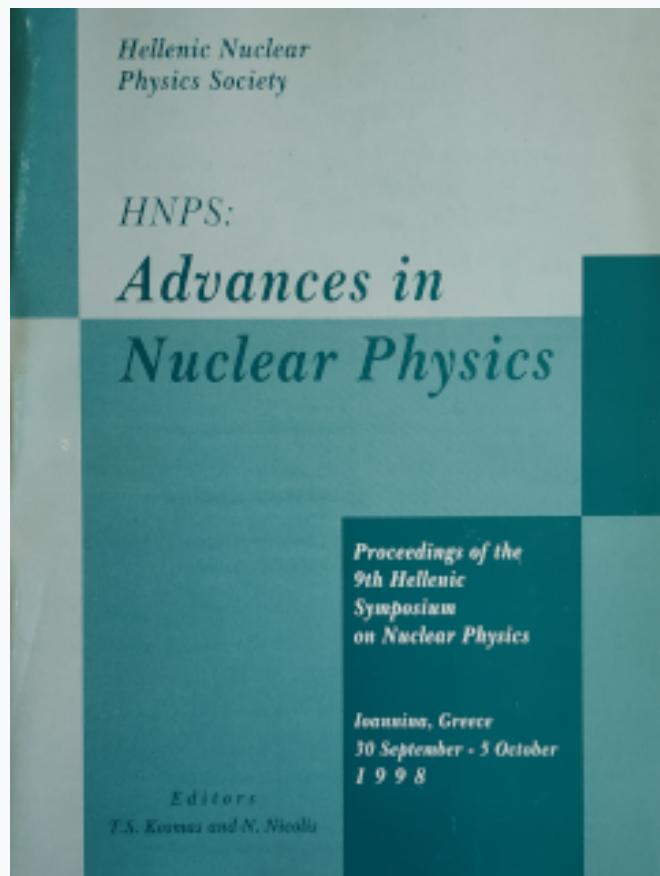


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Modification of pillared layered clays for scavenging radiostrontium from acidic aqueous environments

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Abstract

A Pillared Layered Clay (PILC), code-named FREZEN, has been developed as a potential antidote for trapping radiostrontium in the gastro-intestinal tract of ruminants. The ion exchange behaviour of FREZEN has been studied, with particular emphasis on Sr^{+2} exchange in acidic solutions. As for most sorbents and ion exchangers, strontium uptake by FREZEN remains sufficiently good over a pH range of 5-11, but a sharp diminution is observed at pH values below 4. Furthermore, at lower pH values, hydronium ions (H_3O^+) successfully compete with strontium cations already uptaken by FREZEN. An extended "back-exchange" effect, characterized by fast kinetics, is thus observed.

In order to impede the diffusion and prevalence of H_3O^+ , a modification of the microporous space in FREZEN has been carried out via intercalation of suitable organic molecules. Work currently underway reveals that this approach is capable of improving the performance properties of the PILC. Experimental results with glycerol as the intercalated organic agent will be presented and discussed.

Key words: modified PILCs, radiostrontium, acid solution, glycerol

1 Introduction

The continuous demand for better nuclear waste management techniques as well as previous accidental massive releases of radioactivity, as e.g. the Chernobyl accident, have promoted over many years now the systematic study of natural and synthetic cation exchangers for scavenging radiocontaminants from diverse environments. Resins, clays, zeolites, crown ethers and biomaterials are just a few examples of the material classes which attract research

Table 1
Characteristics of FREZEN

| d_{001} (Å) | Specific surface area ($\text{mm}^2 \text{ g}^{-1}$) | Pore volume (cc g^{-1}) | Micropore (%) | Mesopore (%) | CEC (meq g^{-1}) |
|------------------|---|---------------------------------------|------------------|-----------------|--------------------------------|
| 16.7 | 218 | 0.16 | 28 | 72 | 0.65 |

interest with regard to applications responding to various radioecological needs [6].

