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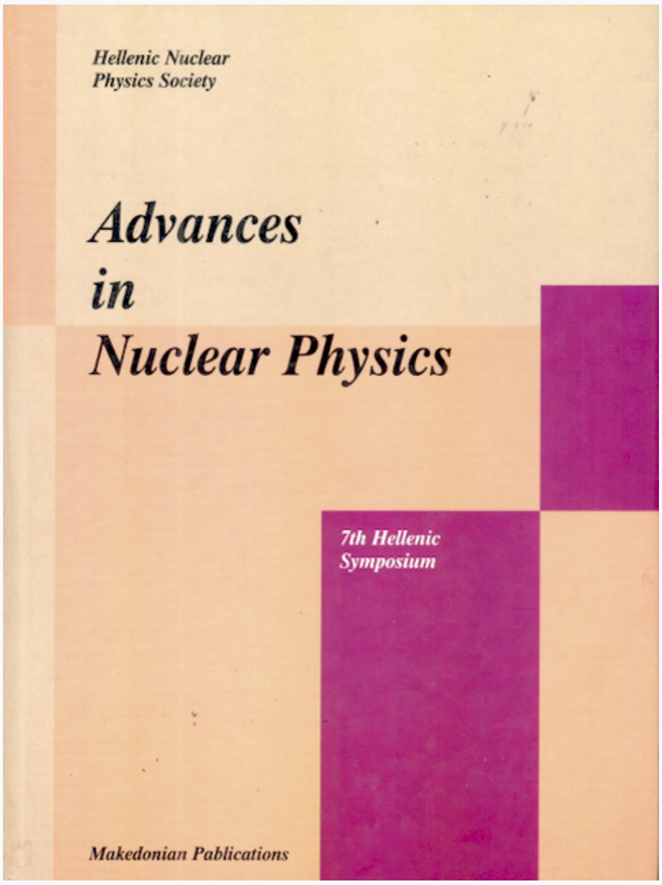

Nuclear Techniques in the Characterisation of Pillared Layered Clays

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Nuclear Techniques in the Characterisation of Pillared Layered Clays

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Abstract

The methods of PIGE and XRF were used to determine the variation of the elemental composition of an aluminum pillared montmorillonite during the material preparation while γ spectroscopy was used to find the extent and the kinetics of caesium and strontium uptake from aqueous solutions.

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1 Introduction

Pillared Layered Clays (PILCs) are a novel class of materials prepared by propping apart the lamellas of expandable layered clays with nano-size pillars of metal oxides and thus creating a two dimensional network of pores in the nm range [1]. The synthesis of PILCs follows basically a three step process. In the first step, a clay suspension is reacted with a solution containing cationic complexes of metals, as e.g. $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$ which by associating with the clay lamellas create flocs of the PILC precursor. In the second step, this precursor is separated from the liquid and the dried material is calcined at about 500° C. In this step, the polyoxo-cations are transformed to metal oxidic particles cross-linked to the clay lamellas and hydronium ions are liberated in the clay interlayer space. Thus, the cation exchange capacity (CEC) of the prepared PILC is substantially lower than that of the starting clay. In the final step, the CEC is restored by neutralising the hydronium ions with a base like NaOH or NH_4OH. This treatment actually replaces the hydronium ions with the easily exchangeable cations of Na^+ or NH_4^+.

Among other applications, PILCs are recently being tested as cation exchangers for the removal of hazardous or precious metals [2, 3]. The elemental composition, the cation exchange capacity (CEC) and the exchange kinetics are characteristic of the PILC material and crucial properties of merit for such an application.

