A new approach for enhancing Sr\(^{2+}\) retention by an Al-PILC in acidic solutions

C.A. Papachristodoulou *, P.A. Assimakopoulos, N-H. Gangas, D.T. Karamanis

Nuclear Physics Laboratory, Department of Physics, School of Sciences, The University of Ioannina, 451 10 Ioannina, Greece

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Abstract

Strontium uptake by an aluminum pillared montmorillonite has been studied in aqueous solutions of pH values ranging from 3 to 8. Desorption of Sr\(^{2+}\) has been observed when the concentration of H\(^{3+}\) in the solution raises. In order to limit this effect, the material has been modified by inserting organic molecules in the interlayer. Results with glycerol and oxalic acid as modifying agents demonstrate that it is feasible to shield the metal cations against hydroxium attack and thus reduce strontium desorption in acidic environments. These results are of a particular interest from a view point of the potential application of PILCs as antidotes against strontium radiocontamination of ruminants. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

A wide range of sorbents, ion exchangers and advanced extractants are currently being developed for removing hazardous radionuclides from nuclear wastes and contaminated groundwater. Zeolites, micas, crystalline silicotitanates, resins and crown ethers are but a few examples of materials that have been identified as acceptable scavenging agents for Cs\(^+\) and Sr\(^{2+}\). While most of these candidates exhibit good to excellent performance for cesium over the whole pH range, only few of them have proved efficient for separating strontium from acidic solutions [1–3].

Equally moderate progress has been made in the development of acceptable prophylactic materials for reducing the retention of radiostrontium in biological systems and especially in large domesticated animals. Although many previous studies have demonstrated that various salts of ferrocyanic acid, conforming to the formula MFe\(^{III}\)Fe\(^{II}\)(CN)\(_{6}\), with M = Li, Na, K, NH\(_4\), enhance excretion of Cs when administered to rats, ruminants and man, none of these analogues has shown encouraging results for Sr decontamination [4]. Sodium alginates, having been successfully tested in rats and human subjects, are considered to be promising antidotes against radiostrontium. However, experiments conducted with big mammals were disappointing [5].

Research for a powerful, non-toxic agent capable of reducing radiostrontium transfer to the tissues of ruminants is attractive and particularly
beneficial, considering that their meat and dairy products are at the top of man’s diet. In this direction, we have synthesized and investigated the ion exchange properties of pillared layered clays (PILCs) belonging to the class of layered aluminosilicates. These materials exhibit fast uptake kinetics for Cs and Sr [6], as well as high selectivity towards biologically abundant competing cations in neutral environment [7]. However, the main adversity arising during in vivo applications is related to the peculiar acidity sequence occurring in the gastrointestinal (GI) system of polygastric species. Their digestive cycle comprises a long period (∼20 h) of microbial digestion in the slightly alkaline forestomachs (pH constantly kept between 7 and 8), followed by a short passage (2–3 h) of the food through the main stomach. There, enzymic digestion is accomplished at a pH adjusted to 3 by continuous production of HCl acid. All electrolytes, including Sr$^{2+}$, follow this course and are principally absorbed in the small intestine. Any potential antidote should therefore provide a means of binding and retaining strontium through the entire GI tract and cause its fecal excretion.

The present work aims first to assess the ion exchange behavior of an aluminum pillared montmorillonite under various pH conditions, concentrating on the adsorption and desorption of Sr$^{2+}$ in acidic environments. At a second stage, the introduction of organic molecules in the PILC is proposed and tested with a view to the ability of the modified materials to better retain Sr$^{2+}$ in acidic solutions. For demonstrating the validity of this new approach, in this paper, we focus on the results obtained using two rather simple molecules: glycerol and oxalic acid. These molecules are not necessarily the optimum candidates for improving the ability of PICLs to retain strontium in aqueous environments of increased acidity.

2. Experimental

2.1. Investigated pillared layered clays

All PILCs used in the present study were prepared from the same starting clay, which was a natural greek bentonite with the commercial name ZENITH-N, kindly provided by Silver & Baryte Min. Co., Athens, Greece. According to the supplier, the main phases present in this bentonite are montmorillonite 85%; feldspars 5%; calcite 3%; quartz 2.5%; illite 2% and christobalite 2%. This starting clay was chosen for establishing a base of comparison of the pillared montmorillonites prepared within this work, seen below PILCs A and B, with a reference material ¹ hereafter referred to as PILC C. This PILC was kindly provided by the chemical engineering department of the National Technical University of Athens, where this material is being routinely prepared since 1993 out of Zenith-N [8,9]. The chemical analysis given by Kaloidas et al. [9] for Zenith-N is in wt.%: SiO$_2$ 57.08; Al$_2$O$_3$ 19.04; Fe$_2$O$_3$ 4.55; CaO 3.01; MgO 3.25; K$_2$O 1.51; Na$_2$O 2.67; TiO$_2$ 0.71; loss on ignition 7.22. In the same work, the following chemical analysis for AZA (PILC C) is also given, SiO$_2$ 52.66; Al$_2$O$_3$ 27.55; Fe$_2$O$_3$ 2.85; CaO 0.84; MgO 2.19; K$_2$O 1.32; Na$_2$O 0.20; TiO$_2$ 0.60; loss on ignition 12.5. To provide a link to a previous study in this laboratory on strontium uptake by aluminum-pillared montmorillonites [6,7], PILC A and B were prepared in 10 g batches by following quite closely the preparative steps used in that study.

