

AN ALUMINUM PILLARED MONTMORILLONITE WITH FAST UPTAKE OF STRONTIUM AND CESIUM FROM AQUEOUS SOLUTIONS

D. T. KARAMANIS,¹ X. A. ASLANOGLU,¹ P. A. ASSIMAKOPOULOS,¹ N. H. GANGAS,¹
A. A. PAKOU¹ AND N. G. PAPAYANNAKOS²

¹ Department of Physics, The University of Ioannina, 451 10 Ioannina, Greece

² Department of Chemical Engineering, National Technical University of Athens, Greece

Abstract—The uptake of Sr and Cs by 2 types of aluminum pillared layered clays (Al-PILC), a reference sample (AZA) and a specially tailored sample (FRAZA), were investigated. The AZA sample was prepared from air-dried precursors and the FRAZA sample from freeze-dried precursors. X-ray diffraction (XRD), pore and grain size measurements revealed that freeze-drying leads to a very fine-grained material with substantial mesoporosity. In contrast, air-drying results in coarse grains and an essentially microporous material. Four different methods were tested for restoring the cation exchange capacity (CEC) of the prepared PILCs. The most effective method proved to be exposing the material to ammonia fumes, then soaking it in a NaCl solution at pH = 10. Strontium and Cs kinetic experiments were carried out with PILCs after restoring their CEC by this method. The results revealed 1 fast uptake component in both materials but with different relaxation times for each PILC.

Key Words—Cation Exchange Capacity, Delamination, Pillared Clay, Radiocesium, Radiostrontium, Uptake.

INTRODUCTION

Nuclear weapons tests, routine emissions from nuclear installations and accidental releases have in the past resulted in a considerable contamination of the environment by radioactive substances. Furthermore, 10 years ago, the incident at Chernobyl demonstrated most vividly the potential hazards from massive releases of radiocontaminants in the case of a nuclear power plant accident. This fact, combined with the long-term problems associated with the generation of large amounts of radioactive isotopes in nuclear reprocessing plants, has created a research impetus aimed at the development of effective countermeasures. In this context, several materials like inorganic exchangers (Narbutt et al. 1994), clays (Adeleye et al. 1994), zeolites (Lukac and Foldesova 1994), crown ethers (Hill et al. 1994), biomaterials (Avery 1995) and other mineral and chemical substances are being tested worldwide for the selective, effective and inexpensive removal of specific radionuclides (Cs, Sr and Co) from complex mixtures. Although some of these materials have proved effective in special circumstances, a general, efficient, low-cost antidote for radiocesium and, especially, radiostrontium removal is still elusive, with the possible exception of a new synthetic Na-4 mica which exhibited high selectivity for Sr²⁺ (Komarneni et al. 1991; Paulus et al. 1992).

Pillared layered clays constitute a novel class of materials prepared by propping apart the lamellae of expandable layered clays with nano-size pillars of metal oxides and thus creating a 2-dimensional zeolite-like network of micropores. Depending upon the prepara-

tion conditions, PILCs may also exhibit extended mesoporosity. As these materials possess, in addition, a substantial CEC, they may prove suitable for the effective removal of radionuclides from complex environments such as the digestive tract of animals and humans. In such and other applications, the rate of the cation uptake is obviously of particular interest, too. The good prospect for application of PILCs is based on the fact that their synthesis makes it possible to tune their structure and properties within wide margins to the requirements for a specific use.

Since the identification of PILCs (Brindley and Sempels 1977), research interest has increased in view of their potential applications in catalysis, selective molecular sorption, electrochemical and optical devices, etc. (Mitchell 1990). As a result, the synthesis and characterization of PILCs have been extensively investigated during the last 2 decades and comprehensive reviews are available (Figueras 1988; Schoonheydt 1991). Furthermore, recent progress (Kaloidas et al. 1995) in the large-scale preparation of PILCs (1 kg/batch) has substantially facilitated the development of applications based on these novel materials.

The employment of PILCs for the removal of hazardous or precious metals has only recently attracted research interest (Bergaoui et al. 1995). Therefore, the present investigation aims at contributing to a better understanding of the pertinent phenomena. Obviously, the CEC and the exchange kinetics are crucial properties of merit for such an application.

