.14 Å, 3.11 Å, 2.86 Å, 2.64 Å, 2.62 Å, 1.82 Å
Kaolinite	9.73	94.3	No obvious change	90.7	No obvious change
Montmorillonite	9.73	40.0	No obvious change	0.3	No obvious change
Clinoptilolite	9.73	34.8	No obvious change	0.1	Smectite formed
Mordenite	9.73	54.2	No obvious change	11.5	Cristobalite ² and smectite(?) formed
Antrim shale	9.73	64.8	La ₂ O ₃ (?) formed	25.7 ³	Illite and chlorite better crystallized; new peaks at 2.85 Å, 3.12 Å, 3.49 Å, 2.64 Å, 2.19 Å, 4.62 Å, 2.01 Å
Brallier shale	9.73	77.1	No obvious change	28.1	No obvious change
Conasauga shale	9.73	66.7	LaCO ₃ OH(?) formed	1.0	Feldspar and pyrite disappeared; new peaks at 2.84 Å, 3.11 Å, 2.63 Å, 2.98 Å, 2.27 Å, 2.19 Å and 2.00 Å
Salona shale	9.73	1.2	LaCO ₃ OH formed	<0.01	LaCO ₃ OH formed
<i>NdCl₃ source</i>					
Chlorite	9.68	20.8	No obvious change	0.8	New peaks at 3.08 Å, 2.35 Å, 3.68 Å, 5.73 Å
Illite	9.68	63.6	No obvious change	6.1	New peaks at 3.08 Å, 2.87 Å, 3.48 Å, 2.96 Å
Kaolinite	9.68	96.4	No obvious change	86.5	No obvious change
Montmorillonite	9.68	37.4	No obvious change	0.04	Nd(OH) ₂ Cl(?)
Clinoptilolite	9.68	27.3	Nd ₂ O ₃ (?) formed	0.0	Nd(OH) ₂ Cl(?), cristobalite and smectite formed
Mordenite	9.68	57.5	One strong unidentified peak at 4.139 Å	10.6	Cristobalite and smectite(?) formed
Antrim shale	9.68	57.4	Feldspar disappeared; Nd ₂ O ₃ (?) formed	19.4 ²	Illite and chlorite better crystallized; feldspar decreased; Nd ₂ O ₃ (?) formed
Brallier shale	9.68	62.7	No obvious change	25.3	New peaks at 3.09 Å, 2.51 Å
Conasauga shale	9.68	54.1	Feldspar disappeared; Nd ₂ O ₃ (?) formed	0.8	New peaks at 2.81 Å, 3.08 Å, 2.34 Å
Salona shale	9.68	0.01	NdCO ₃ OH formed	0.02	NdCO ₃ OH formed

¹ Hydrothermally treated at 200° and 300°C/30 MPa for 12 weeks.

² May have been present in starting material.

³ Indicates leaked runs.

reaction of Sr with these materials may take place in the natural system. The formation of new Sr phases is a desirable waste-backfill or waste-rock interaction because soluble Sr was taken out of solution under the simulated repository conditions.

Reactions with Sr(OH)₂ at 200° and 300°C

All of the clay minerals, zeolites, and shales reacted extensively with Sr(OH)₂ at both temperatures as indicated by the very low percentages (1.1 to 35.7%) of

added Sr remaining in solution and by the formation of new strontium compounds such as SrAl₂Si₂O₈, Sr₂MgSi₂O₇, SrAl₂Si₄O₁₂·2H₂O, and SrCO₃ (Table 3; Figure 1). Despite the low solubility of the starting Sr(OH)₂, no Sr(OH)₂ was detected in the products by XRD indicating that it had reacted with the aluminosilicates to form Sr-aluminosilicates and other Sr compounds (Table 3). That Sr(OH)₂ reacted strongly with the minerals and shales is not surprising because the high pH (~12) Sr(OH)₂ probably decomposed alumi-

Table 7. Cation-exchange capacities of samples and analyses of La, Nd, Na, K, and Ca in solution of mixtures¹ of La or Nd sources with samples.