In spite of considerable progress in this direction, the development of an effective and low cost antidote for removing radiostrontium from the gastrointestinal tract of sheep, cows and other mammals remains still elusive. The difficulty that occurs during such an application is related to the highly acidic ($\text{pH} < 3$) main stomach of all polygastric species. Although most typical cation exchangers are known to be effective in the pH range between 5 and 11, their performance is seriously decreased at lower pH values, since hydronium ions (H_3O^+) successfully compete with other cations for exchange sites.

The present study aims at the investigation of a novel class of materials, Pillared Layered Clays (PILCs), as a potential base material for developing an antidote. More specifically, this study addresses the question whether modified pillared layered clays might effectively scavenge Sr^{+2} cations from acidic aqueous solutions. The approach followed in this study employs the intercalation of suitable organic molecules in order to impede the diffusion and/or reactivity of hydronium ions in the microporous space of a pillared clay. Experimental results with glycerol as the intercalated organic agent will be presented and discussed.

2 Experimental procedure

2.1 Starting montmorillonite

The pillared clay used in this study, referred to as FREZEN, was prepared from a greek bentonite, kindly provided by Silver & Baryte Min. Co., Athens, Greece. A detailed description of the pillaring procedure is given in Appendix A. The structural characteristics of the final material, presented in Table 1, were determined using XRD spectroscopy and nitrogen adsorption-desorption isotherms. Strontium exchange isotherms at neutral pH (Fig. 1) yielded a cation exchange capacity (CEC) of 0.78 meq g^{-1} for the restored material.

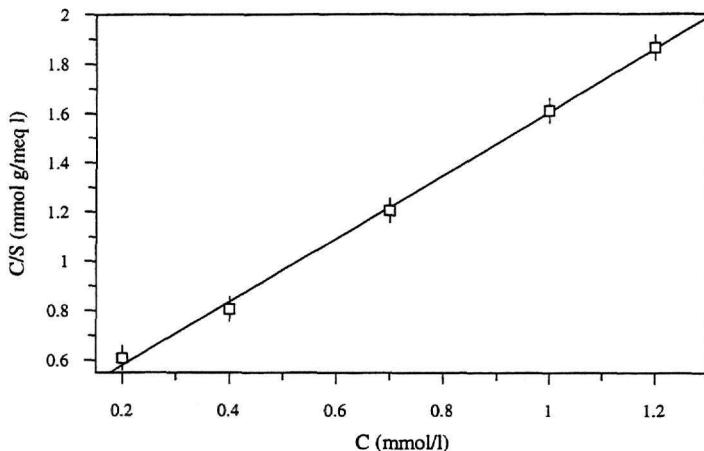


Fig. 1. A Langmuir type isotherm describing strontium uptake by FREZEN at neutral pH.

2.2 Uptake experiments

Strontium uptake was studied in batch experiments, by contacting PILC samples, under gentle stirring, with strontium solutions of known radioactivity. Strontium concentrations were obtained using SrCl_2 salt and ^{85}Sr as a radiotracer, while the pH values were adjusted by adding HCl or $\text{Sr}(\text{OH})_2$. Once equilibrium was reached (after *ca* 1 h), the two phases were separated by centrifugation and the radioactivity of the liquid was measured using a 22%-efficiency intrinsic Ge detector. The amount of strontium adsorbed by FREZEN was thus determined as

$$S = q \times \frac{V \times C_0}{m} \times \frac{R_i - R_f}{R_i} \quad (1)$$

where

- S = strontium concentration in PILC (meq g^{-1})
- V = volume of the adsorption solution (l)
- C_0 = initial strontium concentration in solution (mmol l^{-1})
- m = mass of adsorbent (g)
- q = oxidation number for Sr^{+2} ($= 2 \text{ meq mmol}^{-1}$)
- R_i = solution activity before contact with FREZEN
- R_f = solution activity after equilibrium was reached

2.3 Intercalation of glycerol

Two different ionic forms of FREZEN were prepared, by saturating the material with either Na^+ or Sr^{+2} ions. The labels Na-FREZEN and Sr-FREZEN refer to the corresponding samples. A 500 mg batch of each sample was contacted with 1 M and 10 M aqueous solutions of glycerol for 15 h. The modified samples were then separated by centrifugation, washed twice with deionized water and dried at 50 C. The final materials will be referred to as Na-FREZEN-glycerol and Sr-FREZEN-glycerol respectively.

