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Paul Sylvester[a]; Abraham Clearfield[b]; Ricardo J. Diaz†[b]
[a] Lynntech Inc., College Station, TX, U.S.A. [b] DEPARTMENT OF CHEMISTRY, TEXAS A&M UNIVERSITY, COLLEGE STATION, TEXAS, USA

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Pillared Montmorillonites: Cesium-Selective Ion-Exchange Materials

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PAUL SYLVESTER,* ABRAHAM CLEARFIELD,†
and RICARDO J. DIAZ‡
DEPARTMENT OF CHEMISTRY
TEXAS A&M UNIVERSITY
PO BOX 300012, COLLEGE STATION, TEXAS 77842-3012, USA

ABSTRACT

A zirconia-pillared and an alumina-pillared montmorillonite clay were found to exhibit high K_ds for trace levels of cesium (2.5 ppb) in the presence of high concentrations of Ca^{2+}, Mg^{2+}, and Na^{+} ions with distribution coefficients (K_ds) for ^{137}Cs exceeding 1×10^5 mL/g over a wide range of competing ion concentrations. An excess of K^{+} ions, however, caused a dramatic reduction in the Cs K_ds for both of the materials. These results were in contrast to the parent montmorillonite which exhibited far lower K_ds for ^{137}Cs, particularly in the presence of high concentrations of Mg^{2+} and Ca^{2+}. Batch tests in simulated groundwaters showed that both pillared clays efficiently removed ^{137}Cs from solution, with the best K_ds being approximately 8.5×10^5 mL/g in a potassium-free groundwater. The materials performed less well in a groundwater with a high potassium concentration, but still gave K_ds similar to commercially available zeolites. The rate of ^{137}Cs uptake was found to be rapid with both the alumina- and zirconia-pillared clays extracting $> 90\%$ of the ^{137}Cs from a 0.1 M $NaNO_3$ solution within 5 minutes.

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

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* Current address: Lynntech Inc., 7610 Eastmark Drive, Suite 105, College Station, TX 77840.
† To whom correspondence should be addressed.
‡ Undergraduate Research Scholar.

INTRODUCTION

There is a continuing need to develop new ion-exchange materials for the remediation of wastes produced during United States nuclear weapons 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 the groundwater with radionuclides such as ^{137}Cs and ^{90}Sr (2). Similar groundwater contamination problems also occur at other nuclear sites such as the Idaho National Engineering and Environmental Laboratory (INEEL) (3).

Groundwaters vary considerably in composition and thus exchanger performance is likely to vary significantly from groundwater to groundwater. The main ions present in groundwaters are Ca^{2+}, Mg^{2+}, Na^+, and K^+ which will compete with ^{90}Sr and ^{137}Cs for the available ion-exchange sites in any ion-exchange material. Strontium is typically present at concentrations of a few tenths of a part per million (ppm), but cesium is present at much lower levels, typically parts per billion (ppb) or less. Consequently, ion exchangers will need to exhibit high selectivities for cesium relative to Ca^{2+}, Mg^{2+}, Na^+, and K^+ which are present at concentrations several orders of magnitude greater.

Smectite or swelling clays are layered materials and consist of aluminum or magnesium-oxygen octahedra sandwiched between layers of silica-oxygen tetrahedra. 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 (4). Substitution of aluminum by divalent ions, usually magnesium, occurs in nature and results in a net negative charge on the clay lattice which is counterbalanced by the absorption of cations, usually Na^+ and Ca^{2+}. These cations are readily exchangeable and can be replaced by large polymeric cations such as the Al_{13} Keggin ion, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ or cationic zirconium species based upon the tetrameric unit $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$. After calcination, the clay lamellae are permanently propped open by pillars of alumina or zirconia, leading to microporosity (5–11). A simplified schematic showing the pillaring of a clay by alumina is illustrated in Fig. 1. These materials have relatively high surface areas, uniformly-sized pores, and no longer swell or disperse in aqueous media. A preliminary 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 rather than the host clay, and that pillaring actually increased the ion-exchange capacity of the clays. However, no ion selectivity data was presented, and their results did not take into account that some solubility of the pillar may occur at low or high pHs. Subsequently,

