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The Extraction of ^{137}Cs and ^{89}Sr from Waste Simulants Using Pillared Montmorillonite

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ABSTRACT

Two samples of a silica-pillared montmorillonite produced using 3-aminopropyltrimethoxy silane and an alumina-pillared montmorillonite were evaluated for the removal of ^{137}Cs and ^{89}Sr from a simulated nuclear waste solution and a simulated groundwater, and the results were compared to the parent montmorillonite and two zeolites, AW500 (chabazite) and clinoptilolite. The parent and pillared clays were characterized using x-ray powder diffraction and surface area analysis by nitrogen adsorption/desorption studies. The pillared clays exhibited d -spacings of between 17.43 and 18.32 Å after calcination, and surface areas ranging from 71.3 to 264.4 m^2g^{-1} . Both of the silica-pillared clays and the alumina-pillared clay exhibited excellent K_d s for ^{137}Cs from simulated groundwater with values of 23,650, 23,260 and 144,570 mL/g, respectively. These were far better than the K_d s obtained by clinoptilolite and AW500 which had K_d s of only 14,560 and 9650 mL/g, respectively. None of the pillared clays showed a high selectivity for ^{89}Sr from groundwater or ^{137}Cs from simulated alkaline tank waste. They did, however, show a slight selectivity for ^{89}Sr in the simulated Hanford tank wastes, but this is thought to be due to a precipitation mechanism rather than to ion exchange.

Key Words. Pillared clay; Ion exchange; Montmorillonite; Groundwater

INTRODUCTION

There is a continuing need to develop new ion-exchange materials for the remediation of wastes produced during United States nuclear weapons

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manufacture. Of major concern is the estimated 65 million gallons of waste stored in stainless steel tanks in the Hanford reservation in Washington State which was produced as a result of the reprocessing of irradiated uranium fuel to recover ^{239}Pu for weapons manufacture (1). A number of these tanks have leaked, resulting in contamination of groundwater and the threat of contamination in the nearby Columbia River.

The inventory of each tank is different but they all share some basic characteristics. The waste in each tank is highly alkaline and consists of three primary components which are a salt cake, an alkaline supernate, and a hydroxide sludge (2). The main heat generators in the tanks are ^{137}Cs and ^{90}Sr with half lives of 30.3 and 29.1 years, respectively. Cesium is found primarily in the salt cake and the alkaline supernate while strontium occurs predominantly in the hydroxide sludge with lesser amounts residing in the salt cake and supernate. The proposed disposal route is to vitrify the hydroxide sludge which contains the majority of the actinides and to separate ^{137}Cs and ^{90}Sr from the salt cake and the supernate and to vitrify these isotopes separately. Due to the high alkalinity and high ionic strength of the solutions to be treated, it has been necessary to develop new selective ion-exchange materials which exhibit high selectivity for ppm levels of Cs and Sr in the presence of up to 5 M Na^+ and also are stable in the highly alkaline environment (3–6).

Of equal concern is the contamination of groundwater surrounding the Hanford site and other DOE sites. Here, the chemistry of the waters is far less extreme and the main competition for Cs and Sr uptake will be from Mg^{2+} and Ca^{2+} , and hence a greater number of ion exchangers is likely to prove suitable. Groundwaters vary considerably in both composition and pH, and thus the exchanger performance is likely to vary significantly from groundwater to groundwater.

Smectite or swelling clays are very common naturally occurring minerals and reside in huge deposits around the world. The structure consists of aluminum or magnesium-oxygen octahedra sandwiched between layers of silica tetrahedra as shown in Fig. 1. Montmorillonite is a member of the smectite clay family in which the octahedral positions are occupied by aluminum ions and is termed a dioctahedral clay (7). Substitution of aluminum by divalent ions, usually magnesium, occurs in nature and results in a net negative charge on the clay lattice. This charge deficit diffuses to the outside of the silica tetrahedra where it is counterbalanced by the absorption of cations, usually Na^+ and Ca^{2+} . These cations are readily exchangeable, and hence the montmorillonite exhibits ion-exchange properties. The capacity of the clay is dependent upon the degree of substitution within the octahedral layer but usually falls in the 0.7–1 meq/g range.