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

Material	d_{001} (nm)	BET S (m^2 g^{-1})	V (cm^3 g^{-1})	Micro-pore	Meso-pore	Grain Size (μm)
AZA	1.82±0.02	220±10	0.06-0.08	≈100%		11%<23 50%>200
FRAZA	≈1.76	110±10	0.11±0.01	≈25%	≈75%	50%<23 100%<64

Proton Induced Gamma ray Emission (PIGE) has been established as a useful tool in the analysis of light elements (Z¡15) as it provides a fast and non-destructive analysis at the level of parts per million (ppm) [4]. Methods based in X-rays detection like Proton Induced X-ray Emission (PIXE) or X-Ray Fluorescence (XRF) become inappropriate in that mass region, because the energy of the K_a rays are very low and therefore not detectable. XRF analysis with the detection of the K_α and K_β X-rays is sensitive at the mass region Z¿19 [5]. Consequently, a combination of PIGE and XRF can provide reliable analysis accross the entire mass region.

In the present work, the methods of PIGE and XRF were used to determine the variation of the elemental composition during the Al-PILC preparation while typical gamma ray spectroscopy was used to find the kinetics and saturation level of caesium and strontium uptake from aqueous solutions.

2 Experimental Procedures

Two type of Al-PILCs coded AZA and FRAZA were used. The material AZA was a reference Al-PILC [6] while the material FRAZA was prepared from a Greek bentonite in its Na^+-form (Na-Zenith-N with a CEC of 0.90 meq g^{-1}) at the Nuclear Physics Laboratory (NPL) of the University of Ioannina. A detailed description of the preparation of FRAZA and the CEC restoration of FRAZA and AZA (samples FRAZA-D and AZA-D), is given elsewhere [3]. Structural data of the PILC materials are shown in Table 1. These data reveal that with respect to the spatial organization of the clay lamellas, the Al-PILCs differed both at mm- as well as at μm-scales. Furthermore, FRAZA was a very fine grained material with substantial mesoporosity. In contrast, AZA was a coarse grained and an essentially microporous material [3].

PIGE and XRF elemental analysis of FRAZA was performed at the Institute of Nuclear Physics (INP) at the NCSR "Demokritos" and the NPL of the

University of Ioannina. In PIGE, the 5.5 MeV TANDEM accelerator of the INP was used for the determination of the light elements Al, Si, Mg and Na . A proton beam was utilised at energy E_p=4.0 MeV and the characteristic gamma-rays emitted from the deexcitation of the nuclei ^{27}Al, ^{28}Si, ^{25}Mg and ^{23}Na following (p,p'γ) reactions, were detected. The samples, in the form of pellets, were dried at temperature 200°C before bombardment. Typically, the accumulatde charge for each measurement was 50 μC and the duration 20-30 min. For the normalisation of the efficiency, pellets of known composition were used as standards for each element under investigation.

In the XRF analysis, radiosources of ^{109}Cd (22.1 keV) and ^{241}Am (59 keV) were used for the analysis of elements with Z¿19. The composition was determined via the code COAL [7]. The Al+Si concentration was determined from the intensity of the Rayleigh scattering peak in the ^{241}Am excited spectrum and was found to overlap with the PIGE measurements. Elemental analysis was conducted in samples of the three steps of FRAZA preparation, namely the initial clay (Na-Zenith-N), after calcination (FRAZA) and after CEC restoration (FRAZA-D).

Exchange isotherms and kinetics were conducted at the Nuclear Physics Laboratory of the University of Ioannina with radiotracer methods. A conventional batch technique was used in the exchange isotherms in which a known amount of PILC was contacted with a solution containing chloride salts of Sr^{2+} or Cs^{+} traced with ^{85}Sr or ^{137}Cs respectively. After attaining equilibrium the two phases were separated by centrifugation and the supernatant was measured for γ activity. A similar method was used in the study of exchange kinetics where the two phases were separated by a dialysis tube that contained the solid phase and which was periodically removed for monitoring the solution's γ activity. The kinetics were performed under static or dynamic experimental conditions. The later were produced by a small magnet that was placed inside the tube and was gently stirred. The percentage of strontium or caesium adsorbed by the Al-PILCs was found as the ratio of the difference between initial and final activity to initial activity. All activity measurements were performed with a 22% efficiency, intrinsic Ge detector. In all radiostrontium measurements, the activity was corrected for natural radioactive decay.