Differential Thermal Analysis (DTA) of the glycerol-PILCs has been carried out using a TRDA3 -H Chyo Balance. The samples were heated in an air flow, from 25 C to 600 C at a rate of 4 C min^{-1} , using alumina as the inert substance.

3 Results and discussion

3.1 Strontium uptake from solutions of different pH values

The fraction of strontium adsorbed by FREZEN from solutions of various acidities is shown in Fig 2. In the pH range of 6-11, uptake is found to be

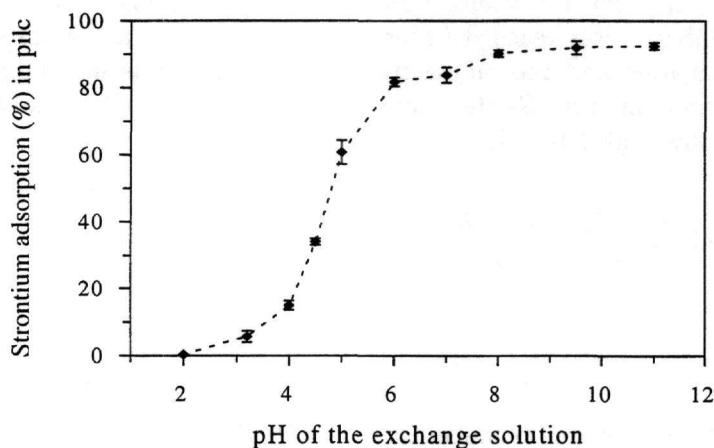


Fig. 1. Fraction (%) of strontium adsorbed by FREZEN from solutions of different pH values. $[\text{Sr}^{+2}] = 10^{-9}\text{N}$, 100 mg FREZEN.

sufficiently good, while a sharp decrease is observed at lower pH values and at pH below 3 the PILC shows practically no adsorption. Although PILCs like FREZEN exhibit a high selectivity for strontium over monovalent competitive

Table 1

Parameters K_L and Q derived from eqn (2) at several pH values

| pH | 3.5 | 4.0 | 5.0 | 7.0 | 8.5 |
|-------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| K_L (1 mmol $^{-1}$) | 7.32 \pm 0.69 | 7.73 \pm 1.10 | 6.01 \pm 1.84 | 3.94 \pm 0.39 | 5.51 \pm 2.54 |
| Q (meq g $^{-1}$) | 0.13 \pm 0.01 | 0.42 \pm 0.01 | 0.64 \pm 0.02 | 0.78 \pm 0.02 | 0.95 \pm 0.08 |

cations [5], H_3O^+ seems to be greatly preferred to the divalent Sr^{+2} . The cation exchange capacity of the material was studied at several pH values between 3 and 9 through Sr^{+2} exchange isotherms. A Langmuir type equation (Appendix B) of the form

$$\frac{C}{S} = \frac{1}{K_L Q} + \frac{1}{Q} C \quad (1)$$

was fitted to the experimental data, where

C = initial strontium concentration in the solution (mmol l $^{-1}$)
 S = strontium concentration in the adsorbent (meq g $^{-1}$),
calculated from eqn (1)
 K_L = distribution coefficient of the adsorbent (1 mmol $^{-1}$)
 Q = cation capacity of the adsorbent (meq g $^{-1}$)

The values of the parameters Q and K_L obtained from eqn (2) at each pH studied are given in Table 2. The distribution coefficient K_L is a measure of the binding strength of the adsorbed cation and is thus expected to be constant. The parameter Q , corresponding to the CEC of the material, is a measure