In view of the above, the present work investigated the extent and kinetics of Cs and Sr uptake from aque-

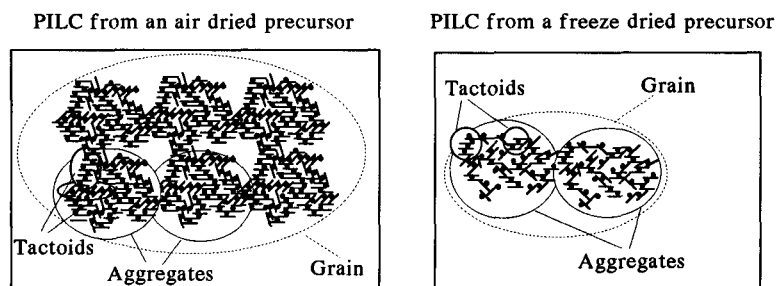


Figure 1. Schematic representation of the spatial organization of the clay lamellae in an air-dried PILC (AZA) and a freeze-dried PILC (FRAZA). Black circles indicate metal oxide particles of nm size, not drawn to scale with respect to the clay lamellae that extend up to a few μm and are represented as short, straight line segments.

ous solutions by 2 Al-PILCs differing mainly with respect to the spatial organization of their pillared clay lamellae. More specifically, the first Al-PILC was a coarse-grained material consisting of aggregates with rather well-ordered clay lamellae, while the second Al-PILC was prepared in a way that led to fine grains comprising aggregates of randomly stacked lamellae. The latter material showed very fast cation uptake, which is a property of high practical value.

SYNTHESIS AND STRUCTURE OF PILLARED LAYERED CLAYS

The synthesis of pillared layered clays basically follows a 3-step process: 1) The 2:1 clay lamellae carry a negative charge due to isomorphous substitution of trivalent metal ions for Si^{4+} in the tetrahedral sites and/or divalent metal ions for Al^{3+} in the octahedral sites. Specifically, a clay suspension is reacted with a solution containing oligo- or polymeric cationic complexes of metals, such as $(\text{Al}_3\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12})^{7+}$, which by associating with the clay lamellae create flocs of the PILC precursor. 2) This precursor is separated from the liquid and dried. 3) The dried material is calcined at about 500°C in order to transform the polyoxocations to metal oxidic particles cross-linked to the clay lamellae. These nano-size particles act as pillars propping apart the lamellae. As a result of the dehydroxylation of the polyoxo-cations during this third step, H_3O^+ ions are liberated in the clay interlayer space and thus the CEC of the prepared PILC is substantially lower than that of the starting clay (Purnell 1992; Schoonheydt et al. 1993). Treatment of the PILC with a base like NaOH or NH_4OH neutralizes the H_3O^+ ions, and this in turn leads to a CEC restoration of up to 80–90% of the CEC value of the starting clay (Molinar et al. 1994; Tang et al. 1995; Cheng and Yang 1995). This treatment actually replaces the H_3O^+ ions with the easily exchangeable cations Na^+ or NH_4^+ .

The evolution of the spatial organization of the clay lamellae during the pillaring process can be roughly described as follows (Figure 1): As the intercalant polyoxo-cations are added to the clay suspension, they

attract the negatively charged clay lamellae and this leads to various local arrangements or “tactoids”. In these, the lamellae are associated either face-to-face or face-to-edge or even edge-to-edge, depending on reaction conditions such as clay concentration, and total charge and number of polyoxo-cations loaded per g of clay. The polyoxo-cations usually hold apart face-to-face associated lamellae, but can also stick on exposed clay surfaces or even graft at the contacts of face-to-edge or edge-to-edge associated lamellae. Aggregates of tactoids form flocs, and start to settle as their weight increases according to Stoke’s law. Obviously, in the freshly sedimented PILC precursor, water fills the voids formed between tactoids as well as between aggregates. Upon freeze-drying of the precursor, these voids remain practically intact, while upon air-drying, the surface tension at the clay–water–air interface drives tactoids as well as aggregates closer. Therefore, air-drying leads to a more compact and ordered arrangement of the tactoids in the PILC precursor. Finally, upon firing the dried precursor, the polyoxo-cations are cross-linked to the clay lamellae and to the contact points of face-to-edge or edge-to-edge associated lamellae. This cross-linking renders to the whole material, from nm- up to mm-scale rigidity. In summary, the building blocks of a PILC, such as the μm -size clay lamellae and the nm-size metal oxides, are organized in space in tactoids, in aggregates thereof and in grains which, as conglomerates of aggregates, may reach a dimension of up to few mm. Such large grains are formed when the precursor has been air-dried, while after freeze drying the grains are much smaller, consisting of only a few aggregates. The process is depicted schematically in Figure 1.

MATERIALS AND METHODS

Preparation of Al-Pillared Clays

An aluminum pillared Greek montmorillonite (with the commercial name of the source bentonite: Zenith-N), coded AZA, was kindly provided for the purposes of this research by Kaloidas et al. (1995) who prepared this material at the 1 kg/batch scale following air-dry-

ing of the precursor. The interlayer opening, or $d(001)$ spacing, of AZA is 1.82 ± 0.02 nm, its specific surface area is 220 ± 10 m²/g and its pore volume lies between 0.06 and 0.08 cm³/g. A second Al-PILC, coded FRAZA, was prepared by the authors of this paper at the g/batch scale from the same starting clay as AZA and according to the following procedure.