Typically, clays tend to be relatively nonselective ion exchangers and are difficult to separate from aqueous media due to their small particle size and

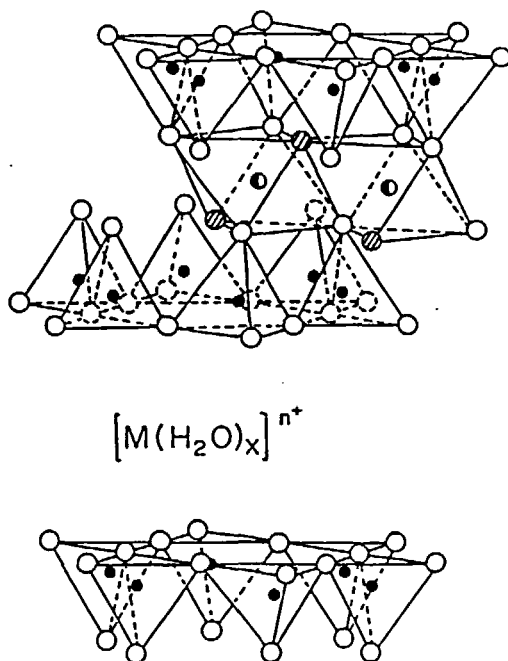


FIG. 1 Representation of the structure of a smectite clay showing the tetrahedral-octahedral-tetrahedral layer structure. M is typically Na^+ or Ca^{2+} .

tendency to form dispersions. Consequently, they have found limited applications in industrial processes. However, it is possible to pillar clays to produce porous materials in which the clay lamellae are permanently propped apart by inorganic pillars (8–11). These materials have relatively high surface areas and uniformly-sized pores and, since they no longer swell or disperse, can be handled much more easily in aqueous media. A study of the ion-exchange properties of pillared clays was undertaken by Dyer and Gallardo (12) who showed that the ion-exchange properties of pillared clays were associated with the pillar and not the host clay, and that pillaring actually increased the ion-exchange capacity of the clays. However, no ion selectivity data were presented, and their results did not take into account that some solubility of the pillar may occur. Subsequently, Molinard et al. (13) showed that some alumina does dissolve in both acid and base, and if not taken into account may lead to misleading results in ion-exchange titration data.

The present study investigated the ^{137}Cs and ^{89}Sr selectivity of two montmorillonites pillared with silica and alumina and compared the results to the

TABLE 1
The Composition of NCAW (Neutralized Current Acid Waste)
and N-Springs Simulants

Compound	NCAW (mol/L)	N-Springs (mol/L)
NaNO ₃	0.258	—
KNO ₃	0.120	—
Na ₂ SO ₄	0.150	—
Na ₂ HPO ₄	0.025	—
NaOH	3.40	—
Al(NO ₃) ₃	0.430	—
Na ₂ CO ₃	0.230	1.25×10^{-4}
NaF	0.089	1.05×10^{-5}
NaNO ₂	0.430	—
RbNO ₃	5.00×10^{-5}	—
CsNO ₃	5.00×10^{-4}	—
Ca(NO ₃) ₂	—	9.55×10^{-5}
CaCl ₂	—	2.26×10^{-5}
Ca(OH) ₂	—	6.09×10^{-4}
Ba(OH) ₂	—	1.12×10^{-7}
MgSO ₄	—	2.16×10^{-4}
Sr(NO ₃) ₂	—	1.48×10^{-6}

parent clay of the silica-pillared montmorillonite. Two simulants were prepared according to information supplied by the Pacific Northwest National Laboratory (PNNL) (14) and spiked with either ¹³⁷Cs or ⁸⁹Sr as appropriate. The composition of these simulants is given in Table 1. NCAW (neutralized current acidic waste) represents Tank 102 AZ diluted to 5 M Na⁺ and is thought to contain the highest levels of Cs in the Hanford site. N-Springs represents a groundwater found in the Hanford 100 area and contains relatively high concentrations of magnesium and calcium but no potassium. Since Mg²⁺ and Ca²⁺ primarily compete with Sr²⁺ while K⁺ competes with Cs⁺, any ion exchangers would be expected to exhibit relatively high *K_d*s for Cs because of the lack of K⁺ in the N-Springs simulant.

EXPERIMENTAL

A sample of montmorillonite, SWy-1 (from Crooks County, Wyoming), was obtained from Source Clays, University of Missouri-Columbia. This raw mixture was then purified by wet sedimentation and characterized by XRD prior to use. The purified montmorillonite was used to synthesize silica-pillared clays according to the following procedures.