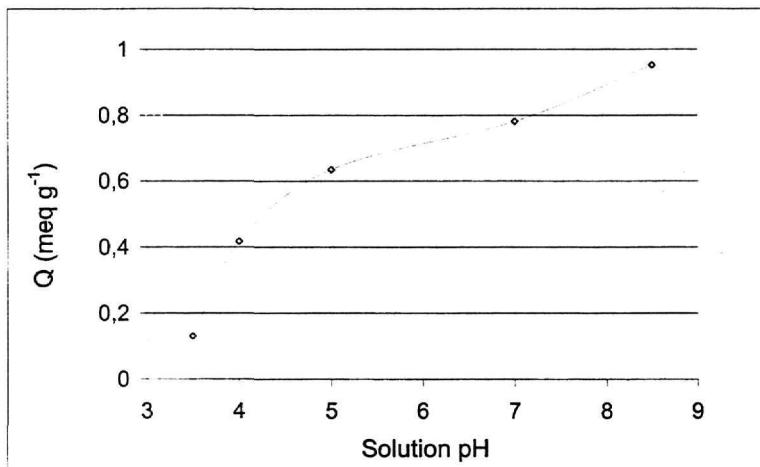


Fig. 2. The cation exchange capacity of FREZEN as a function of the solution pH.

of the negative sites on the PILC surface, which will attract the strontium cations. As shown in Fig 3, the CEC of FREZEN shows a smooth increase

from 0.78 meq g⁻¹ at neutral pH to 0.95 meq g⁻¹ at pH=8.5, whereas a steep decrease to 0.115 meq g⁻¹ is observed at pH=3.5.

3.2 Desorption of strontium in acidic solutions

The desorption of strontium cations in acidic solutions was also examined using the following procedure: the PILC was saturated with Sr⁺² in solution of pH=7 and the amount of Sr⁺² adsorbed was determined. The pH was then reduced to 3 by adding HCl and the amount of Sr⁺² desorbed was measured. These steps were chosen because they reproduce the pH sequence occurring in the digestive system of ruminants. As shown in Fig 4, a decrease in the pH of the uptake solution causes a back-exchange effect and strontium cations already uptaken by FREZEN are being replaced by hydronium ions. This desorption is practically complete at pH≈3 and is characterized by fast kinetics.

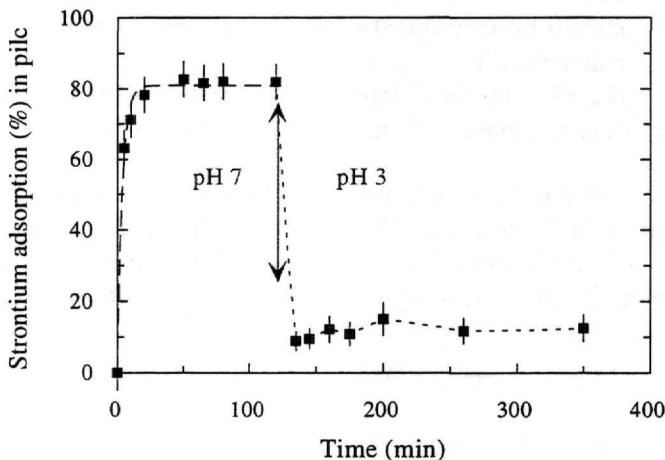


Fig. 3. Radiostrontium adsorption and desorption kinetics on FREZEN, at Sr⁺² concentration 10⁻⁹N.

In order to apply FREZEN as an antidote against radiostrontium contamination of ruminants, it is necessary to limit the back-exchange described above. For this purpose, a modification of the PILC is proposed, aiming to replace the water content of the interlayer by adequate organic molecules. Such a modification would hinder the mobility of hydronium ions and impose geometrical constraints to the strontium cations already present in the micropores, preventing their desorption. Glycerol, CH₂(OH)-CH(OH)-CH₂(OH), which is a tertiary alcohol known to be easily intercalated in montmorillonites even from dilute aqueous solutions, has been selected.