The Na⁺-saturated form of the starting clay was obtained by washing the raw clay several times, first with 1 M NaCl and then with deionized water. The <2 μm clay fraction was separated by sedimentation upon dispersing the Na⁺ clay in deionized water. A 1 wt% aqueous suspension of this fraction was then reacted with a solution containing Al oxo-hydroxo cationic complexes. The intercalant solution was prepared by adding dropwise (1 mL/min) and under vigorous stirring a 0.2 M NaOH to a 0.2 M AlCl₃ water solution up to a ratio OH/Al = 1. The final Al concentration was 0.1 M. The clay suspension was added rapidly and under vigorous stirring to the intercalant solution until a loading ratio of 2 mmol of Al/g clay was reached. The pH in the reaction volume was maintained at 3.60 and the mixture was allowed to react for 2 h. For removing the excess Al ions, the coagulated intercalated clay was centrifuge-washed several times with water acidified with HCl to the same pH value. The material was then freeze-dried and calcinated at 500 °C for 4 h.

Characterization Methods

X-RAY DIFFRACTION. XRD patterns were obtained for dry powder samples by a Philips PW 1011 X-ray diffractometer with CoK α radiation.

SURFACE AREA, PORE-SIZE DISTRIBUTION AND GRAIN SIZE. Surface area and porosity of the AZA and FRAZA materials were measured by nitrogen adsorption-desorption isotherms. The BET equation was used for the determination of the surface area while the Kelvin equation was used to determine pore size distribution. Grain size of the 2 materials was obtained by wet-sieving the samples through sieves of different mesh size.

CATION EXCHANGE CAPACITY. CEC was determined from ⁸⁵Sr radioactivity measurements (see below) on PILCs whose interlayer cations had been exchanged with Sr²⁺ ions traced with this isotope.

Uptake Experiments

The uptake of Sr²⁺ or Cs⁺ by AZA and FRAZA has been investigated via equilibration and exchange kinetic measurements. These were carried out in deionized water containing the corresponding chloride salts and adjusted to a pH of ~6. The conventional batch technique was employed for the equilibration measurements in which a known amount of PILC (typically 0.1 g) was contacted with a 200-mL solution containing chloride salts of Sr²⁺ traced with ⁸⁵Sr or

chloride salts of Cs⁺ traced with ¹³⁷Cs. After attaining equilibrium, the 2 phases were separated by centrifugation and the γ activity of the clear supernatant was measured. Typical contact times for equilibrium attainment were about 72 h for AZA and 20 h for FRAZA. The percentage of Sr²⁺ or Cs⁺ adsorbed by the Al-PILCs, calculated from the initial and final activities, was converted to equivalent cationic charge sorbed per g of PILC. A dialysis method was used in the exchange kinetic measurements in which the dialysis bag held the PILC material in a minimum amount of deionized water. It also contained a very small magnet and was gently stirred in order to minimize any solution and solution-particle interface diffusion effects. The rate of cation uptake was determined by periodically removing the dialysis bag and measuring the remaining solution activity. The shortest contact time at the beginning of an exchange kinetic measurement was 2 min. It was also experimentally checked that kinetic measurements conducted with the batch method and under stirring, followed by centrifugation or filtration, led, within experimental errors, to the same results as in the dialysis method measurements. The latter was followed because of convenience.

All activity measurements were performed with a 22%-efficiency intrinsic Ge detector. In all radiostrontium measurements, the activity was corrected for natural radioactive decay. Glass or plastic vessels were used in the experiments and it was experimentally checked that background losses were less than 2% in both the equilibration and kinetic measurements. The temperature in all experiments was between 20–30 °C. Uptake experiments were initially tested in duplicate but, because of the small mean deviation, no further replicate experiments were performed.

Restoration of the CEC

In this work, 4 different CEC restoration methods were employed:

- 1) The PILC was contacted under stirring with an aqueous solution of 1 M NaCl adjusted to pH = 10.00 with 1 M NaOH. As the pH of the mixture was decreasing with time, it was readjusted with drops of 1 M NaOH. After about 30 h, no further pH decrease was observed. Then the sample was centrifuge-washed until no Cl ions were detected with the standard AgNO₃ test and no pH reduction was observed. The sample was finally air-dried for 15 h at 80 °C.
- 2) The PILC was left for 12 h in an ammonia atmosphere produced by the evaporation of a concentrated NH₄OH water solution. Then the material was degassed at room temperature and under vacuum for 2 h.