Before pillaring, the clay fraction, mainly montmorillonite, of the starting bentonite was brought to its Na$^+$-homoionic form. Specifically, ZENITH-N was repeatedly contacted with 1 M NaCl solutions and washed with de-ionized water until Cl$^-$ free, as indicated by the AgNO$_3$ test. Then, a 1 wt.% aqueous suspension of the thus treated Na$^+$-ZENITH-N was prepared and left to stand for 24 h. The upper 80% of the colloid column was then separated, centrifuge-washed and finally gently ground after drying at room temperature.

2.1.1. Pillared layered clay A

The pillaring solution was prepared by hydrolyzing, at 70°C and under vigorous stirring, a 0.2 M

¹ This reference PILC, known as AZA, has been prepared for the needs of the Concerted European Action on Pillared Layered Structures (European Commission Project BREU CT-91-0462, 1991–1995).
solution of AlCl$_3$ with a 0.2 M solution of NaOH up to a ratio Al/OH equal to 1 and a final Al$^{3+}$ normality equal to 0.3 mN. The clay fraction powder was added to the pillaring solution at a ratio of 3.5 mmol Al per g clay and left to react for 1 h under vigorous stirring at 70°C. Once the exchange process was completed, the PILC precursor was repeatedly washed with de-ionized water until a conductivity of 30 $\mu$S cm$^{-1}$ was reached and then freeze dried. This drying method was employed for imparting to the PILC mesoporosity, a feature substantially enhancing the rate of cation exchange [7]. Heating the PILC precursor in air at 500°C for 4 h delivered the final PILC in powder form. Its cation exchange capacity was restored by bringing this powder to contact first with an ammonia atmosphere overnight and then with a 1 M NaCl solution for approximately 30 h keeping its pH = 10 by addition of NaOH. This latter step aimed at converting the PILC to its Na$^+$-homionic form. The PILC was recovered by centrifugation and centrifuge-washed several times with de-ionized water and dried at 80°C. The dried solid lumps were then ground in an agate mortar to pass through a mesh of 95 $\mu$m. The powder thus gained is referred to hereafter as PILC A. Strontium exchange isotherms taken for this material yielded a strontium saturation concentration of 0.64 meq g$^{-1}$ at neutral pH. A more detailed description of the PILC preparation processes is given by Karamanis et al. [6].

2.1.2. Pillared layered clay B

Another PILC employed in this study was prepared by slightly modifying the pillaring process described above. Specifically, the as-prepared PILC precursor was left to soak in water for two days before proceeding to the usual end-washing step. This prolonged soaking aimed at bringing about some additional hydrolysis of the intercalated Al-hydroxy moieties, which might allow them either to better distribute in the lamellar space [10] or/and to further polymerize [11]. The final washing, freeze drying and calcination of the PILC precursor, as well as the restoration of its cation exchange capacity were carried out as already described for PILC A. The strontium saturation concentration of PILC B was measured through strontium isotherms and found equal to 0.66 meq g$^{-1}$ at neutral pH.

2.1.3. Pillared layered clay C

Before using PILC C in the present work, this material too was submitted to the cation exchange capacity restoration treatment described above. Strontium isotherms at neutral pH gave the value 0.63 meq g$^{-1}$ for the saturation concentration of PILC C.

2.2. Characterization techniques

2.2.1. X-ray diffraction

X-ray diffraction patterns were obtained for dry powder samples using a Philips PW 1011 X-ray diffractometer with CoK$\alpha$ radiation.

2.2.2. Surface area and pore-size distribution

Nitrogen adsorption–desorption isotherms of PILC samples previously outgassed at 120°C for 12 h under a vacuum of 1 Pa were obtained with a Carlo Erba 1800 Sorptomatic. For all three PILCs, BET surface areas were determined between $P/P_0 = 0.01$ and 0.15, while the pore size distributions were calculated via the Kelvin equation.