3.3 Strontium desorption from the modified PILC

The two-step procedure described above was also used to investigate the back-exchange of strontium from the glycerol-PILC. The pattern of strontium adsorption by the glycerol samples at neutral solutions was found to be identical to that of the pristine-PILC. However, desorption was found to be limited by the presence of glycerol in the interlayer and this effect seems to be influenced by the type of the exchangeable cation. More specifically, the amount of radiostrontium bound to the modified FREZEN increases if glycerol is intercalated in a Sr^{+2} -saturated instead of a Na^+ -saturated sample. In the former case, 17% of the radiostrontium uptaken is retained in the PILC when the pH is reduced to 3, compared to 11% in the latter case and 3% in the case of pristine-FREZEN (Fig 5).

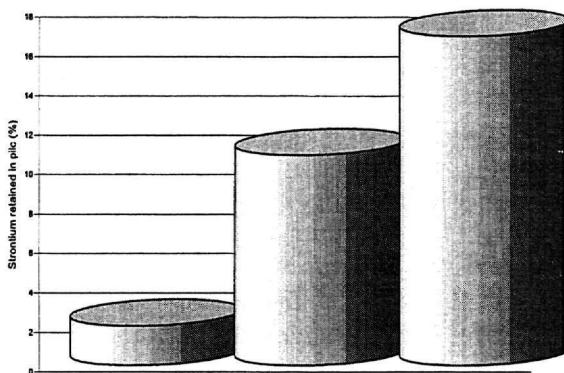


Fig. 4. Amount of strontium retained by the PILCs, after reducing the pH from 7 to 3, at $[\text{Sr}^{+2}] = 10^{-9} \text{N}$. 1:FREZEN; 2:Na-FREZEN-glycerol; 3:Sr-FREZEN-glycerol.

Many previous studies have focused on the factors influencing the adsorption of organic molecules by montmorillonites. It has generally been found that the adsorption of polar molecules, such as alcohols, involves electrostatic ion-dipole forces between the molecule and the saturating cation present in the interlayer [1, 2]. The adsorption of glycerol is therefore enhanced in the case of the divalent Sr^{+2} which has a larger charge density than the monovalent Na^+ .

The nature of glycerol bonding in the Na-FREZEN-glycerol and Sr-FREZEN-glycerol samples has also been investigated by the DTA technique. As shown in Fig 6, the two glycerol samples exhibit a similar endothermic peak from 50 to 100 C, which corresponds to loss of physi-sorbed water upon heating. At higher temperatures, the following trend is observed in the DTA diagrams of the two samples: i) in the Na-FREZEN-glycerol, a large endotherm appears between 120 and 320 C, which consists of two peaks, around 240 C and 320

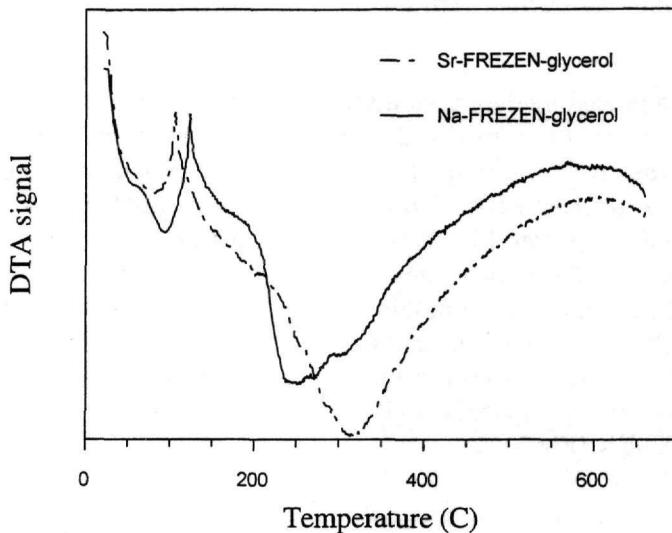


Fig. 5. DTA diagrams for the glycerol-modified PILCs.