3 Results and Discussion

The elemental analysis data during the preparation steps of FRAZA-D are shown in Table 2. The structural formulae derived from the elemental composition and according to the method described by Van Olphen [8], were:

- Na-Zenith-N: ¡$Na_{0.81}K_{0.16}Ca_{0.019}$¿$[Si_{7.75}Al_{0.25}]\{Al_{3.14}Mg_{0.75}Fe_{0.05}Ti_{0.06}\}O_{20}(OH)_4$ $+ 0.14SiO_2 + 0.08Fe_2O_3$ (outer oxides)
- FRAZA: ≈ ¡$Na_{0.036}K_{0.18}Ca_{0.018}$¿$[Si_{7.75}Al_{0.25}]\{Al_{3.22}Mg_{0.67}Fe_{0.05}Ti_{0.06}\}O_{22} + 2(H_2O)$ $+ 0.08Fe_2O_3$ (outer oxides) $+ 0.49Al_2O_3$ (pillars)
- FRAZA-D: ≈ ¡$Na_{0.66}K_{0.18}Ca_{0.018}$¿$[Si_{7.75}Al_{0.25}]\{Al_{3.26}Mg_{0.63}Fe_{0.05}Ti_{0.06}\}O_{22} + 2(H_2O)$ $+ 0.08Fe_2O_3$ (outer oxides) $+ 0.49Al_2O_3$ (pillars)

Table 2
Elemental analysis of the initial clay (Zenith-N), the pillared clay FRAZA and the pillared with restored CEC (FRAZA-D).

Element	Zenith-N	FRAZA	FRAZA-D
		Weight %	
Si[1]	25.89	24.06	24.04
Al[1]	10.42	14.43	14.07
Fe[2]	1.84	2.01	2.12
Ca[2]	0.08	0.08	0.08
Mg[1]	2.02	1.80	1.63
K[2]	0.47	0.78	0.78
Na[1]	2.05	0.09	1.68
Ti[2]	0.29	0.33	0.33

[1]PIGE [2]XRF

In Table 2, the percentage weight of Al increased after the pillaring due to the intercalation of aluminum pillars in the interlammelar space. In contrast, the percentage weight of the structural Mg in Na-Zenith-N, reduced in FRAZA and FRAZA-D as a result of the molecular weight increase. This reduction is characteristic in the pillaring process [9]. The percentage weight of the interlayer Na$^+$ which is the exchangeable cation contributing mainly to the CEC, was dramatically reduced up to 95% in FRAZA and was restored up to 80% in FRAZA-D. This restoration is schematically depicted in Fig. 1 through the variation of the peak 440 keV of ^{23}Na in the three samples.

This deficit in the CEC restoration may be due to the presence of hydronium ions remaining in the pillared structure that cannot be removed either by NH_3 or NaOH and/or to the charge carried by the pillars. Indeed, by converting the weight percentages to equivalent concentrations (meq/g-material), one finds that the sum of the exchangeable cations Na$^+$, K$^+$ and Ca^{2+} is 1.11 meq g^{-1} for the initial clay Na-Zenith-N and 0.96 meq g^{-1} for FRAZA-D. This means that the pillars in FRAZA-D still carry a positive charge of about 0.15 meq g^{-1}.

The dependence of Sr^{2+} or Cs^{+} exchange on the initial concentration was studied on both FRAZA-D and AZA-D. These exchange isotherms were of the Langmuir type and an equation of the form

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

was fitted to the experimental data (Fig. 2). In eq. (1), C is the cation concentration in the solution at equilibrium (mmol L^{-1}), S the concentration in the material (mmol g^{-1}), Q the material capacity and K_L the distribution coefficient which characterises the binding strength of the adsorbed cations. The results of the fits are given in Table 3. The values of the parameters Q were around 0.70 meq g^{-1} and confirmed the 80% CEC restoration of the initial clay (Na-Zenith-N) that was observed in the elemental analysis. The higher values of parameter K_L for FRAZA-D over AZA-D and for Sr^{2+} over Cs^{+} indicated a stronger binding of strontium in material FRAZA-D.