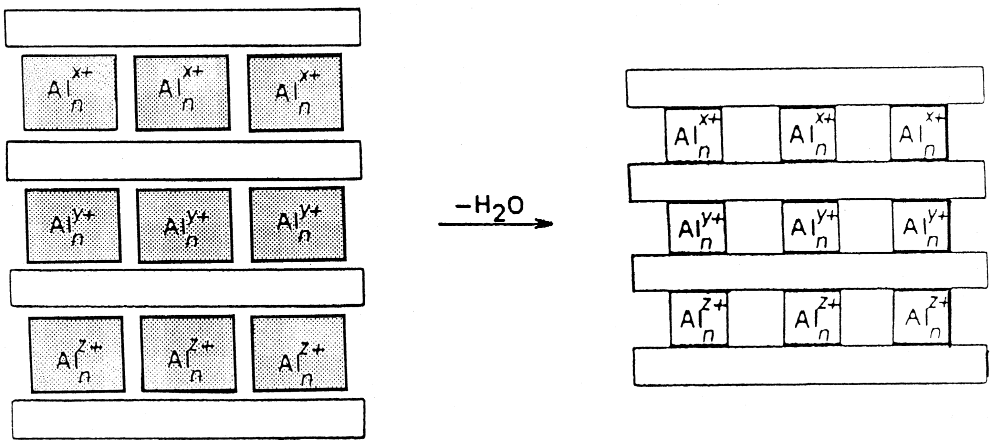

FIG. 1 Synthesis of an alumina-pillared montmorillonite: Intercalation of an aluminum polymer followed by calcination to generate the pillar.

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 selectivity of alumina and zirconia-pillared montmorillonite and compared the selectivity to that of the parent clay. The alumina-pillared material had previously been shown to be selective for cesium (14) and to have greater selectivity than a montmorillonite pillared by silica (15). The cesium selectivities of these alumina and zirconia-pillared clays were determined in calcium, magnesium, sodium, and potassium nitrate solutions and then their performance in two groundwater simulants was assessed and compared with the parent montmorillonite and commercially available zeolites. Two groundwater simulants were prepared according to information supplied by the Pacific Northwest National Laboratory (PNNL) (16) and INEEL (17), and spiked with ^{137}Cs to give a total cesium concentration of approximately 2.5 ppb. The composition of these simulants is given in Table 1. N-Springs represents an unusually alkaline groundwater found in the Hanford 100 area and contains relatively high concentrations of magnesium and calcium but no potassium. Since Mg^{2+} and Ca^{2+} primarily compete with Sr^{2+} while K^+ competes with Cs^+, most ion exchangers would be expected to exhibit relatively high K_ds for Cs because of the lack of K^+ in the N-Springs simulant. The TAN (Test Area North) simulant was developed in-house at Texas A&M University and contains the major cations found in a sample of groundwater taken from the TSF-05 injection well at INEEL (3). Contaminants of concern in this groundwater include chlorinated hydrocarbons, ^{90}Sr, and ^{137}Cs. This groundwater is less alkaline, has a greater total ionic strength than the N-Springs, and also contains significant potassium (2.45 ppm).

TABLE 1
The Composition of the N-Springs and TAN Groundwater Simulants

	Concentration (ppm)	
Ion	N-Springs	TAN Groundwater
Na^+	6.00	89.0
K^+	—	2.45
Mg^{2+}	5.25	19.7
Ca^{2+}	29.1	54.5
Ba^{2+}	0.02	0.14
Fe^{3+}	—	1.75
Zn^{2+}	—	0.40
Sr^{2+}	0.13	0.32
pH	11.2[a]	7.5–8.5[b]

[a] Theoretical simulant pH.
[b] pH range of actual groundwater.