C. The former peak can be attributed to the liberation of physically sorbed glycerol on the mesopores or external surfaces of the material, since it occurs at temperatures below the boiling point of glycerol (290 C). The latter peak results either from desorption or combustion of glycerol strongly bound in the micropores and around the Na^+ cations. ii) in the Sr-FREZEN-glycerol, an endotherm appears in the same temperature region as in the Na-FREZEN-glycerol sample. However in this sample, only the second peak centered around 320 C is observed.

These differences in the shape of the DTA curves indicate that glycerol is more readily removed from Na-FREZEN than Sr-FREZEN, which agrees well with the data presented by Brindley [3] in a study of the effect of heat on glycerol complexes with montmorillonite saturated with various cations. The alcohol is thus arranged in a more packed way around the Sr^{+2} cations, while it is more loosely bound around Na^+ cations. Consequently, the glycerol molecules inserted to the Sr-FREZEN sample offer a more efficient shielding of the strontium cations.

4 Conclusions

The uptake of strontium by the aluminum pillared montmorillonite used in this study has been found to depend on the hydronium concentration of the exchange solution. Experimental results presented here show that it is possible to inhibit strontium desorption from PILCs, caused when the pH of the

exchange solution is reduced. Although the inhibition is not complete, work in progress hints that it might be made more effective.

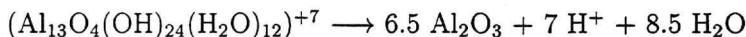
Acknowledgments

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Appendix A

The parent clay was a bentonite, containing a large amount (>80%) of montmorillonite. The cation exchange capacity of this starting material was 0.98 meq g⁻¹, as determined through strontium exchange isotherms.

The intercalant solution was prepared by adding dropwise and under vigorous stirring a 0.2M NaOH solution to a 0.2M AlCl₃ solution up to a ratio of Al/OH=1, while the temperature was kept at 70 C. The clay powder was immediately added to the intercalant solution and left to react for 1 hour under vigorous stirring, at 70 C. Once the exchange process was completed, the PILC precursor was repeatedly washed with deionized water, freeze-dried and calcined at 500 C for 4 h. During this latter step, the pillar precursor, which mainly consists of the Keggin ion (Al₁₃O₄(OH)₂₄(H₂O)₁₂)⁺⁷, is converted to aluminum oxide according to the reaction:



The protons liberated during this procedure cannot be readily replaced by other counterions and thus the CEC of the initial clay is heavily reduced at this step. A method has been applied to restore the CEC of the pillared sample [4], which included two steps:

- i) the PILC was first contacted with an ammonia atmosphere for 20 h. During this step the protons of the interlayer are converted to ammonium ions according to the reaction NH₃ + H⁺ \longrightarrow NH₄⁺.
- ii) the ammonium ions were then replaced by sodium ions by contacting the PILC with a NaCl water solution for 30 h. The pH during this step was adjusted to 10 by continuous addition of NaOH.

The final PILC was centrifuge washed with deionized water until Cl⁻ free and dried at 50 C for 15 h. The restored CEC was found to be 0.78 meq g⁻¹.

Appendix B

The Langmuir model was originally developed to represent chemisorption on a set of distinct localized adsorption sites and it is based on the following assumptions:

1. Molecules are adsorbed at a fixed number of well-defined localized sites.
2. Each site can hold one adsorbate species.
3. All sites are energetically equivalent.
4. There is no interaction between species adsorbed on neighbouring sites.

The general formula of the Langmuir equation describing the dynamic sorption of an ion by a porous medium is:

$$\frac{\partial S}{\partial t} = K_a C Q - K_b S (1 + K_L C) \quad (1)$$

In the state of equilibrium, the equation above reduces to the simple form:

$$S = \frac{K_L Q C}{1 + K_L C} \quad (2)$$

where

C = ion concentration in the solution (mol l^{-1}),

S = ion concentration in the media (mol g^{-1}),

K_L ($= K_a / K_b$) = distribution coefficient of the media (1 mol^{-1}) and

Q = ion capacity of the media (mol g^{-1}).

The last two parameters, K_L and Q , depend on the experimental conditions and can be determined by fitting eqn (4) to the experimental data.

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