2.3. Uptake experiments

Strontium sorption and desorption were studied in batch experiments using natural Sr and radiostrontium ($^{85}$Sr) as a radiotracer. In each batch, 0.1 g of PILC was reacted under gentle stirring with 200 ml of an aqueous strontium solution, whose initial $\gamma$-activity had been previously measured with a 22%-efficiency intrinsic Ge detector. Preliminary experiments showed that the exchange equilibrium was reached in less than 2 h, after which the solid and aqueous phase were separated by centrifugation. Then, the $^{85}$Sr $\gamma$-activity of the aqueous phase was measured again and the amount of strontium taken up or desorbed by the PILC was calculated. All sorption and desorption experiments were performed in duplicate, while background contributions during the equilibration measurements were determined to be less than 5%.
2.3.1. Strontium adsorption isotherms

To assess Sr$^{2+}$ uptake levels in a range of pH values, strontium exchange isotherms were obtained as described above for a series of independent batch measurements covering the whole pH range of interest. Specifically, a set of aqueous solutions of different ionic strengths between 10^{-4} and 1.2 \times 10^{-3} \text{ M} were prepared by dissolving SrCl$_2$ in de-ionized water and adjusting their pH with HCl to acidic or with Sr(OH)$_2$ to alkaline values. Small amounts of a $^{85}$Sr radiosource solution were added, keeping the concentration of the radioisotope in the order of 10^{-9} \text{ M}. Therefore, the initial Sr$^{2+}$ concentration in solution was determined from the amount of chloride salt dissolved. In alkaline solutions, the amount of strontium hydroxide added was also taken into account. Then, in each solution 0.1 g of PILC was immersed.

From the difference in $^{85}$Sr $\gamma$-activity of each solution before and after exchange, the amount of Sr$^{2+}$ adsorbed by the PILC was calculated and the strontium uptake saturation level at each specific pH value was determined through Langmuir isotherms, as described in Section 3.2.

2.3.2. Strontium desorption curves

Following a similar methodology, in another set of experiments strontium desorption in acid solutions was followed. Samples of 0.1 g PILC were first contacted with separate equal volumes of an aqueous stock solution of ionic concentration equal to 10^{-9} \text{ N} and neutral pH. Once equilibrium was reached, the amount of $^{85}$Sr adsorbed by the PILC was determined through Langmuir isotherms, as described in Section 3.2.

2.4. PILC modification via organic molecules

With a view to diminish strontium desorption in acidic aqueous environments, the idea was tested to somehow shield Sr$^{2+}$ against hydronium attack (see Section 3.4) by introducing organic molecules into the PILC. The results presented hereafter involve strontium adsorption–desorption patterns of PILCs modified by either glycerol or oxalic acid. These results were obtained in several independent experiments using PILCs A or B from different preparation batches and PILC C from one preparation batch.

2.4.1. Glycerol

Samples of Na$^+$- and Sr$^{2+}$-homoionic forms of the investigated PILCs were modified by contacting them with aqueous solutions of glycerol. Specifically, 0.5 g of each PILC were contacted first with 0.1 M water solution of glycerol and then, after washing twice, with 1 M water solution of glycerol. Each contact was prolonged overnight to allow adsorption of the alcohol molecules in the porous medium. Finally, the glycerol-modified PILCs were washed twice with de-ionized water and dried at 50°C overnight. Labels NaAG and SrAG refer to the modified PILCs derived from pristine PILC A. Similarly, labels NaBG and SrBG, NaCG and SrCG refer to the modified PILCs derived from pristine PILC B and C, respectively.

2.4.2. Oxalic acid

A 0.5 g sample of PILC A was immersed in 50 ml of a 0.01 M solution of dihydrate oxalic acid overnight. The PILC was then re-gained via centrifugation, washed twice with de-ionized water and dried at 50°C overnight. Label NaAO refers to the modified product.

2.5. Thermogravimetry and FTIR spectra

TGA and DTA measurements were taken with a TRDA$_3$–H Chyo Balance. Fifty mg samples were heated in air flow at a rate of 4°C min$^{-1}$, from 25°C to 600°C, using alumina as the reference material. Before measurement, the samples were passed through a 95 µm sieve with no further treatment.

Infrared spectra were recorded between 4000 and 400 cm$^{-1}$ on a Perkin Elmer GW FT-IR Spectrometer. Pellets, 0.3 inch in diameter, were prepared by mixing, at a ratio 1:55, PILC and KBr powders, previously ground to a particle size less than 45 µm. All pellets were kept at room temperature and humidity before measurement. The
FTIR spectra were obtained for samples of PILC A, modified by either glycerol or oxalic acid, before and after their overnight contact with de-ionized water. These measurements aimed at detecting whether the inserted organic compounds wash out during strontium uptake from aqueous solutions. No notable variation in the spectra has been observed, particularly at the frequency regions characteristic for the aforementioned compounds, i.e., around 2950–2850 and 1400 cm$^{-1}$. This finding does not preclude some quantitative changes, it though gives evidence that the guest organic molecules have not been extensively expelled from the interlayer after immersing the modified PILCs in water.