EXPERIMENTAL

All materials were of reagent grade or better. ^{137}Cs was obtained from Amersham Life Science and had a specific activity of 2.5×10^4 Ci/g total Cs. The Los Trancos montmorillonite and the alumina-pillared derivative (Al-PILC) of this clay (Batch 4812) were obtained from Laporte Absorbents, Widnes, Cheshire, England. The Al-PILC was used “as received” without any further purification while the Los Trancos montmorillonite was dried overnight at 65°C prior to use. AW500 pellets were purchased from Aldrich, IE-96 powder was obtained from UOP, and a sample of a natural clinoptilolite, originating from the Mud Hills deposit in the Mojave Desert, California, was donated by British Nuclear Fuels Plc. AW500 is a small pore molecular sieve listed as a sodium potassium aluminosilicate. IE-96 is a high alumina ($Si/Al \cong 2$) zeolite, chabazite, containing Na^+ or Ca^{2+} as the exchange ions. It is highly selective for Cs^+ and selective but less so for Sr^{2+}. Solution activities were measured on a Wallac 1410 liquid scintillation counter using Fisher Scientific Scintisafe Plus 50% scintillation cocktail. Surface area measurements were performed on a Quantachrome Autosorb 6 using N_2 gas as the adsorbate. X-ray diffraction was performed on a Scintag PAD V diffractometer using CuKα radiation at a scan rate of 1°/min at 40 kV and 30 mA.

Synthesis of Pillared Clays

The Al-PILC was obtained from Laporte Absorbents and had been produced by intercalating the Al_{13} Keggin ion into the Los Trancos montmorillonite followed by calcination at 550°C for 4 hours. The zirconia-pillared clay (Zr-PILC), was synthesized according to the method described by Dyer et al. (18). Clay (33 g) was stirred for 24 hours at room temperature with 1000 mL of a 0.1 M $ZrOCl_2$ solution. The clay was then centrifuged and washed repeatedly with deionized water until the washings were free of chloride ions and did not cause a precipitate with silver nitrate solution. The product was then calcined at 300°C for 24 hours and characterized using surface area analysis and x-ray powder diffraction. The adsorption–desorption isotherm of this material after calcination is given in Fig. 2. The final calcined product was designated RD-58, and all references to Zr-PILC in this paper refer to this material.

The synthetic conditions were varied and the temperature of reaction and ratio of zirconium to clay changed to see the effect on the selectivity of the final pillared clay. In one experiment, RD-61, the $ZrOCl_2$ solution was aged by