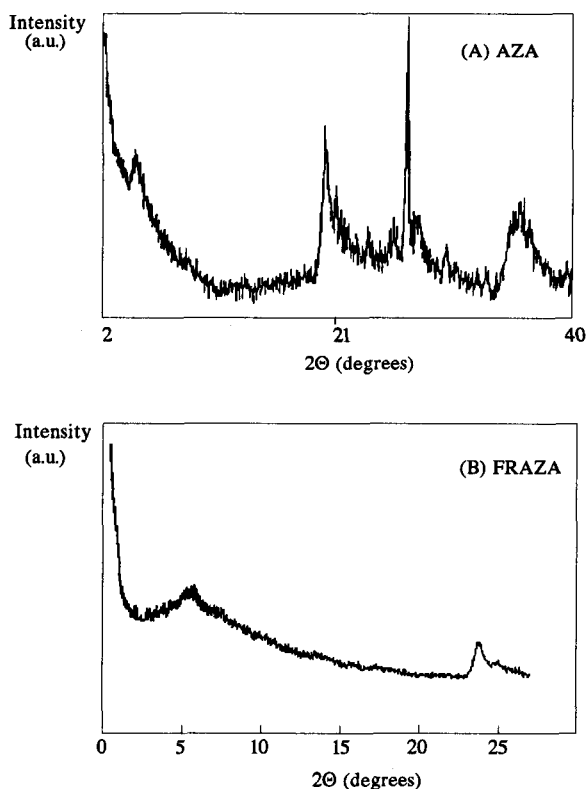


Figure 2. XRD powder diffraction pattern of materials AZA ($\text{CuK}\alpha$ source) and FRAZA ($\text{CoK}\alpha$ source).

- 3) The PILC was contacted first with a NaCl alkaline solution and then with an ammonia atmosphere, as described above.
- 4) The reverse sequence of contacts was followed in the fourth method. This last method proved to be the most efficient CEC-restoring treatment (see below).

The materials obtained through each of the restoration methods described above were coded for identification purposes as AZA-A, AZA-B, FRAZA-A, etc.

RESULTS AND DISCUSSION

Characterization of AZA and FRAZA

Inspection of the XRD spectra in Figure 2 reveals that, although the peak at low angles is in approximately the same position for both AZA and FRAZA, for the latter PILC the peak is considerably broader. This peak is associated with the (001) reflection and consequently its position provides a measurement of the interlayer spacing. Furthermore, as the peak width is related to the number of clay lamellae contributing coherently (Brindley 1980), it is deduced from Figure 2 that in FRAZA only a small fraction of the tactoids consist of several face-to-face stacked clay lamellae. The remaining and a larger part of FRAZA consists

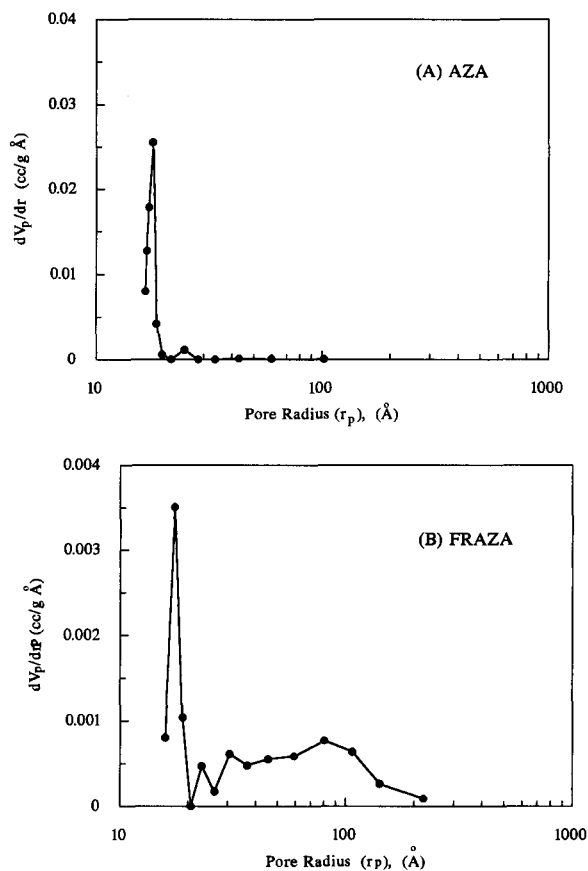


Figure 3. Pore-size distribution of materials AZA and FRAZA.

