Journal of Radioanalytical and Nuclear Chemistry, Vol. 242, No. 1 (1999) 3–9

Characterization of an aluminum pillared montmorillonite with cation exchange properties

D. T. Karamanis,* X. A. Aslanoglou, P. A. Assimakopoulos, N. H. Gangas

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

(Received December 1, 1998)

The methods of PIGE and XRF were used to determine the elemental composition and the structural formulae of a specially tailored PILC material during the steps of its preparation. The CEC, a crucial property for the characterization of a cation exchanger, was monitored through all stages of preparation. In addition, the charge carried by the pillars, a critical quantity of the pillaring process, was estimated. Exchange isotherms of strontium and cesium were performed through the use of radiotracers' exchange isotherms of ^{137}Cs and ^{85}Sr with typical γ-ray spectroscopy. These isotherms were of the Langmuir type and PILCs adsorption capacity was determined. The latter property was compared with the CEC determined by the elemental analysis and was found equal to the amount of the exchangeable interlamellar sodium ions.

Introduction

Pillared layered clays (PILCs) are a novel class of nano-composite materials prepared by propping apart the lamellas of expandable layered clays with nano-size pillars of metal oxides.[1] They have very interesting features such as the complementary zeolite-like network of pores with adjustable size pores in the nm range, high thermal stability, high specific surface area and high stability with respect to ionic concentration of complex environments.

PILCs are usually synthesised as follows: initially, a clay suspension in its Na-form is reacted with a solution containing cationic complexes of metals, e.g., $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. In a second step, the clay with the adsorbed polyoxo-cations is separated from the liquid and the dried material is calcined at about 500 °C. In this step, the complexes are transformed to metal oxidic particles cross-linked to the clay lamellas and hydronium ions are liberated in the clay interlayer space. Although the resulting material has been scaled up for several proposed applications such as catalysts, selective sorbents, membranes etc., the cation exchange capacity (CEC) of the starting clay is highly reduced in the prepared PILC. A further preparation step is thus needed in order to restore the PILC's CEC.

Hydrothermal treatment of the PILC[2] or treatment with a base, like NH_4OH or NaOH[3], have been proposed and employed for the restoration of PILCs' CEC. Hence, this type of cation exchangers with restored CEC is very promising for the separation of hazardous radionuclides and metals from complex environments, as e.g., in the treatment of nuclear wastes or in the digestive tract of animals and humans. Obviously, the elemental composition and the accurate and precise CEC variation during the material preparation are very important in the PILCs' prospect as cation exchangers.

Analytical techniques based on the detection of either γ-rays or X-rays have been widely used in the past for the determination of both bulk and trace elements.[4] Methods based on the detection of X-ray fluorescence (XRF) and proton induced X-ray emission (PIXE) are used for the determination of heavy elements ($Z > 17$). X-rays corresponding to light elements have low energy and are absorbed by air or by the window of the detector and this fact makes these elements "invisible" to XRF or PIXE. Detection of γ-rays emitted by nuclear reactions after bombardment with proton induced gamma ray emission (PIGE) has been used in the past for the determination of light elements in a variety of materials.[5–9] Consequently, a combination of PIGE and XRF can provide a non-destructive, fast, clear, accurate and reliable analysis across the entire atomic number region relevant for clays and PILCs. The merits of these analytical tools versus conventional wet chemical analysis and methods as inductively coupled plasma (ICP) with digestion of the solid sample are evident.

In the present work, the methods of PIGE and XRF were used to determine the variation of the elemental composition during the preparation of a specially tailored Al-PILC with restored CEC while γ-ray spectroscopy was used to find the adsorption capacity of cesium and strontium uptake from aqueous solutions.