Sample	Cation-exchange capacity (meq/100 g)	200°C		300°C	
		La or Nd uptake (meq/100 g)	Na + K + Ca released (meq/100 g)	La or Nd uptake (meq/100 g)	Na + K + Ca released (meq/100 g)
LaCl ₃ source (NdCl ₃ source)					
Chlorite	0.8	110.0 (159.5)	1.1 (0.3)	197.3 (199.7)	0.4 (0.7)
Illite	25.5	73.9 (73.2)	7.8 (9.0)	161.4 (189.1)	31.3 (30.2)
Kaolinite	2.4	11.9 (7.3)	12.4 (0.3)	9.8 (13.6)	0.9 (0.9)
Montmorillonite	120.0	126.1 (126.0)	17.6 (18.0)	209.4 (201.2)	68.7 (47.7)
Clinoptilolite	159.0	137.0 (146.4)	5.3 (7.0)	209.8 (201.2)	187.5 (169.4)
Mordenite	135.0	96.3 (85.5)	16.7 (17.3)	185.8 (179.9)	164.6 (160.7)
Antrim shale	—	73.9 (85.7)	6.9 (9.3)	156.0 (162.3)	36.7 (35.2)
Brallier shale	—	48.2 (75.1)	3.0 (4.2)	150.9 (150.4)	10.7 (14.0)
Conasauga shale	12.0	70.0 (92.5)	5.9 (6.7)	208.0 (199.7)	27.3 (30.4)
Salona shale	—	207.6 (201.2)	14.7 (40.3)	210.0 (201.2)	58.2 (209.3)

¹ Hydrothermally treated at 200° and 300°C/30 MPa for 12 weeks.

nosilicate minerals, releasing large quantities of Si and Al into solution to form new phases such as SrAl₂Si₂O₈, Sr₂MgSi₂O₇, and SrAl₂Si₄O₁₂·2H₂O (Table 3). Large concentrations of Si and Al were detected in capsule fluids (Table 5) which supports the above decomposition process by Sr(OH)₂. No correlation was found between the Sr-uptake and the cations released (Table 4), indicating that ion exchange alone cannot account for these reactions. These results point out that the Sr released as Sr(OH)₂ from either SrZrO₃ or spent fuel elements (Komarneni, 1981) or SrTiO₃ of synroc waste (Nesbitt *et al.*, 1981) may be extremely reactive with such backfill materials or surrounding shale wall rocks to form relatively insoluble Sr compounds such as SrCO₃ and SrAl₂Si₂O₈ (Seidell, 1965; Fleer and White, 1981).

Reactions with LaCl₃ at 200° and 300°C

The samples generally removed less than half of the added La at 200°C (except for the Salona shale) and more than 75% at 300°C, as indicated by the low percentages of the added La remaining in solution (Table 6). The principal mechanism of La-uptake does not appear to be ion exchange, because the uptake of La exceeded the CEC of the samples (by as much as 200 times in the case of chlorite), as well as by the amounts of exchangeable cations released into solution (Table 7). Lanthanum was probably taken out of solution as La(OH)₃ or La₂O₃ at 200°C by reaction with most of the minerals and shales, except the Salona shale where La hydroxy carbonate crystallized by reaction with calcite. The prediction of La(OH)₃ formation is based on an analogy with the behavior of Mg which formed brucite by hydrolysis and reaction with SrZrO₃ (Komarneni, 1981) due to a decrease in pH (Braithwaite and Molecke, 1980) under hydrothermal conditions. At 300°C, unidentified crystalline phases developed with chlorite, illite, and the Antrim and Conasauga shales. Clinoptilolite and mordenite transformed to clay-like

phases in the presence of La at 300°C (Figure 2) but did not alter in the blank runs (Table 2). The d spacing of this clay phase expanded from 15.5 Å to about 17 Å with ethylene glycol treatment indicating that it is a smectite (Figure 2). The mechanism of smectite formation probably involves hydrolysis of La to form La(OH)₃ and H⁺-exchange saturation of the zeolite, followed by its decomposition (Breck, 1974) and recrystallization. Studies are in progress to test the above hypothesis of smectite formation. The calcite-rich Salona shale reacted almost completely with La to form La hydroxy carbonate both at 200° and 300°C (Table 6).