3. Results and discussion

3.1. Characterization of PILCs A, B and C

Fig. 1 presents the XRD-diagrams obtained for PILCs A, B and C. The well-defined peaks shown around $2\theta \approx 5^\circ$ reveal the presence of quite well-defined pillared clay tactoids consisting of few montmorillonite layers. Table 1 presents data for $d_{001}$-spacings, BET surface area and total volume of micropores (width less than 2 nm) and mesopores (width between 2 and 50 nm) for all three materials. This volume has been calculated from the pore size distributions derived from the nitrogen desorption data. The last column of the table quotes the fraction of the micropore volume with respect to the listed total volume.

The slight increase in the BET surface area in the order PILCs A, B and C is in agreement with the increase in their $d_{001}$-spacings. As the pillar height becomes comparable to or smaller than $\approx 0.72$ nm, i.e., twice the molecular diameter of nitrogen, coverage by a complete nitrogen mono-layer of both interlayer surfaces of each gallery is doubtful or even geometrically impossible. However, the substantial mesoporosity of PILCs A and B compensates to a certain extent for the surface area reduction due to partial nitrogen coverage of their micropores.

Fig. 1 and the data in Table 1 bear out that all three PILCs employed in this work have a well-defined pillared structure, which differs with respect to mesoporosity and pillar height. This indicates that this set of hosts is in principle apt for detecting the likely effect of organic guest molecules on the retention of strontium by PILCs in acidic aqueous environments.

3.2. Strontium adsorption isotherms at different pH values

A typical exchange isotherm at pH 7 is presented in Fig. 2. The Langmuir equation in the form

![Fig. 1. XRD diffraction patterns for PILCs A, B and C.](image-url)
was fitted to the experimental data. In Eq. (1), \( Q \) stands for the Sr\(^{2+} \) concentration in the PILC at equilibrium (meq g\(^{-1} \)), \( C_e \) stands for the Sr\(^{2+} \) concentration in the solution at equilibrium (meq l\(^{-1} \)), while the parameters \( K_L \) (l meq\(^{-1} \)) and \( Q_L \) (meq g\(^{-1} \)) are obtained through the fit and correspond to the distribution coefficient and the strontium saturation concentration in the PILC, respectively.

\[
\frac{C_e}{Q} = \frac{1}{K_L Q_L} + \frac{C_e}{Q_L}
\]  

(1)

The pH variation of parameter \( Q_L \), shown in Fig. 3, was determined by fitting Eq. (1) to the exchange isotherms obtained in solutions of different pH values. At neutral pH, PILC A is found to adsorb 0.64 meq of strontium per gram, while at low alkaline solutions (pH = 8.5), an additional 0.18 meq g\(^{-1} \) is taken up. The curve shows a smooth decrease in the strontium uptake until pH \( \approx 5 \), while the rate of reduction increases as more acidic values are reached. It is clear that the presence of H\(_3\)O\(^+ \) in the solution drastically suppresses the uptake of Sr ions. Thus, at pH \( \approx 4 \), the saturation concentration in the PILC is about half its value at pH = 8.5, while at pH < 3 it is practically nil.

The observed moderate increase of the Sr uptake at alkaline pH is due to the extra exchange sites, which are formed by deprotonation of Al–OH groups on the pillars, as the hydroxyl concentration in the bulk solution rises [12,13]. On the other hand, the decrease in the Sr uptake observed at low pH values can be partly attributed to the positive charge, which develops on the PILC edges according to the process noted by Avena et al. [14]:

\[
\text{SO}^- + \text{H}^+ \rightarrow \text{SOH} \text{ and } \text{SOH} + \text{H}^+ \rightarrow \text{SOH}^2^+,
\]

where S stands for any surface site. However, it has previously been reported [15] that the clay sheets of montmorillonites remain negatively charged at pH values down to 3, since the positive charge of the edges does not exceed the charge of the sheets. It can therefore be concluded that the Sr uptake at acidic pH values is suppressed, because the remaining negative charge of the PILC is preferentially compensated by H\(_3\)O\(^+ \) ions. This provides a supplement to the results reported in a recent study [7] with a PILC similar to PILC A, which was found to exhibit high uptake selectivity for Sr\(^{2+} \) over competitive monovalent ions in the order: Sr\(^{2+} \) > K\(^+ \) > Na\(^+ \). Hydronium ions, although monovalent, behave mostly as di or trivalent ion and can be added to this selectivity order as H\(_3\)O\(^+ \) > Sr\(^{2+} \) > K\(^+ \) > Na\(^+ \). The same pattern is known to be obeyed in non-pillared exchanging clays [16].