Table 3
Langmuir parameters for Sr or Cs uptake by FRAZA-D or AZA-D.

Parameters	Sr-FRAZA-D	Sr-AZA-D	Cs-FRAZA-D	Cs-AZA-D
Q (meq g^{-1})	0.70±0.03	0.73±0.05	0.69±0.03	0.71±0.04
K_L (L meq^{-1})	7.9±1.1	2.7±0.3	4.2±0.3	2.5±0.2

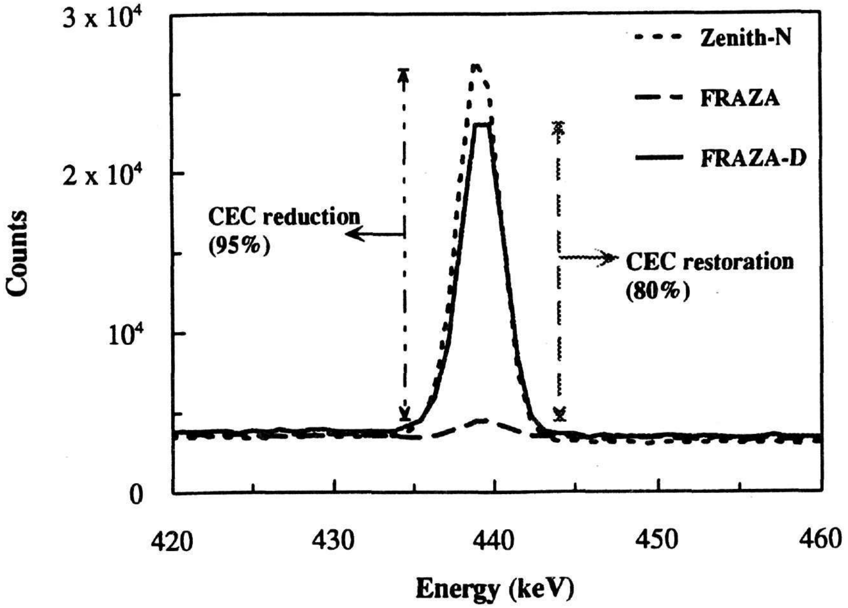

Fig.1 Characteristic peak of ^{23}Na in PIGE of the initial clay (Na-Zentih-N), the pillared FRAZA and the sample with restored CEC (FRAZA-D).

Strontium or caesium exchange kinetic measurements were conducted for the materials AZA-D and FRAZA-D under both static or dynamic experimental conditions. Typical strontium exchange kinetics are presented in Fig. 3. In this figure, the cation adsorbed in the PILC material (S) was determined as

$$S = C_o \cdot f \cdot \frac{V}{m} \tag{2}$$

where C_o is the initial equivalent concentration in the solution (meq L^{-1}), V the solution volume (L), m the PILC mass (g) and f the fractional uptake defined from the radioactivity in the solution as

$$f = \frac{ACT_{INI} - ACT_t}{ACT_{INI}} \tag{3}$$

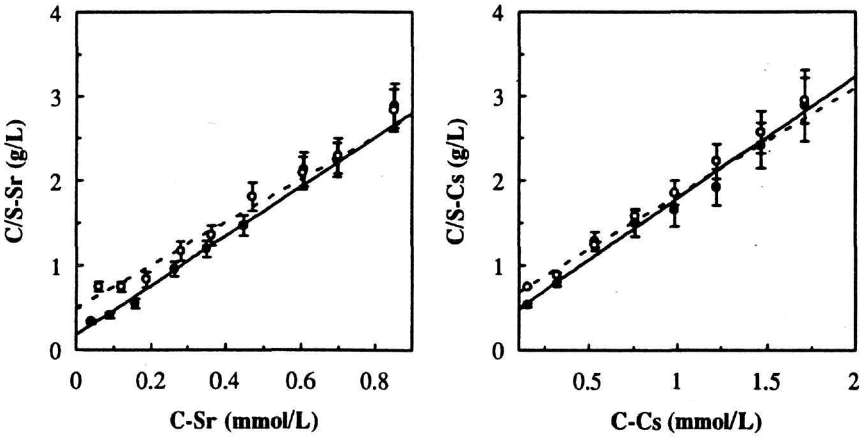

Fig.2 Langmuir type isotherms of Sr^{2+} and Cs^+ in materials FRAZA-D (black symbols, solid lines) and AZA-D (open symbols, dashed lines).