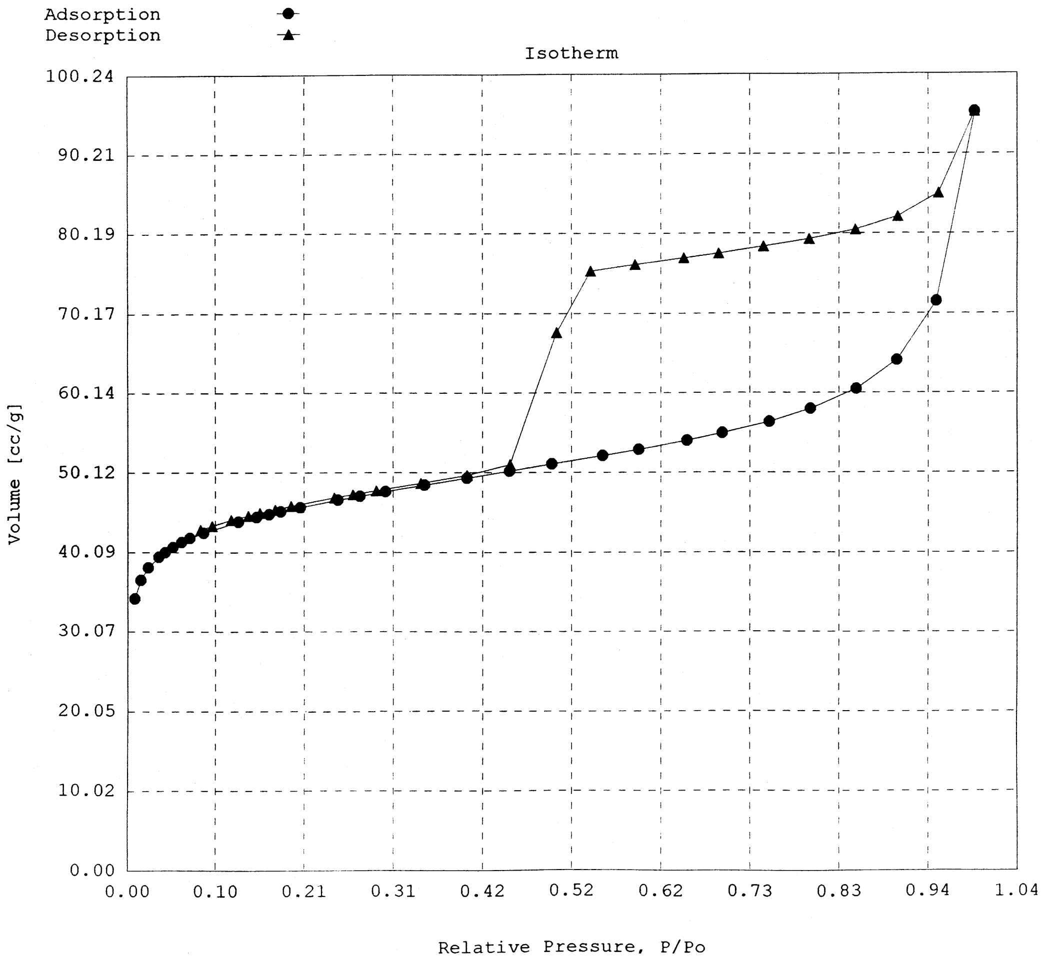

FIG. 2 The N_2 adsorption–desorption isotherm for RD-I-58 calcined at 300°C.

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refluxing for 2 hours and stirred overnight at room temperature in an attempt to encourage polymerization of the zirconium tetramers and thus allow the incorporation of larger polymers into the interlayer space of the clay.

Ion-Exchange Studies

The Cs selectivities of the parent Los Trancos clay and the PILCs were evaluated in pure Na^+, K^+, Ca^{2+}, and Mg^{2+} nitrate solutions. The pH of these solutions was approximately 7, thus ensuring no degradation of the pillar or host clay occurred. Al-PILC (0.05 g) was weighed into a scintillation vial and 10 mL of the salt solution (from 1 M to 10^{-4} M), spiked with ^{137}Cs, was added. The total concentration of cesium was approximately 2.5 ppb (1.8×10^{-8} M). The vial was then capped and placed on a rotary shaker for approximately 24 hours. The mixture was filtered through a 0.2-μm membrane and the aqueous phase analyzed by liquid scintillation counting. K_ds were then calculated according to

$$K_d = (A_i - A_f)/A_f \cdot V/m \tag{1}$$

where A_i = initial activity/cpm
A_f = final activity/cpm
V = volume of solution/mL
m = mass of exchanger/g

All determinations were performed at least twice, and the results reported are an average of the two or more K_ds obtained. In general, duplication was good and the majority of replicates gave K_ds within 5% of each other.

The materials were also evaluated in two simulated groundwaters and compared with three commercially available zeolites, namely IE-96, AW500, and clinoptilolite (Tables 2 and 3). AW500 is a synthetic calcium chabazite with the idealized formula $Ca_2Al_4Si_8O_{24}\cdot 13H_2O$ while the Mud Hills clinoptilolite, a naturally occurring zeolite, has an approximate formula $Na_{2.20}Mg_{0.40}$

TABLE 2
K_ds and % Cs Removal from N-Springs Groundwater Simulant

	$V{:}m = 200$		$V{:}m = 1000$	
Sample	K_d (mL/g)	% Cs removed	K_d (mL/g)	% Cs removed
AW500	4.37×10^4	99.55	4.91×10^4	98.04
IE-96	2.33×10^4	99.15	4.59×10^4	97.87
Clinoptilolite	1.64×10^4	98.79	3.94×10^4	97.62
Clay	1.88×10^3	90.34	1.65×10^3	61.20
Zr-PILC	$>8.50 \times 10^5$	>99.98	8.63×10^5	99.89
Al-PILC	1.15×10^5	99.83	2.46×10^5	99.60