3.3. Strontium desorption in acidic solutions

Given the affinity of PILC A to hydronium ions, a series of additional experiments was carried...
out in order to follow the course of strontium desorption in acidic solutions. According to the procedure described in Section 2.3.2, the fraction of strontium finally retained by the material at pH $\hat{x}$ was calculated as

$$\frac{[\text{Sr adsorbed at pH } 7] - [\text{Sr adsorbed at pH } x]}{[\text{Sr adsorbed at pH } 7]}.$$ (2)

The results presented in Fig. 4 shows that the decrease in pH causes a back exchange of strontium cations previously taken up by the material. This Sr$^{2+}$ depletion process, corroborating the selectivity of PILC A for H$_3$O$^+$, is virtually complete at pH $\approx$ 3 and takes place within a few minutes (Fig. 5). This fast depletion reveals a rapid migration of H$_3$O$^+$ ions from the external solution towards the interlayer exchange sites by mere rearrangement of hydrogen bonds between adjacent water molecules. Such a transfer of protons from one water molecule to the next is obviously facilitated in a PILC interlayer with ample water molecules.

3.4. Shielding Sr$^{2+}$ against hydronium attack

A conceivable way to hinder the aforementioned transfer of protons is to replace a least part of the interlayer water with organic molecules. These might impede the H$_3$O$^+$ transfer in the PILC interlayer with the consequence of a strontium back exchange to the external solution. Furthermore, interlayer organic molecules might trap Sr$^{2+}$ ions in the PILC by

1. posing geometrical constraints on their desorption, since the presence of organic molecules is expected to impede the free movement of Sr$^{2+}$ ions in the micro- and mesopores,
2. assuring their firm bonding in the interlayer via mechanisms in addition to the simple electrostatic attraction to the negative fixed charges of the clay lamellas, since it is known that many organic moieties successfully coordinate with Sr$^{2+}$. Therefore, the formation of such in situ Sr$^{2+}$ complexes or compounds may hinder strontium depletion of the PILC in acidic environments.

In selecting adequate candidates, the chemistry of metal coordination has been taken into account. Several studies have focused on the coordinative principles of metal cations with conventional and macromolecular ligands in different systems. Neutral compounds possessing oxygen and nitrogen coordination sites, such as polyalcohols, acyclic polyethylene glycols, glymes and amine derivatives have been recognized as potent complexing agents for the strontium cation. Their chelate effect is large enough to make Sr$^{2+}$ prefer their coordination over that of water [17,18]. Anionic ligands and especially carboxylate anions belong to another category of powerful metal chelators. The M$^{2+}$-carboxylate interactions are particularly favored in the case of the medium-charge
density such as cations Ca$^{2+}$, Sr$^{2+}$ and Na$^+$. Apart from complying with the principles of co-ordination chemistry, the candidate organic molecules have also to comply with the spatial restrictions posed by the porous structure of the host material. Moreover, they should be easily introduced into the interlayer region, either from the gas or the liquid phase.

In view of the above, two molecules were selected, one from the class of the electrically neutral oxygen donor ligands and a second from the class of multiply charged carboxylate ligands. The first is glycerol, CH$_2$(OH)CH(OH)CH$_2$(OH), which is known to form complexes with all metal cations and in particular with alkaline earth ions. The interaction of glycerol with montmorillonites has been extensively described in the past [19,20]. The second is oxalic acid, HOOCCOOH, the smallest dicarboxylic acid, which forms an insoluble salt with the Sr$^{2+}$ ion. Several studies have been reported on the formation of complexes of carboxylic acids with montmorillonite, and it has been shown that such species can be held through physisorption or chemisorption to the clay surfaces [21].

3.5. Strontium adsorption–desorption in the presence of glycerol

Strontium desorption from the glycerol modified PILC was followed as the solution pH decreased to pH ≈ 3 after initial strontium uptake at pH ≈ 7. This two-step procedure was adopted with a view to the potential application of PILCs as scavengers of Sr$^{2+}$ ions under conditions of varying pH, as, e.g., is the case in the digestive system of ruminants. Although strontium exchange equilibrium in a glycerol-modified PILC is established within less than 2 h, the exchange reaction at pH ≈ 7 was left to proceed overnight, in order to allow any redistribution of the glycerol molecules around strontium cations.