of quite randomly aggregated tactoids of few clay lamellae and/or of tactoids with varying interlayer spacing. This interpretation is also supported by the pore size distributions for AZA and FRAZA as determined from nitrogen adsorption. More specifically, as shown in Figure 3, AZA appears to be practically 100% microporous, while only a small fraction (25%) of the pore volume of FRAZA consists of micropores (radii < 2 nm). The remaining pore volume is made up of pores with radii in the mesoporous region, that is, between 2 and 20 nm. This noteworthy difference in the spatial organization of the clay lamellae in these 2 PILCs can be mainly attributed to the different ways of drying the corresponding PILC precursors. As portrayed in the "Synthesis and Structure of PILCS" section, freeze-drying tends to preserve not only edge-to-face or edge-to-edge associations of the clay lamellae, but also the big voids resulting from such a "card house" structure (Pinnavaia et al. 1984). Thus, in the freeze-dried FRAZA, the aggregation of tactoids is less compact compared to AZA, which results from an air-dried precursor. In accordance with the above picture is the finding that grain size in the thus-prepared PILCs is also quite different. In FRAZA, all grains are

Table 1. Structural data for the PILC materials coded AZA and FRAZA.

Material	$d(001)$ (nm)	BET S (m^2/g)	Pore volume (cm^3/g)	Micropore (%)	Mesopore (%)	Grain size (μm)
AZA	1.82 ± 0.02	220 ± 10	0.06–0.08	≈ 100	—	21% < 45 μm ; 55% > 200 μm
FRAZA	≈ 1.76	110 ± 10	0.11 ± 0.01	≈ 25	≈ 75	70% < 45 μm ; 100% < 63 μm

<63 μm , while in AZA more than 55% of the grains are >200 μm . Therefore, each FRAZA grain contains only a few aggregates, while each AZA grain comprises several aggregates compactly arranged.

In summary, the data given in Table 1 reveal that, with respect to the spatial organization of the clay lamellae, the Al-PILCs used in this study differ both at μm as well as at mm scales. The end result of this dual structural difference (Figure 1) on the modalities of the cation exchange process is revealed by the uptake experiments discussed below. At this point, it is noted only that the specific surface area of FRAZA is unexpectedly low for a freeze-dried PILC and that this finding could be due to either or both of the following reasons: 1) some of the pores are inaccessible to the nitrogen molecules due to their blocking by the randomly stacked clay lamellae; and/or 2) part of the clay remained nonpillared. However, none of these reasons would inhibit the exchange of small cations as Cs, K, Na or Sr.

Restoration of CEC

Upon calcination of a PILC precursor around 500 °C, the dehydroxylation of the intercalated oxo-hydroxy cations liberates protons. Although most of these protons stay in the interlayer space, some migrate through the hexagonal cavities formed by the basal SiO_2 tetrahedra towards the octahedral sheet that carries the negative charges (Vaughan et al. 1981; Tenakoon et al. 1987). As a result, in the thus-prepared PILCs, the CEC is dramatically lower than that of its precursor. However, by neutralizing the liberated protons with a base like NaOH or NH_4OH (Vaughan et al. 1981; Malla and Komarneni 1990; Tichit and Figueras 1990; Molinard et al. 1994; Tang et al. 1995; Cheng and Yang 1995), one can restore the CEC al-

most completely. It should be noted that, as CEC values are quoted in meq/g of material, the value quoted for a PILC is *a priori* lower than that of the starting clay, since each clay lamella weighs more when it carries a pillar. Nevertheless, this is a small effect, since the weight of the pillars usually makes up less than 10% of the total weight of a pillared clay and, in practice, CEC values for PILCs are quoted without making the corresponding weight correction.

The data presented in Table 2 show the CEC restoration efficacy of the 4 different methods employed in this study. More specifically, all of these methods end up with CEC values for the treated PILCs definitely lower than 0.9 meq/g clay, the value determined for the starting clay. This deficit can be accounted for by the presence of H_3O^+ ions remaining in the pillar structure that cannot be removed either by NH_3 or NaOH and/or by Al ions that are not electrically compensated by their ligands in the pillar structure. Obviously, the latter ions cannot be replaced by NH_4^+ or Na^+ ions via a cation exchange treatment. For these reasons, the CEC obtained after restoration did not exceed 70% of the value of the starting clay.

Uptake Experiments

EXCHANGE ISOTHERMS. In a first series of experiments, the dependence of Sr^{2+} or Cs^+ uptake (meq/g) on the initial concentration (mM) of these cations was studied on both Al-PILCs after restoration of their CEC via method D. The dependence shown by the exchange isotherms contained in Figure 4 agrees with the fact that the cation exchange is a stoichiometric reaction (Grim 1968). These isotherms reveal also that the Sr^{2+} uptake attains the same saturation level in both PILCs and at almost the same starting concentrations, that is, $0.5 \times 10^{-3} M$. The same behavior is observed in the

Table 2. CEC of the initial clay Zenith-N and of AZA and FRAZA before and after restoration via different methods.†

Sample code	CEC in meq/g material				
	Before restoration	After restoration via method:			
		A	B	C	D
Zenith-N‡	0.95 ± 0.03	—	—	—	—
	0.90 ± 0.03	—	—	—	—
AZA	0.09 ± 0.01	0.43 ± 0.02	0.54 ± 0.03	0.44 ± 0.03	0.63 ± 0.05
FRAZA	0.10 ± 0.01	0.40 ± 0.02	0.52 ± 0.04	0.47 ± 0.04	0.63 ± 0.04

† A) Washed in Na^+ solution of pH ~ 10.00 ; B) In NH_3 atmosphere; C) First (A) and then (B); D, First (B) and then (A).