TABLE 3
K_ds and % Cs Removal from the TAN Groundwater Simulant

	V:m = 200		V:m = 1000	
Sample	K_d (mL/g)	% Cs removed	K_d (mL/g)	% Cs removed
AW500	3.68×10^4	99.46	4.37×10^4	97.82
IE-96	5.32×10^4	99.63	5.86×10^4	98.32
Clinoptilolite	1.63×10^4	98.79	2.04×10^4	95.27
Clay	1.58×10^3	88.91	9.94×10^2	50.47
Zr-PILC	5.45×10^4	99.64	3.88×10^4	97.44
Al-PILC	1.87×10^4	98.94	2.54×10^4	96.18

$K_{0.89}Ca_{0.99}Sr_{0.07}Al_6Si_{30}O_{72}\cdot xH_2O$ (19) which indicates that Na^+ is the predominant exchangeable cation. IE-96 and clinoptilolite were used without prior conditioning. The AW500 was purchased in the form of 1.6 mm pellets which were ground to powder prior to use. It should also be noted that the AW500 pellets contain approximately 20% clay binder and consequently Cs K_ds for the pure zeolite would be expected to be greater than those for the pelletized material. The previously described experimental technique was used to determine Cs K_ds, except that the materials were evaluated at a V:m ratio of 1000:1 as well as 200:1. Total cesium concentration in both of the groundwater simulants was approximately 2.5 ppb.

Kinetic Experiments

The rate of uptake of ^{137}Cs from 0.1 M $NaNO_3$ solution was investigated for the Los Trancos clay, the Al-PILC, and the Zr-PILC. Material (0.05 g) was weighed into a scintillation vial and 10 mL of $NaNO_3$ solution, spiked with ^{137}Cs, added. The vial was then capped and placed on a rotary shaker. After a specific period of time the vial was removed and the aqueous phase sampled immediately using a syringe equipped with a 0.2-μm filter. The aqueous phase was then analyzed using liquid scintillation counting and the percentage removal of cesium from the aqueous phase calculated.

RESULTS AND DISCUSSION

The physical characteristics of the Los Trancos clay and the PILCs are shown in Table 4. X-ray powder diffraction showed that the Los Trancos clay was relatively pure with the only obvious impurity being a minor amount of quartz. Earlier work (15) showed this clay to have a cation-exchange capacity of approximately 1 meq/g with the main exchangeable ion being Ca^{2+} along with minor amounts of Na^+ and K^+. Both pillared clays were microporous

TABLE 4
Physical Characteristics of the Los Trancos Clay, the Zr-PILC, and the Al-PILC

Clay	Pillar	Calcination temperature (°C)	Surface area (m^2/g)	Microporosity (%)	*d*-Spacing (Å)
Los Trancos	None	65	73.7	45	15.1
Al-PILC	Alumina	550	264	82	18.3
Zr-PILC	Zirconia	300	171	84	Not seen

materials with surface areas of 264 and 171 m^2/g for the Al-PILC and the Zr-PILC, respectively. These values compared well with data supplied by Laporte Absorbents and previous work by Dyer et al. (18) who recorded surface areas of 250 and 134 m^2/g for the Al-PILC and Zr-PILC, respectively. The majority of the surface areas are associated with micropores which suggests that the clays have been successfully pillared as opposed to delaminated. The strong peak observed on the Al-PILC XRD pattern at 18.3 Å confirmed that the material was pillared, but the Zr-PILC did not show any well-defined peaks corresponding to the interlayer spacing after calcination, so it is not certain that pillaring has occurred. A similar result for the Zr-PILC was also obtained by Dyer et al. (18). Pore size measurements gave a mean micropore diameter of approximately 6.2 Å for the Al-PILC and 5.6 Å for the Zr-PILC.

Variations in the zirconia pillaring procedure did not produce any materials with well defined *d*-spacings after calcination. The Cs K_ds of each of these Zr-pillared materials was determined in 10^{-2} M $NaNO_3$ solution and were found to be less than the initial Zr-PILC, RD-58. Consequently, all further ion-exchange experiments were performed using the Zr-PILC designated RD-58. The synthetic conditions for the other zirconia-pillared clays and their ^{137}Cs K_ds are summarized in Table 5.