Reactions with NdCl₃ at 200° and 300°C

Significant amounts of Nd were taken out of solution by all the shales and minerals except kaolinite as indicated by the fractions (0 to 86.5%) of added Nd remaining in solution (Table 6). A comparison of the La and Nd results indicates that both of these elements behaved similarly in their reaction with the various minerals and shales (Table 6). Several mechanisms are probably involved in Nd uptake by the various minerals and shales. Some ion exchange may be involved, but it is not the principal mechanism because the Nd uptake is very much greater than the CECs of most of the samples (Table 7). The amounts of cations released by the minerals are much smaller than the amounts of Nd uptake by the various minerals and shales at both temperatures (Table 7), further supporting the above hypothesis. The reaction of Nd with the shales and minerals at 200°C probably resulted in the precipitation of Nd₂O₃ or Nd hydroxy carbonate, as in the case of Salona shale by reacting with calcite (Table 6). At 300°C, more than 80% of the added Nd was taken out of solution by most samples by the formation of unidentified new phases whose d-spacings are listed in Table 6. Such phases were not formed in the control runs without the addition of Nd (Table 2). The clinoptilolite-Nd reaction formed a

smectite clay mineral (Table 6, Figure 2), similar to the clinoptilolite-La reaction.

CONCLUSIONS

Backfills, such as clay minerals and zeolites, and wall rocks, such as shale, removed Sr from solution by ion exchange and/or by forming new Sr phases under simulated repository conditions. The reaction of soluble Sr with backfills or wall rocks to form sparingly soluble Sr phases, such as $\text{SrAl}_2\text{Si}_2\text{O}_8$, SrCO_3 , $\text{Sr}_2\text{MgSi}_2\text{O}_7$, and $\text{SrAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$, is significant because these phases fix Sr, one of the most mobile and hazardous elements in nuclear wastes.

The reaction of La and Nd (simulating Am and Cm) strongly depend on temperature and mineralogy of the reactant materials. La and Nd were taken out of solution almost completely by some of the investigated backfill and wall rock materials by the formation of LaOHCO_3 , NdOHCO_3 , and, possibly, oxides and hydroxides of La and Nd. The zeolites, clinoptilolite and mordenite were transformed to smectite in the presence of La and Nd. If La and Nd are good simulators of Am and Cm, the present data suggest that Am and Cm can be immobilized (taken out of solution) under repository conditions.

Among the backfill and wall rock materials tested, Salona shale containing calcite was found to be the most reactive with Sr, La, and Nd under the simulated repository conditions used in this study.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy through sub-contract with the Office of Nuclear Waste Isolation, Battelle Memorial Institute, Contract E512-03400.

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(Received 6 January 1982; accepted 14 May 1982)

Резюме—Исследовались реакции Sr, La, и Nd (последние два элемента симулирующие Am и Cm) с потенциальными минералами для засыпки хранилища радиоактивных отходов и с породами стен хранилища, такими как сланцеватые глины в условиях симулирующих хранилище, при температурах 200° и 300°C в течение 12 недель, при давлении 30 МПа. Твердые продукты реакции и продукты, выделенные из растворов, использовались для определения природы и степени протекания реакции. Хлорит, иллит, каолинит, монтмориллонит, клиноптилолит, морденит, и четыре сланца удаляли из раствора 61,2 и 98,5% добавленных SrCl_2 и $\text{Sr}(\text{OH})_2$, соответственно, путем обмена ионов и/или путем образования новых соединений стронция таких, как $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, SrCO_3 (стронцианит), и $\text{SrAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ (Sr-ваиракит). Образование этих едва растворимых фаз Sr путем реакции растворимых соединений Sr с такими засыпковыми материалами указывает на то, что засыпки могут служить в качестве барьера в течение термального периода отходов во время существования хранилища. Эти самые минералы и сланцы удаляли из раствора 99,99% добавленного La или Nd при 300°C путем образования новых фаз таких, как LaOHCO_3 , NdOHCO_3 , и, вероятно, окисей и гидроокисей La или Nd. Цеолиты реагировали с La и Nd, образуя смектит. Таким образом, если La и Nd действительно симулируют реактивность Am и Cm, засыпки, приготовленные соответствующим образом, могут служить в качестве барьера перед миграцией трансурановых элементов ядерных отходов. [E.C.]