Approximately 3 g (dry weight) of purified SWy-1 was suspended in 200 mL of deionized water and the mixture heated to 100°C. In a separate vessel, 5 g of 3-aminopropyltrimethoxy silane, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$, was added to 150 mL of deionized water and brought to reflux temperature. The hot clay suspension was then added dropwise to the silane solution while stirring vigorously. This resulted in flocculation of the clay, making stirring difficult, so an additional 100 mL of deionized water was added, giving a total volume of approximately 450 mL. This mixture was allowed to reflux for 18 hours. The solid product was separated by centrifugation, washed with deionized water, and dried at 65°C. Mass of product obtained = 4.5 g. Pillaring was achieved by calcining the material at 500°C in air for 18 hours to burn off the organic material, leaving behind a silica pillar in the interlamellar region. This pillared material was designated "II-41."

In an attempt to cause further polymerization of the silane prior to reacting it with the clay, the above experiment was repeated except that 10 g of 3-aminopropyltrimethoxy silane was added to 300 mL of water and allowed to reflux for 20 hours. This silane solution was then added to a dispersion of 3 g (dry weight) of SWy-1 in 200 mL of deionized water, 100 mL of additional water was added to facilitate stirring, and the mixture refluxed for 24 hours. The solid product was then separated by centrifugation, washed with deionized water, and dried at 65°C. Mass of product = 4.5 g. As in the previous sample, pillaring was obtained by calcining in air at 500°C for 18 hours. The pillared product was designated "II-55."

A sample of a Los Trancos alumina-pillared calcium montmorillonite was obtained from Laporte Absorbents, Widnes, Cheshire, UK. This had been prepared by intercalating the Al_{13} Keggin ion, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, into a calcium montmorillonite followed by calcination at 550°C for 4 hours to dehydrate the Keggin ion and fix the pillars. This pillared product (AL-PILC) was used as received without any further treatment. This material had been developed as a potential scavenger for organic species in aqueous media, and its ion-exchange properties had not been fully evaluated.

Ion-Exchange Studies

The selectivities of the three pillared clays and the parent SWy-1 for ^{137}Cs and ^{89}Sr were investigated using simple batch studies. Approximately 0.05 g of material was contacted with 10 mL of solution (giving a $V:m$ ratio of 200) spiked with ^{137}Cs or ^{89}Sr , as appropriate, for 20 hours with constant rotary mixing. The solution was then filtered through a Whatman No. 42 filter paper (which had previously been shown to be sufficient to exclude all of the clay fines from the supernate), and the activity in the aqueous phase

measured using liquid scintillation counting. Distribution coefficients (K_d s) were then calculated according to:

$$K_d = [(C_i - C_f)/C_f]V/m \quad (1)$$

where C_i = initial activity of solution

C_f = final activity of solution

V = volume of solution (mL)

m = mass of exchanger (g)

The radiotracers added resulted in a total cesium concentration in the N-Springs groundwater of approximately 2 ppb and a total strontium concentration of approximately 0.1 ppm in the NCAW. The contributions of the radiotracers to the total strontium in the groundwater (1.48×10^{-6} M) and the total cesium in the NCAW (5.0×10^{-4} M) were negligible.

Instrumentation

X-ray powder diffraction patterns were obtained on a Scintag PAD V diffractometer using nickel-filtered $\text{CuK}\alpha$ radiation. Surface area measurements were obtained on a Quantachrome Autosorb 6 unit using nitrogen adsorption-desorption at 77 K. Radioisotope counting was obtained using a Wallac 1410 Liquid Scintillation Counter.

RESULTS AND DISCUSSION

The XRD patterns of SWy-1 (Na-form, dried at 65°C), II-55, and II-55 after calcination are given in Fig. 2. All of the materials are poorly crystalline, but a distinct reflection remains after calcination which corresponds to the interlayer spacing of the silica-pillared clay and reveals the increase in layer spacing due to the silica pillar. (The sharp peak at 3.35 \AA corresponds to quartz which wasn't removed during the purification procedure.) The XRD patterns of II-41 were similar to those of II-55 and these, together with the surface area data, are summarized in Table 2.