The ion-exchange studies in Ca^{2+}, Mg^{2+}, Na^+, and K^+ nitrate solutions are summarized in Figs. 3(a), 3(b), and 3(c). There is a striking difference between the behavior of the PILCs and the parent Los Trancos clay. Mg^{2+} and Ca^{2+} ions had very little effect on the Zr-PILC, and Cs K_ds remained greater than 1×10^5 mL/g, even in 1 M Ca^{2+} and Mg^{2+} solutions (Fig. 3a), indicating negligible affinity of the Zr-PILC toward either of these ions. The Al-PILC (Fig. 3b) showed similar behavior, though the Cs K_ds in Mg^{2+} and Ca^{2+} solutions were generally nearly an order of magnitude lower than the Zr-PILC. By contrast, the Los Trancos clay (Fig. 3c) showed a steady decrease in Cs K_ds as the concentration of Mg^{2+} and Ca^{2+} increased, and the Cs K_ds in 1 M solutions of these ions were only approximately 300 mL/g.

Increasing the concentration of Na^+ had a greater effect on the PILCs than either Mg^{2+} or Ca^{2+}. K_ds were reduced from greater than 6.65×10^5 mL/g to 5.40×10^3 mL/g and from 9.70×10^4 mL/g to 1.60×10^3 mL/g for the Zr-

TABLE 5
Summary of Synthesis Conditions for the Zirconia-Pillared Clays and Their ^{137}Cs K_ds from 10^{-2} M $NaNO_3$ Solution

Sample	mmol Zr/g clay	Temperature (°C)	Reaction time (hours)	K_d (mL/g)
RD-58	3	25	24	1.98×10^5
RD-59A	3	90	24	6.84×10^4
RD-59B	3	60	24	1.38×10^5
RD-61A	10	65	3[a]	2.91×10^4
RD-61B	4	65	3[a]	4.75×10^4

[a] Three hours at 65°C, then the mixture was allowed to cool to room temperature and stirred for a further 18 hours.

PILC and the Al-PILC, respectively, as the Na^+ concentration was increased from 10^{-4} M to 1 M. Again, the parent clay performed poorly with a K_d of only 142 mL/g in 1 M $NaNO_3$ solution.

The concentration of K^+ had a great effect on the Cs K_ds for all three materials. There was very little difference in the K_ds of the PILCs and the clay over the entire range of K^+ concentrations investigated. Only in solutions where the K^+ concentration was 0.001 M or less were appreciable Cs K_ds for any of the materials recorded.

Kinetics

The results from the kinetics experiments are summarized in Table 6. The rate of ^{137}Cs uptake was found to be relatively rapid for both of the PILCs with at least 90% of the ^{137}Cs being absorbed after a contact time of 5 minutes. This initial rapid absorption was followed by a gradual increase in Cs removal as the contact time was increased from 5 minutes

TABLE 6
Kinetic Study of the Uptake of ^{137}Cs from 0.1 M $NaNO_3$ Solution by the Zr-PILC, the Al-PILC, and the Parent Los Trancos Clay

	% Cs removal at							
Sample	5 min	10 min	20 min	30 min	1 h	2 h	5 h	24 h
Clay	75.81	76.75	77.24	77.96	77.97	76.01	74.89	82.09
Zr-PILC	96.02	97.06	97.91	98.18	98.38	99.09	99.30	99.57
Al-PILC	90.00	92.66	94.68	94.89	96.23	97.14	97.81	97.87