3.5.1. Glycerol modified PILC A

Adsorption–desorption experiments conducted with solutions containing only $^{85}$Sr ([Sr$^{2+}$] = 10$^{-9}$ N) revealed that, if the PILC is modified by glycerol adsorption prior to radiostrontium uptake, back exchange is reduced. More specifically, the arithmetic mean of duplicate experiments showed that pristine PILC A, referred hereafter as NaA, retains at pH ≈ 3 (2 ± 2)% of the radiostrontium initially taken up, which increases to (11 ± 2)% for NaAG and reaches (17 ± 2)% in the case of SrAG. These results indicate a shielding of strontium by the adsorbed organic molecules, which appears to depend on the nature of the interlayer cation initially present in the PILC. In fact, Sr$^{2+}$ being more polarizing than Na$^+$ is expected to enhance the adsorption of glycerol by the PILC.

Previous research has often illustrated the key role of the exchangeable cation in the adsorption process of alcohols in montmorillonite. In the classic work of MacEwan, [22] it is reported that, although exchangeable cations do not influence the number of layers formed during the intercalation of organic agents in montmorillonites, the type of cation influences the ways of molecular packing established in its neighborhood. In addition, Bissada et al. [23], in a study on the nature of complexes of montmorillonite with ethanol, reported that the number of molecules adsorbed depends on the interlayer cation, and adsorption is favored when divalent cations are present. They were thus led to the conclusion that the association between the intercalated organic molecules and the interlayer cations is governed mainly by electrostatic ion–dipole interactions. Similarly, German and Harding [24] studied the adsorption pattern of aliphatic alcohols in montmorillonite and found that Na-montmorillonite adsorbs less alcohol than Ca-montmorillonite. Annaby-Bergaya et al. [25] showed that adsorption isotherms for methanol in montmorillonite decrease in the order Li$^+$ > Ba$^{2+}$ > Na$^+$ in agreement with the relative polarizing power of the cations.

Apart from being more efficiently adsorbed by the Sr$^{2+}$-form of the PILC, glycerol is also expected to be held more firmly due to co-ordination with Sr$^{2+}$ instead of Na$^+$ cations. It is well known that the formation of chelate complexes between a

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2 The electric field of a cation is proportional to $v/r^2$, where $v$ is the valency and $r$ the ionic radius. Thus, the polarizing factor of Sr$^{2+}$ is 1.44, while that of Na$^+$ is 0.96 only.
metal ion, $M^{z+}$, and a considerably polar ligand, such as glycerol, is determined by the polarizing power of the ion. The stability of such co-ordination complexes increases with an increasing polarizing power of the $M^{z+}$ ion. In the case of neutral oxygen donor ligands, such as glycerol, the ligand may even replace water molecules in the cation's first co-ordination sphere [26].

3.5.2. Thermal desorption of glycerol from $Na^+$ and $Sr^{2+}$ exchanged PILC A

In order to gain further insight into the mechanisms of complex formation of glycerol within the PILC, DTA and TGA data were obtained for NaA and two modifications thereof: NaAG and SrAG. In the DTA diagrams shown in Fig. 6, a similar endothermic pattern, attributed to the loss of physisorbed water, is observed for all three materials between 50°C and 100°C. Above this temperature region, the DTA diagrams differ. A quite broad endotherm appears between 120°C and 500°C in NaA. The low temperature part of this endotherm can be associated with the loss of water chemisorbed by or co-ordinated to the pillars, while the middle temperature part with the dehydroxylation of the pillars themselves. Finally, the high temperature part is related to the dehydroxylation of the clay lattice, since this process starts in PILCs at lower temperature (i.e., below 600°C) than in non-pillared clays.

In the DTA diagram for NaAG, desorption of water chemisorbed by the pillars is again observed in the region of 150°C, while around 240°C and 320°C, two quite separate peaks are discernible. The former peak can be mainly ascribed to the removal of physisorbed glycerol, as its boiling point is 290°C, while the latter peak to the removal or combustion of chemisorbed glycerol. The DTA structure for SrAG is again less distinct, although it actually follows up to about 200°C the same pattern as NaAG. In the higher temperature region, however, a clear difference between the diagrams of SrAG and NaAG is noted (Fig. 6, enlarged scale). In SrAG, only one broad endotherm appears in the vicinity of 320°C, a temperature corresponding, as in the case of NaAG, to the desorption of chemisorbed glycerol. Thus, from the overall shape of this broad endotherm, it may be deduced that chemisorbed glycerol is the predominant phase in SrAG, whereas in NaAG, glycerol is held mainly by physisorption.

The aforementioned interpretation of the detected endotherms agrees well with Brindley's findings [19], who studied the effect of heat on glycerol complexes with montmorillonites saturated with various cations. It was found that in a two-layer complex within a Na-montmorillonite, the first layer is removed in the region of 115–170°C, while the second layer breaks down between 160°C and 210°C. These regions shift to higher temperatures when the clay is saturated with divalent cations as, e.g., $Mg^{2+}$, $Ca^{2+}$ and $Ba^{2+}$. With such cations, the second layer is removed at temperatures between 230°C and 350°C.