The kinetics were analysed through the laws of isotopic exchange [10]. The rate determining step was the film diffusion in kinetics under static conditions and the particle diffusion under dynamic conditions. The experimental data were fitted with a first order kinetic equation of the form

$$S = S(\infty)[1 - \exp(-Rt)] \tag{4}$$

where R is the rate of uptake.

As seen in Fig. 3, the strontium exchange kinetics were faster in FRAZA-D than in AZA-D in the static conditions of the time scale of hours as a result of the different macroscopic grain size of the two materials. In the dynamic conditions of the time scale of minutes, the strontium kinetics were faster in

FRAZA-D than in AZA-D as a result of the substantial mesoporosity that the material FRAZA-D possessed. The kinetic isotherms for caesium were similar to those for strontium but the rate was even higher than in the case of the latter cation under the dynamic conditions. This behavior was attributed to the smaller hydrated radius of the caesium ion, which leads to a faster accessibility of the exchange sites. However, the difference in the rate and the total time of caesium uptake for the two materials still remained.

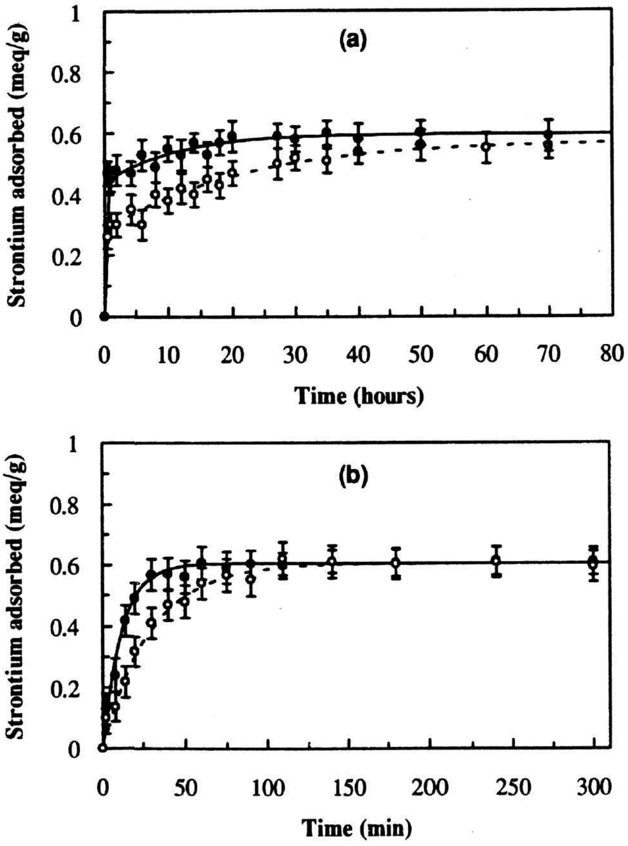

Fig.3 Sr^{2+} exchange kinetics on FRAZA-D (black circles, solid curves) and AZA-D (open circles, dashed curves) under (a) static and (b) dynamic experimental conditions.

4 Conclusion

In this work, the methods of PIGE and XRF were used to study the variation of the elemental composition of a PILC material during its steps of preparation. Moreover, the CEC, a crucial property for the characterisation of a cation exchanger, was monitored through the preparation. Also, the charge carried by the pillars after the CEC restoration which is a critical quantity of the pillaring process, was estimated. The use of radiotracers of ^{137}Cs and ^{85}Sr in caesium or strontium kinetics lead to the recognition and understanding of the principal factors controlling the diffusion of typical ions inside the pores of PILCs.

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