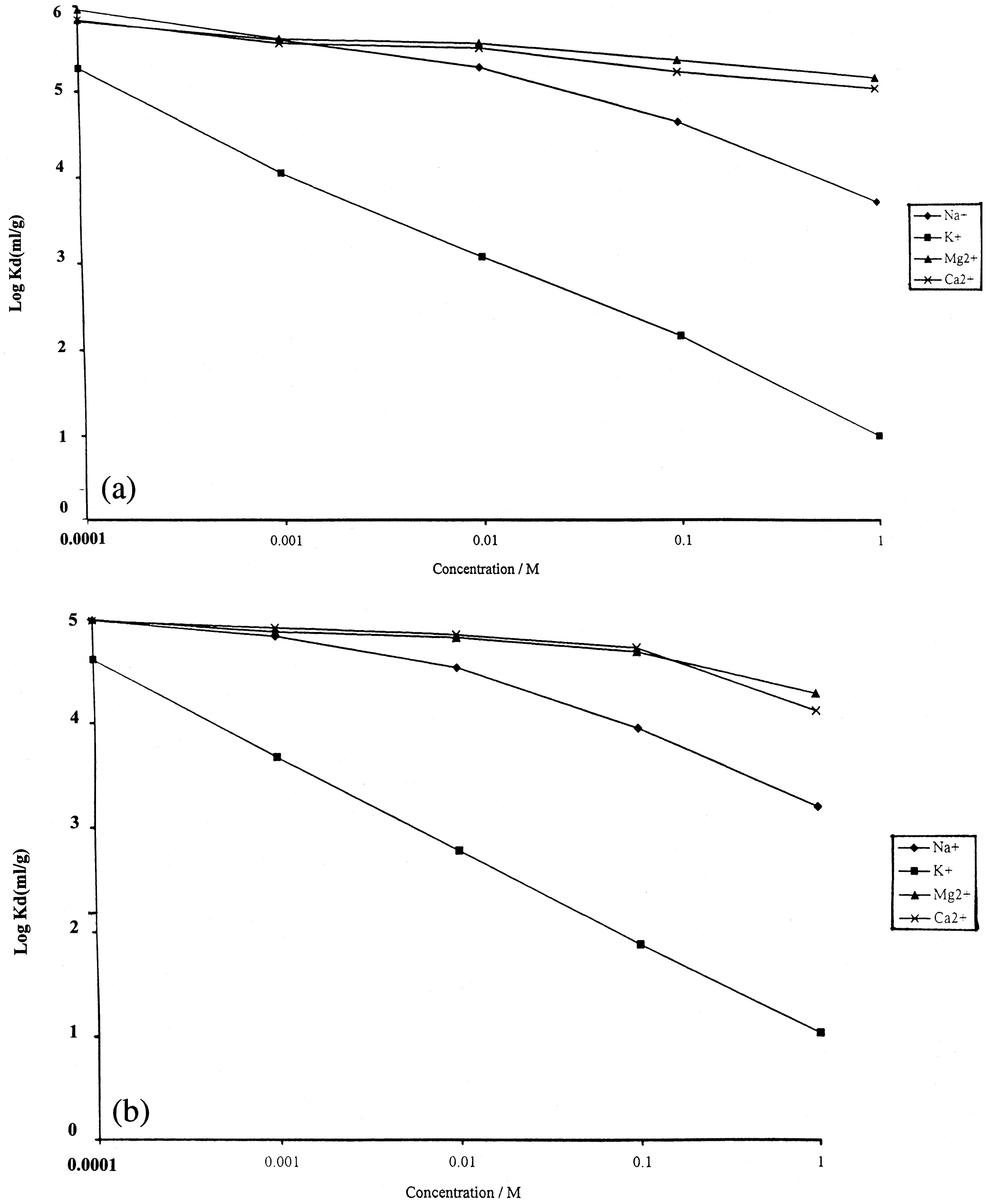

FIG. 3 Log Cs K_ds versus the log of Na^+, K^+, Mg^{2+}, and Ca^{2+} concentrations for (a) Zr-PILC, (b) A1-PILC, and (c) Los Trancos clay. (Total Cs^+ concentration was approximately 1.8×10^{-8} M.)

to 5 hours. Further increasing the contact time to 24 hours only caused a relatively slight increase in Cs uptake with the amount removed from solution increasing from 99.30 to 99.57% and from 97.81 to 97.87% for the Zr-PILC and the Al-PILC, respectively. This rapid uptake of cesium agrees well