The TGA diagrams shown in Fig. 7, support the above DTA findings. In the region between 50°C and 100°C, all samples lost less than 3% of their initial weight due to the removal of physisorbed water. At higher temperatures, NaA exhibits a gradual loss, attributed to the removal of

![Fig. 6. DTA diagrams for NaA, NaAG and SrAG. In the inserted figure the NaAG and SrAG curves are superimposed in the temperature region from 100°C to 500°C.](image-url)
chemisorbed water and to the dehydroxylation of the PILC. However, the materials previously exposed to glycerol display a large weight reduction starting around 180° C and amounting to 12–15\%.

In NaAG, this weight reduction reaches saturation at temperatures around 320° C, whereas in SrAG, saturation is obtained around 380° C. The higher temperature needed to liberate glycerol from the SrAG suggests a stronger bonding of the alcohol with the strontium ions.

Based on the TGA data, one can roughly estimate that glycerol intercalation leads to a loading of about 1.6 mmol glycerol per gram of NaA. Assuming that each glycerol molecule occupies a volume of about $5 \times 4 \times 4$ Å\(^3\), the total space occupied by 1.6 mmol glycerol does not exceed 0.077 cm\(^3\). This figure suggests that, even in the extreme case that all glycerol molecules were adsorbed exclusively on internal surfaces, less than half of the total micro- and mesopore volume of 0.16 cm\(^3\) available in one gram of NaA would be filled with glycerol. In this connection, it should be noted that a single glycerol layer in montmorillonites leads to a basal spacing of $\approx 14$ Å \[19\], while a double glycerol layer requires $\approx 17.8$ Å \[20\]. These considerations indicate that the $d$-spacing ($\approx 16.7$ Å) of NaA does not allow the formation of a double glycerol layer. It might, therefore, be presumed that strontium retention could be increased if glycerol was intercalated into a PILC having a $d$-spacing closer to 17.8 Å or larger.

3.5.3. Glycerol-modified PILCs B and C

In view of the above considerations, strontium back exchange was also studied in glycerol-modified PILCs B and C, which have larger $d_{001}$-spacings than PILC A. Exchange isotherms of SrAG, SrBG and SrCG at neutral pH reveal that strontium saturation concentrations remain unchanged ($\approx 0.64$ meq g\(^{-1}\)) after glycerol adsorption. Yet, when the solution pH is reduced to 3 (Fig. 8), the parameter $Q_L$ of the Langmuir equation assumes the following values:

1. $0.073 \pm 0.005$ meq g\(^{-1}\) in SrAG,
2. $0.201 \pm 0.001$ meq g\(^{-1}\) in SrBG,
3. $0.063 \pm 0.002$ meq g\(^{-1}\) in SrCG.

The substantial increase in the amount of Sr\(^{2+}\) retained by SrBG would at first sight favor the hypothesis that the $d$-spacing $\approx 17.5$ Å of this PILC allows the formation of a double glycerol layer and thus a better strontium protective shielding. However, the unexpectedly low strontium retention by SrCG, which has a basal spacing of 18.2 Å, indicates that this is not the parameter that crucially determines the degree of shielding. The controversy can be reconciled by noting that PILC C is a completely microporous material, whereas PILCs A and B have substantial mesoporosity. This fact suggests that strontium retention is mainly due to the shielding of strontium...
cations by glycerol molecules located in mesopores.

3.6. Intercalation of oxalic acid

Oxalic acid can be intercalated in a PILC from dilute aqueous solutions, which contain neutral molecules as well as oxalate and hydronium ions originating from the equilibrium reactions

\[
\text{HOOC–COOH} + \text{H}_2\text{O} \rightleftharpoons \text{HOOC–COO}^- + \text{H}_3\text{O}^+ \\
pK_1 = 1.23
\]

\[
\text{HOOC–COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{–OOC–COO}^- + \text{H}_3\text{O}^+ \\
pK_2 = 4.19
\]

Apart from the non-dissociated state, which is expected to enter the interlayer, oxalate anions might be taken up too, since the hydroxyl groups of the pillars are known to protonate (–OH₂)⁺ in acid environments and might act as anion exchangers [12]. Once inside the PILC, oxalate species will either be retained in their ionic form or they will react with the H₃O⁺ of the interlayer and be converted to the parent acid. In the case of PILC A, e.g., when the process is completed, neutral oxalic molecules, oxalate, hydronium ions and some of the initial Na⁺ exchangeable ions, will coexist in the interlayer.