The data displayed in Table 2 show that both of the silane pillaring attempts were successful and a pillared material was produced. However, despite the fact that both silane materials exhibited similar interlayer spaces before and after heating, II-41 had a low surface area after calcination. This may be due to less polymerization of the silane prior to contact with the clay, resulting in the intercalation of a number of silane species in addition to the desired pillaring species. On calcination, this would result in the blocking of the pores and consequently a low surface area. In II-55 by contrast, the silane has

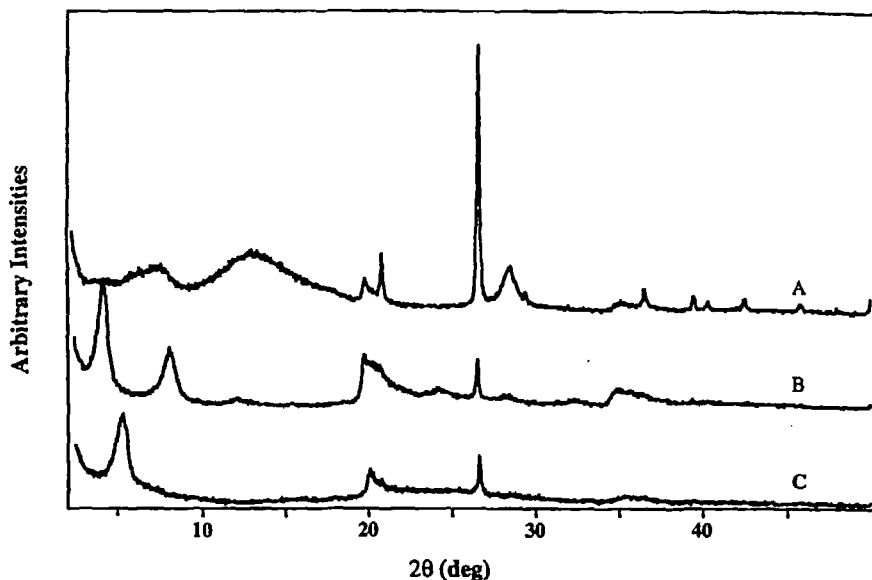


FIG. 2 X-ray diffraction patterns of (A) montmorillonite SWy-1, (B) II-55, and (C) II-55 calcined at 500°C.

undergone greater polymerization with the intercalation of a far greater proportion of the preferred polymer.

The pillaring of layered materials using 3-aminopropyltrimethoxy silane has been studied in previous publications (15–17), and some information on the nature of the pillaring species has been determined. Intercalation of the aminosilane into the clay gave d -spacings of 21.33 and 21.46 Å for II-41 and II-55, respectively. Assuming a thickness of the clay lamellae of 9.4 Å, this gives an approximate pillar length of 12 Å prior to calcination, which com-

TABLE 2
XRD and Surface Area Data for the Pillared Clays and the Montmorillonite SWy-1

Sample	d (Å) (65°C)	d (Å) (500°C)	BET surface area (m ² /g)	Percent of surface area due to micropores
SWy-1	9.65	—	41.8	38.8
II-41	21.33	17.43	71.3	36.6
II-55	21.46	17.63	169.7	56.2
Al-PILC	—	18.32	264.4	81.9

pares well with the predicted pillar length of 12.74 Å for an octameric poly-aminosilane hypothesized by Roziere et al. (16). When such a polymer is directly intercalated into α -zirconium phosphate (α -ZrP), a "stuffed" nonporous material results after calcination. In the case of the montmorillonite in this study, the intercalation of the same polymeric silane resulted in an open porous structure with a surface area comparable to conventional alumina-pillared clays. The reason for this is the difference in charge density between the α -ZrP and the montmorillonite. α -ZrP has a theoretical ion-exchange capacity of 6.6 meq/g, which is between 7 and 10 times the capacity of the clay. Consequently, a far greater number of silane species will be intercalated to satisfy the layer charge as compared to the clay. Additionally, the charge in α -ZrP is associated with specific —P—OH groups while in the clay it is a diffuse charge rather than a point charge. Hence, the intercalated polymers will be spread out across the layer rather than associated with specific localities within the structure. The resulting clay will contain fewer intercalated silane species which, on calcination, produces a porous, open structure.

The preparation of alumina-pillared clays is well known and has been the subject of numerous reviews (9–11). Consequently, the structure and mechanism of pillaring will not be discussed further. However, it is worth noting that the initial layer charge on the montmorillonite was satisfied by the intercalation of the Al_{13} Keggin ion. Calcination of the Keggin ion results in dehydration of the pillar and the liberation of protons. It is these protons which account for the ion-exchange behavior of the pillared material and not a residual charge from the parent clay.