‡ Two independent measurements for Zenith-N.

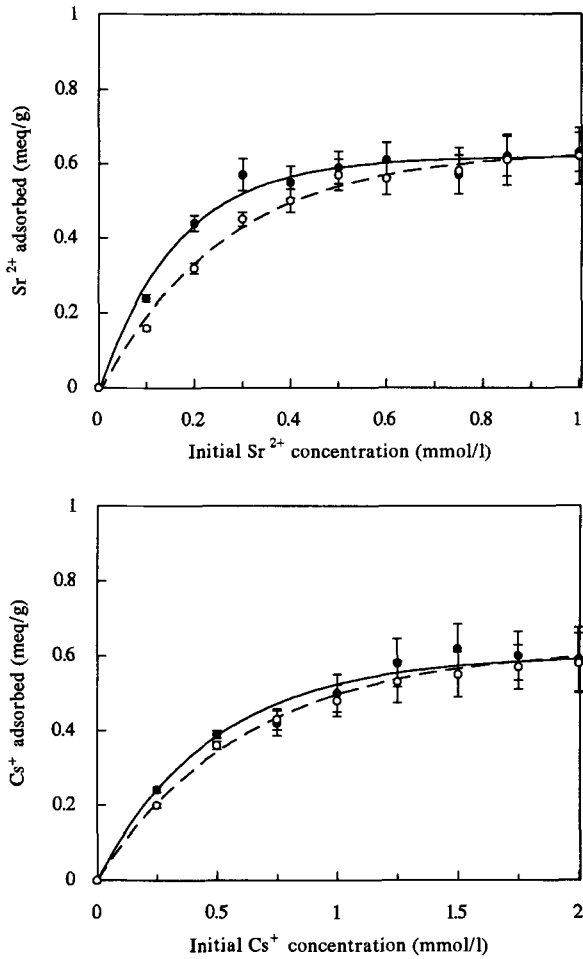


Figure 4. Sr^{2+} and Cs^+ exchange isotherms on AZA-D D (open circles, dashed line) and FRAZA-D (black circles, solid line) at room temperature and $\text{pH} \approx 6.00$.

uptake of Cs^+ , but here saturation is attained in both materials at higher concentrations, around $1.5 \times 10^{-3} M$. The saturation levels reached are, as expected, in all cases equal to about 0.63 meq/g material, that is, equal to the CEC value achieved after restoration via method D (Table 2). The difference in the Sr^{2+} and Cs^+ concentrations needed for reaching saturation is due to the higher replacing power of the divalent Sr^{2+} compared to that of the monovalent Cs^+ (Grim 1968).

Since the investigation pertains to Sr^{2+} and Cs^+ uptake from slightly acidic aqueous environments, the exchange isotherms were carried out in this study in water of pH approximately 6.00. However, as shown by Dyer and Calladro (1990) in Cs^+ and Sr^{2+} uptake experiments conducted in alkaline solutions of $\text{pH} > 8$, the saturation levels they observed were higher than the full CEC of the starting clay. These authors attribute this finding to the exchange of H_3O^+ ions attached to the pillars.

EXCHANGE KINETICS. Exchange kinetic measurements were conducted for both AZA-D and FRAZA-D in aqueous solutions either with a concentration of $0.5 \times 10^{-3} M$ in Sr^{2+} or $1 \times 10^{-3} M$ in Cs^+ . Since the time dependence of the kinetic isotherms systematically revealed the presence of a fast exponential component, the experimental data shown in Figures 5, 6 and 7 have been fitted with a first-order kinetic model according to the equation:

$$S = C(1 - e^{-t/\tau_0}) \quad [1]$$

where S (meq/g) expresses the sites occupied at time t by Sr^{2+} or Cs^+ and C (meq/g) represents the uptake at equilibrium. The best fit was obtained by minimizing the corresponding χ^2 function through a modified version of code MINUIT (James and Roos 1975) with