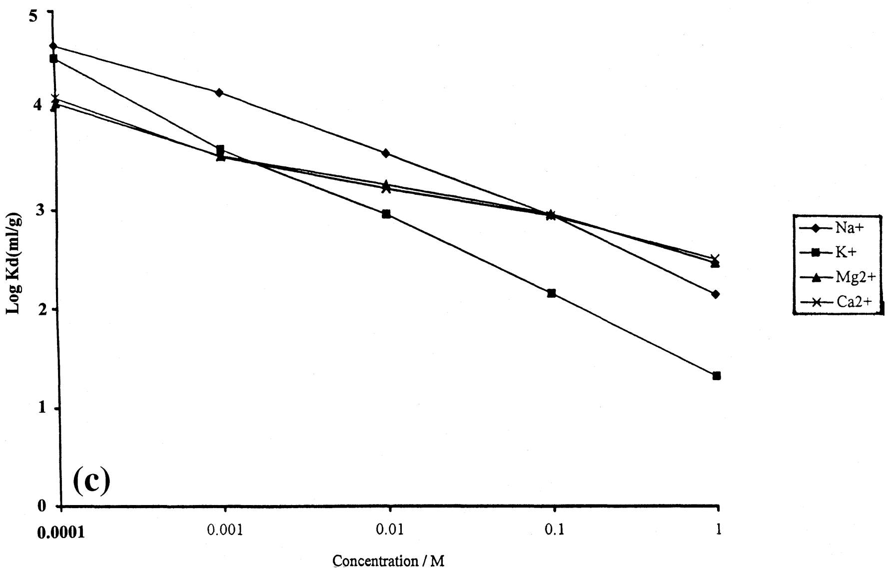

FIG. 3 Continued

with observations made by Karamanis et al. (20). By contrast, Cs uptake by the Los Trancos clay was variable and ranged between 74.89 and 82.09% and no distinct increase in uptake with time was noticeable. Similar results were obtained by Gokturk and Dyer (21) who also performed kinetic experiments to evaluate the absorption of alkali metals on the Los Trancos montmorillonite.

CONCLUSIONS

It has been shown that both of the PILCs are cesium-selective ion-exchange materials with little affinity for Ca^{2+}, Mg^{2+}, or Na^{+}. The pillaring process is responsible for the observed selectivity as can be seen by comparing the results with the parent Los Trancos montmorillonite which showed very low Cs K_ds in the presence of high concentrations of these ions. Preliminary pore size measurements suggest that the difference in the Cs selectivity for the two PILCs may be due to the slight variations in the micropore size. The Zr-PILC has a micropore diameter of 5.6 Å which is 0.6 Å smaller than the Al-PILC and thus may improve the specificity of the exchange sites for the Cs^{+} cation. In groundwaters with very low concentrations of potassium, these PILCs would be suitable to extract cesium selectively and, on the basis of batch K_d experiments, would be expected to perform far better than the zeolites AW500, IE-96, or clinoptilolite. In solutions containing appreciable potassium, the PILCs are far less efficient at removing cesium, though they both perform better than the sample of clinoptilolite used in this study. Zr-PILC has a similar performance to both IE-96 and AW500.

The kinetics of exchange for both the Al-PILC and the Zr-PILC are initially very rapid with the majority of the cesium being extracted after 5 minutes, though the amount removed then continued to increase steadily with time. The uptake of Cs by the parent clay is also very fast but is more or less complete after 5 minutes. This suggests that the ion-exchange reaction in the PILCs is a bulk phase reaction and some time is required for the reacting ions to diffuse into and out of the ion-exchange sites after the accessible surface sites have been saturated. The exchange characteristics of the Los Trancos clay suggest that diffusion is not as important, indicating that the ion exchange is predominantly a surface reaction rather than a bulk effect.

Both the Al-PILC and the Zr-PILC are inexpensive to synthesize, mainly due to the very low cost of natural clays and the pillaring solutions, none of which need to be particularly pure. Consequently, the PILCs have potential applications as backfill materials around nuclear waste disposal sites or as underground barriers to limit the spread of ^{137}Cs in contaminated groundwaters. Alternatively, they could also be utilized to remove traces of Cs^+ or K^+ from solutions of Group II metals to produce ultrapure chemicals or in the separation of ^{137}Cs from other fission products, such as ^{90}Sr, to produce a pure radionuclide for pharmaceutical applications.

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