The ion-exchange behavior of the pillared materials is quite unlike that of the parent montmorillonite, SWy-1. It can be inferred from the K_d s listed in Table 3 that the introduction of pillars into the montmorillonite has engineered a high selectivity for cesium from groundwater with the alumina-pillared

TABLE 3
 K_d s for ^{89}Sr and ^{137}Cs from N-Springs Simulant^a

Sample	^{137}Cs K_d (mL/g)	^{89}Sr K_d (mL/g)
SWy-1	560	665
II-41	23,650	276
II-55	23,260	513
II-55 (U)	542	n.d.
Al-PILC	144,600	441
AW500	9,650	30,650
Clinoptilolite	14,560	27,190

^a n.d. = not determined, (U) = uncalcined sample.

TABLE 4
 K_d s for ^{89}Sr and ^{137}Cs from NCAW Simulant

Sample	^{137}Cs K_d (mL/g)	^{89}Sr K_d (mL/g)
SWy-1	36	274
II-41	7	3600
II-55	12	6620
Al-PILC	27	3300
AW500	44	260
Clinoptilolite	7	48

material, exhibiting a K_d of nearly 150,000 mL/g. This is a several orders of magnitude greater than that of SWy-1 which only exhibited a K_d of 560 mL/g. The silica-pillared materials give very similar K_d s which was expected from the initial XRD patterns. Although these values are far less than the alumina PILC, they are comparable to the conventional "benchmark" ion-exchange materials chabazite (AW500) and clinoptilolite.

To ensure that the K_d s obtained for ^{137}Cs from N-Springs groundwater were due to the silica pillars, the ion-exchange experiment was performed using the uncalcined precursor of II-55. This material contains the uncalcined aminosilane and as such would be expected to exhibit negligible ion-exchange selectivities. This is confirmed, as can be seen in Table 3 where a K_d for ^{137}Cs of only 542 mL/g was noted, indicating that the pillaring of the clay is the true cause of the selectivity toward cesium.

The measured K_d s in NCAW are given in Table 4 where it is evident that the pillared materials exhibit negligible selectivity toward cesium though this is not surprising since NCAW is approximately 5 M in Na^+ , 0.12 M in K^+ , and a mere 5×10^{-4} M in Cs^+ . There is a slight selectivity for strontium though [probably present as $\text{Sr}(\text{OH})^+$], with the best material, II-55, exhibiting a K_d of 6,620 mL/g. This is impressive when compared to the conventional zeolites clinoptilolite and AW500 which gave K_d s of 48 and 260 mL/g, respectively, but is very poor when compared to other materials such as sodium nonatitanate, $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$, which gave a K_d of over 200,000 mL/g in NCAW under identical conditions (18). After contact with the three pillared materials, particularly II-41 and II-55, it was noted that there was a slight yellow color to the solution, suggesting partial dissolution of the material. Since this color was not evident for the parent clay SWy-1, it was assumed that this was due to partial dissolution of the silica pillars. Considering the high alkalinity of the NCAW, partial dissolution of both the parent clay and the pillars over a contact time of 20 hours is almost certain.

CONCLUSIONS

This study has shown that it is possible to modify a natural montmorillonite clay by permanently propping apart the lamellae with a stable inorganic oxide to produce a selective ion exchanger. The choice of the pillar clearly has a major effect on the selectivity of the final product as exemplified by the difference between the alumina- and silica-pillared clays. ^{137}Cs was efficiently removed by the pillared materials from a low ionic strength groundwater simulant containing a large excess of sodium and alkaline earth cations. The parent clay and the uncalcined precursor both exhibited negligible cesium uptake. Negligible selectivity for strontium was observed in all of the materials.

In NCAW, the materials proved unable to remove trace levels of cesium in the presence of 5 M Na^+ . However, some removal of strontium was observed though the removal mechanism is unlikely to be ion exchange. In such strongly basic solutions, considerable dissolution of both the host clay and the alumina and silica pillars will occur, so it is possible that the strontium uptake is a result of the precipitation of strontium silicates or aluminosilicates.

Consequently, it can be concluded that alumina-pillared clays are suitable materials for the selective removal of Cs^+ from groundwater since they perform better than currently available zeolites and are inexpensive to synthesize, resistant to radiolysis, and chemically stable in typical groundwaters. Their use is limited by the chemical stabilities of the host clay and the pillar, but they have potential applications for the removal of cesium from low alkaline effluents such as fuel storage pondwaters. Further work is underway to fully evaluate the ion-exchange properties.

Alumina-pillared clays have to date shown the greatest Cs^+ selectivity, but since it is possible to use a range of pillaring species, including Cr, Ti, Zr, and Fe oxides, and to use other lamellar hosts in place of clays, it may be possible to synthesize more selective and more chemically stable materials with wider applications within the nuclear industry.

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