As long as the weak acid groups remain non-dissociated, the cation capacity of the PILC is due to the exchangeable sodium and hydronium ions. However, once these groups dissociate, the carboxylate anions may act as fixed charges which must be balanced by counter ions. The dissociation of carboxylic acids is a pH-dependent process and takes place only when the pH of the solution rises above the pK value of the acid. Nevertheless, one should note that the acidity inside the PILC differs from that in the bulk solution. The acid strength of surfaces is usually expressed in terms of the Hammett and Deyrup acidity function \( H_0 \), which is a measure of the ability of a surface to convert an adsorbed neutral base to its conjugate acid. A variety of surfaces have been studied by Benesi [27], who found that \( H_0 \) is between +1.5 and −3.0 for dry Na-montmorillonite. Furthermore, as Walling [28] had previously noted, the acid strength of a dried clay decreases and thus the \( H_0 \) value increases in the presence of water. In the case of oxalic acid and its conjugate base, which is the oxalate anion, \( H_0 \) may be written as

\[
H_0 = pK_1 - \log \left( \frac{[\text{COOH}_2^-]}{[\text{HOOC}^-\text{COO}^-]} \right). 
\]

In this expression, only the first dissociation is assumed to take place with \( pK_1 = 1.23 \) for the first dissociation constant of oxalic acid in water. As can be deduced from Eq. (3), if \( H_0 < pK_1 \), the acid will act as a base and the non-dissociated form will predominate in the interlayer region, whereas if \( H_0 > pK \), dissociation of the acid will take place.

When contacting the PILC modified with oxalic moieties with solutions of increasing pH, it is expected to achieve a transition from the non-dissociated to the dissociated state. The modified PILC will therefore exhibit an additional apparent cation exchange capacity, which will depend on the external pH conditions.

To test these considerations, the uptake of Sr²⁺ ions by NaAO has been studied via strontium isotherms in solutions of various acidities. Uptake kinetics is again fast (<2 h), but the exchange was allowed to proceed for more than 15 h in order to permit arrangement and reactions between the interlayer acid and cations. Strontium saturation concentrations were obtained through Eq. (1) and are shown in Fig. 9 as a function of the external pH. It is noticed that the saturation concentrations in NaAO and NaN are practically the same in acid solutions and begin to differentiate only at pH values higher than 5. In the neutral and slightly alkaline region, additional exchange sites seem to be formed in NaAO, compared to pristine NaN, inducing an increase of 0.24 meq g⁻¹ at pH ≈ 7 and 0.30 meq g⁻¹ at pH ≈ 8, in the former sample. This enhancement in strontium uptake supports the idea that oxalic molecules constitute ionogenic groups that may contribute to the overall cation exchange capacity of the modified PILC under certain experimental conditions.

For examining the influence of oxalic acid on the back exchange of Sr²⁺ for H₃O⁺ ions, strontium adsorption–desorption experiments on NaAO...
were carried out. Samples of NaAO were first contacted with Sr solutions at pH ≈ 8 and the amount of Sr taken up after equilibrium was measured. Then the pH was reduced to 3 and Sr desorption from the material was followed. By fitting Eq. (1) to the data shown in Fig. 10, the value $Q_L^{\pm} = (1.089 \pm 0.032)$ meq g$^{-1}$ is obtained for NaAO at pH 8 and $Q_L^{\pm} = (0.215 \pm 0.012)$ meq g$^{-1}$ at pH 3. The strontium surplus uptaken by NaAO at pH 8 is thus partly back exchanged at pH 3.

However, the amount of Sr$^{2+}$ still retained by NaAO at pH 3 far exceeds the $\approx 0.04$ meq g$^{-1}$ retained by pristine PILC A at the same pH value. Such an improved performance indicates that the oxalate group acts as a chelating agent for the strontium cation, forming compounds that resist solvation in acid media.

4. Conclusions

The results of this work clearly hint that the back exchange of Sr$^{2+}$ ions from a pillared montmorillonite in acidic external solutions may be suppressed by intercalating the PILC with suitable organic molecules. This effect can be attributed to an in situ co-ordination of strontium cations with neutral or anionic ligand groups of the organic guest molecules. Although the enhancement in strontium retention is considerable, in the case of the PILC modified with oxalic acid retention at pH 3 amounts to about 24%, compared to less than 5% for the pristine PILC, there is no a priori theoretical obstacle for maximizing this effect. For such a goal, the choice of the organic guest molecules vis à vis their chemical affinity to strontium cations, on the one hand, and the tuning of the PILC structural features, as, pore size distribution and pillars size, on the other hand present principal issues for consideration.

Our work is currently proceeding along the new approach delineated in this paper, to the study of the shielding effect of other molecules, belonging to the class of neutral O and N-donor ligands as well as to carboxylic anion ligands. Such an extended study is needed for identifying an organic compound that would present no health hazards. This is an additional prerequisite for ending up with an antidote for radiostrontium contamination of ruminants, and mammals in general.

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References