Experimental

An aluminium pillared montmorillonite coded FRAZA, was prepared from a starting commercial Greek bentonite in its Na^+-form with a CEC of 0.90 $meq \cdot g^{-1}$ (Na-ZENITH-N). The CEC was restored by first exposing the prepared FRAZA in an NH_3 atmosphere and then contacting the degassed sample with a sodium alkaline solution. A detailed description of the methods

---

* E-mail: dkaramanis@cc.uoi.gr

0236–5731/99/USD 17.00

Elsevier Science B. V., Amsterdam
Akadémiai Kiadó, Budapest

Table 1. Materials' data for the PILC coded FRAZA[3]

Material	d_{001}, nm	BET S, m^2/g	Pore volume, cm^3/g	Micropore, %	Mesopore, %	Grain size
FRAZA	≈1.76	110 ± 10	0.11 ± 0.01	≈25	≈75	70% <45 μm; 100% <63 μm

used for FRAZA preparation and the restoration of its CEC (sample FRAZA-D) are given elsewhere.[3] The material's data, shown in Table 1, reveal that FRAZA is a very fine-grained material with substantial mesoporosity.

PIGE and XRF elemental analysis of FRAZA was performed at the Institute of Nuclear Physics (INP) at the National Center for Scientific Research (NCRS) "Demokritos" in Athens, Greece and the Nuclear Physics Laboratory (NPL) of the University of Ioannina, Greece. The PIGE measurements were performed using the 5.5 MV terminal Voltage TN11 TANDEM accelerator of the INP. The purpose of these measurements was the determination of light elements as Al, Si, Mg and Na. A proton beam with energy $E_p = 4.0$ MeV was used and the γ-rays emitted from the deexcitation of the residual nuclei following (p,p'γ) reactions, were detected. The γ-rays monitored were the $E_\gamma = 1014$ keV of ^{27}Al, $E_\gamma = 1179$ keV of ^{28}Si, $E_\gamma = 585$ keV of ^{25}Mg and $E_\gamma = 440$ keV of ^{23}Na. The samples, in the form of pellets, were dried for an hour at temperature 200 °C before bombardment. The beam was directed to the target via a set of two collimators of 4-mm diameter. Typically, the accumulated charge for each measurement was 50 μC during 20–30 min bombardment. The detector used was an intrinsic Ge γ-ray detector placed at an angle 90° with respect to the beam, to avoid line broadening due to Doppler effect. The resolution of the detector was 1.9 keV at the 1333 keV γ-ray lines. The target was placed at an angle of 45° with respect to the beam and was cooled to 10 °C to withstand high beam currents. An electric potential of 300 Volts was set on the target for electron suppression in order to assure accurate beam current measurement. For the normalisation and the extraction of quantitative results, pellets of powder graphite and cellulose containing less than 10% of the element under determination were used as standards.

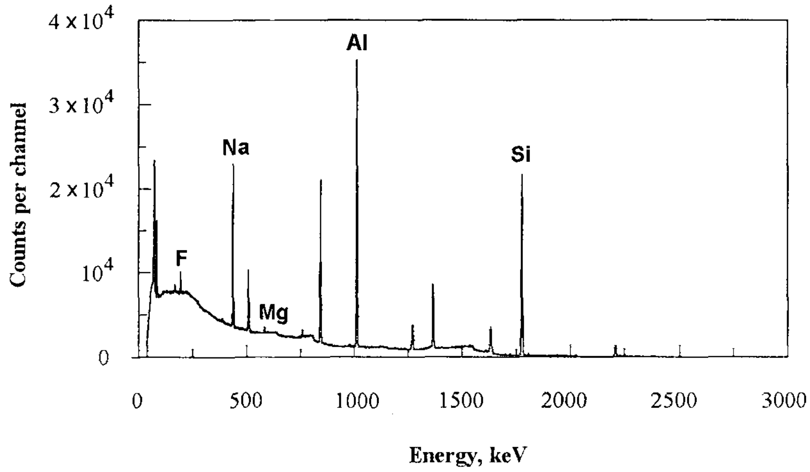

Fig. 1. Gamma-ray spectrum of FRAZA-D after bombardment with protons of $E_p = 4$ MeV. The peaks used for the elemental analysis of the PIGE method are noted