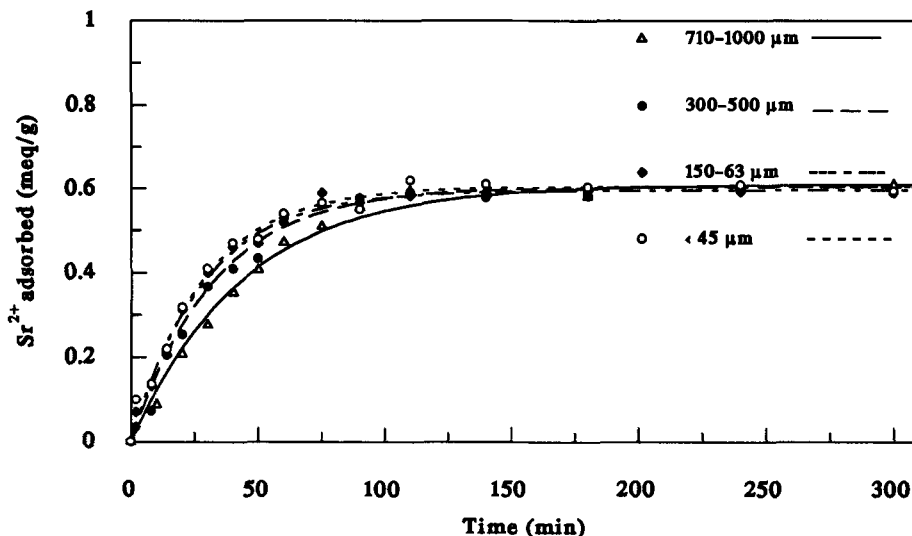


Figure 5. Sr^{2+} exchange kinetics on different grain sizes of AZA-D; Sr^{2+} concentration $0.5 \times 10^{-3} M$ and $\text{pH} \approx 6.00$.

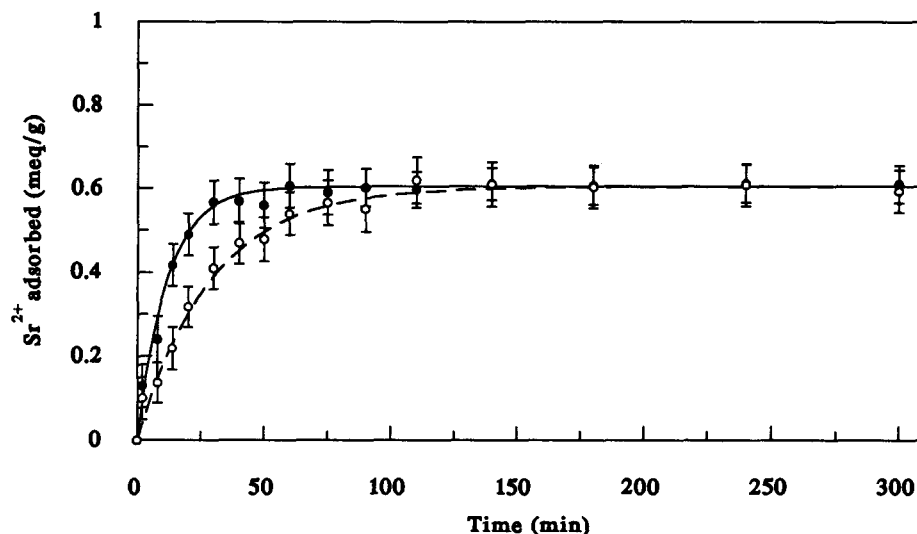


Figure 6. Sr^{2+} exchange kinetics on AZA-D (open circles, dashed line) and FRAZA-D (black circles, solid line) at Sr^{2+} concentration $0.5 \times 10^{-3} M$ and $\text{pH} \approx 6.00$ and for grain fractions $< 45 \mu\text{m}$.

C and τ_0 treated as free parameters. The results of the fits are given in Table 3.

In an initial set of experiments, prior to the direct comparison of the 2 materials, the effect of grain size on cation exchange rates was investigated. Thus, Sr^{2+} exchange kinetic measurements were conducted for different grain sizes of the AZA-D material. A study of the isotherms for Sr^{2+} and different grain size of AZA-D (Figure 5) reveals that the grain size is not the principal rate controlling factor of Sr^{2+} uptake. Indeed, no difference was observed in the Sr^{2+} kinetics for various grain sizes up to $150 \mu\text{m}$, whereas only a small delay occurred for larger grains which can be attrib-

uted to a macroscopic grain diffusion processes. Nevertheless, in order to exclude grain size effects, sizes between 2 and $45 \mu\text{m}$ were used in all subsequent experiments.