Resümee—Reaktionen von Sr, La, und Nd (die beiden letzten Elemente simulieren Am und Cm) mit möglichen Trägermineralen für die Lagerung radioaktiver Abfälle und mit lagerungsgesteinen, wie z.B. Schieferton, wurden unter simulierten Lagerungsbedingungen von 200°C und 300°C über 12 Wochen und bei maximalen Drücken von 30 MPa untersucht. Die festen Reaktionsprodukte und die Reaktionslösungen wurden untersucht, um die Art und das Ausmaß der Reaktion zu bestimmen. Chlorit, Illit, Kaolinit, Montmorillonit, Mordenit, und Klinoptilolith sowie Schiefertone entfernten bis zu 61,2 bzw. 98,5% des zugefügten SrCl_2 und $\text{Sr}(\text{OH})_2$ aus der Lösung entweder durch Ionenaustausch und/oder durch die Bildung neuer Strontium-Verbindungen wie z.B. $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, SrCO_3 (Strontianit), und $\text{SrAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ (Sr-Wairakit). Die Bildung dieser kaum löslichen Sr-Phasen durch die Reaktion von löslichen Sr-Verbindungen mit derartigen Trägerstoffen deutet darauf hin, daß die Aufnahme durch diese Minerale als Schranke während der thermischen Periode des Abfalles wirken kann. Die gleichen Minerale und Schiefertone entfernten bei 300°C bis zu 99,99% des zugefügten La oder Nd aus der Lösung durch die Bildung neuer Phasen, wie LaOHCO_3 , NdOHCO_3 , und möglicherweise La- oder Nd-Oxide und -Hydroxide. Zeolithe reagierten mit La und Nd unter der Bildung von Smektit. Wenn daher La und Nd wirklich die Reaktivität von Am und Cm simuliert, dann kann eine richtig durchgeführte Rückfüllung als eine Schranke gegen die Wanderung von Transuranen aus radioaktiven Abfällen wirken. [U.W.]

Résumé—Les réactions du Sr, La, et Nd (les deux derniers éléments simulants Am et Cm) avec des minéraux pouvant servir de rembourrage (backfill) pour le stockage de déchets radioactifs, et avec les surfaces des roches du milieu de dépôt telles l'argilite, ont été étudiées sous des conditions de dépôt simulées de 200° et 300°C pendant 2 semaines sous une pression du milieu de 30 MPa. Les produits des réactions, solides et en solution, ont été identifiés pour déterminer la nature et l'étendue de la réaction. Chlorite, illite, kaolinite, montmorillonite, mordenite, et clinoptilolite, et quatre argilites ont extrait de la solution jusqu'à 61,2 et 98,5% du SrCl_2 et $\text{Sr}(\text{OH})_2$ ajoutés, respectivement par échange ionique et/ou par formation de nouveaux composés de strontium tels que $\text{SrAl}_2\text{Si}_2\text{O}_8$, $\text{Sr}_2\text{MgSi}_2\text{O}_7$, SrCO_3 (strontianite), et $\text{SrAl}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$ (Sr-wairakite). La formation de ces phases peu solubles du Sr par la réaction des composés solubles du Sr avec de tels éléments de rembourrage indique qu'il peut servir de barrière durant la période thermique du déchet dans le cycle d'un dépôt. Ces mêmes minéraux et argilites ont extrait jusqu'à 99,99% du La ou Nd ajoutés, de solution à 300°C par formation de nouvelles phases telles LaOHCO_3 , NdOHCO_3 , et peut-être d'oxydes et hydroxydes de La ou Nd. Les zéolites réagissent avec La et Nd pour former de la smectite. D'où, si La et Nd reflètent réellement la réactivité d'Am et de Cm, un rembourrage approprié peut servir de barrière à la migration des éléments transuraniens des déchets nucléaires. [D.J.]