The kinetic isotherms in Figures 6 and 7 and their corresponding fitting results in Table 3 show that Sr^{2+} or Cs^+ exchange in PILCs is a fast process but with different relaxation times for the 2 materials studied. (In this paper, we have characterized the process of cation uptake by FRAZA as "fast". The characterization of the speed of exchange is of course a matter of terminology. Although there is no common practice in the bibliography, with reference to Amacher's time

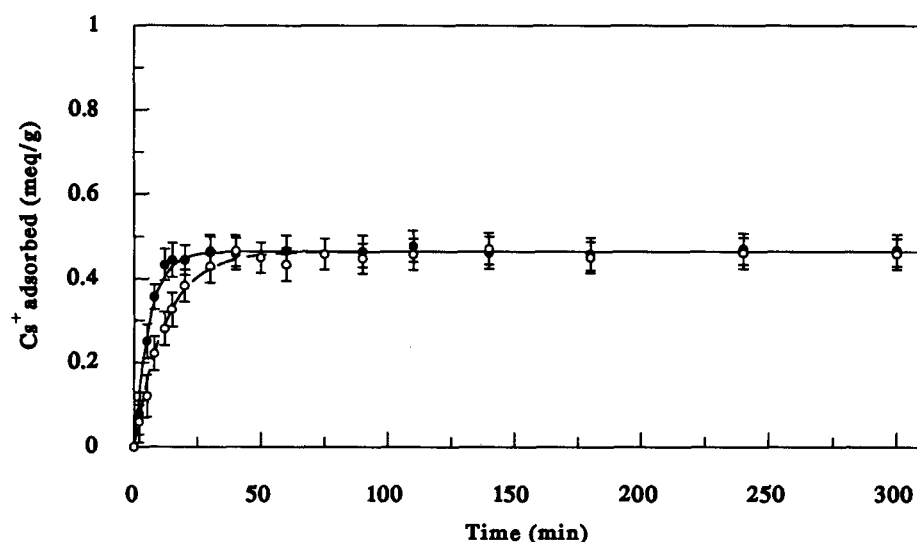


Figure 7. Cs^+ exchange kinetics on AZA-D (open circles, dashed line) and FRAZA-D (black circles, solid line) at Cs^+ concentration $1 \times 10^{-3} M$ and $\text{pH} \approx 6.00$ and for grain fractions $< 45 \mu\text{m}$.

Table 3. Parameters determined by fitting of Equation [1] to the experimental data of Figures 6 and 7.

Conditions	PILC	C (meq/g)	τ_0 (min)
Sr ²⁺ (0.5 × 10 ⁻³ M)	FRAZA-D	0.605 ± 0.020	13.0 ± 0.8
	AZA-D	0.605 ± 0.018	28.9 ± 0.8
Cs ⁺ (1 × 10 ⁻³ M)	FRAZA-D	0.46 ± 0.01	5.8 ± 0.4
	AZA-D	0.46 ± 0.02	12.2 ± 0.7

scale diagram (Sparks et al. 1993 and references therein), we have adopted for the various processes (including ion exchange) the terms “instantaneous” for the scale of μsec , “very fast” for seconds, “fast” for minutes and “slow” for hours.) Strontium kinetic experiments show that the exchange is accomplished in less than 1 h for FRAZA-D and less than 2 h for AZA-D. The kinetic isotherms for Cs⁺ (Figure 7) are similar to those for Sr²⁺, but the relaxation time is even smaller than in the case of the latter cation for both materials. This might be due to the smaller hydrated radius of the Cs⁺ ion, a fact leading to a faster accessibility of the exchange sites. However, the difference in the relaxation time and the total time of Cs⁺ uptake for the 2 materials still remains. These differences can be attributed to the different microstructure of the 2 PILCs studied. Furthermore, the substantial mesoporosity that FRAZA possesses and its less compact structure (Figure 1) facilitates the accessibility of the exchange sites and accelerates the exchange process in contrast to the slower cation diffusion through the spatially restricted network of micropores in AZA-D.

CONCLUSIONS

The present investigation provided direct evidence that the rate of cation exchange in PILCs is clearly affected by the spatial organization of its building blocks, that is, of the clay lamellae and the metal oxide particles cross-linked to the lamellae. Furthermore, the method of drying the precursor during the synthesis of such a material appears to critically control the cation exchange rates. More specifically, as the freeze-drying method leads to large voids between the tactoids of pillared clay lamellae, the cation exchange sites become easily accessible, in contrast to air-drying, which results in closely compacted tactoids. Evidently, several other aspects of the cation exchange process in PILCs, as for example the role of different competing cations, deserve clarification before this complex process in these novel materials can be fully understood. In any case, the findings of this study corroborate that the structure of PILCs can be modified in such a way that fast uptake of cations from aqueous environments is possible. Uptake times of the order of a few minutes have been observed, and this fact opens up new application possibilities for PILC.

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