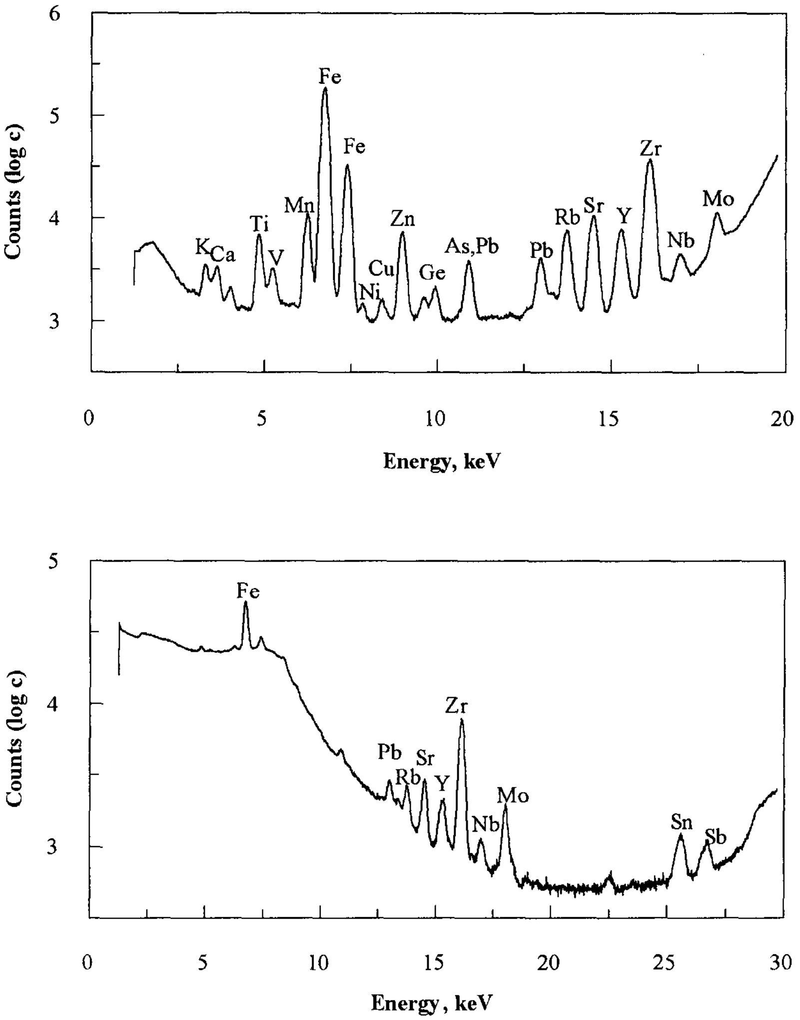

Fig. 2. X-ray spectrum of FRAZA-D after irradiation with a ^{109}Cd source (a) and with an ^{241}Am source (b). The peaks used for the elemental analysis of the XRF method are noted

In the XRF measurements, a vertical Si(Li) detector with a Be window of 25 μm was used. The resolution of the system was 180 eV at the 5.9 KeV line of Mn. The exciting radiation was provided by a ring shaped radioisotope source housed in a cylindrical container and shielded from the detector. A 5 mCi ^{109}Cd source emitting Ag X-rays (22 keV) and a 20 mCi ^{241}Am source emitting 60 keV X-rays were used. The sample, in the form of a pellet of diameter 2.5 cm and carrying 1 g of material, was placed at the top of the assembly in a π geometry. Induced X-rays reach the detector through a small hole in the shielding material. The sensitivity of the system for various elements was determined experimentally using monatomic targets of known thickness evaporated on kapton.

XRF and PIGE elemental analyses were conducted at the main stages of the PILC preparation, namely in the starting clay (Na-Zenith-N), after calcination (FRAZA) and after CEC restoration (FRAZA-D). Typical PIGE and XRF spectra for FRAZA-D are shown in Figs 1 and 2, respectively.

Exchange isotherms were determined at the Nuclear Physics Laboratory of the University of Ioannina with radiotracer methods. The conventional batch technique was used in which a known amount of FRAZA-D was contacted with a solution containing chloride salts of Sr^{2+} or Cs^{+} traced with ^{85}Sr or ^{137}Cs, respectively. Typical contact times needed for equilibrium were about 20 hours (Fig. 3). After attaining equilibrium, the two phases were separated by centrifugation and the supernatant was measured for γ-activity. All activity measurements were performed with a 22% efficiency, intrinsic Ge detector, shielded with lead for the isolation of external background radiation. In all radiostrontium measurements, the activity was corrected for natural radioactive decay.

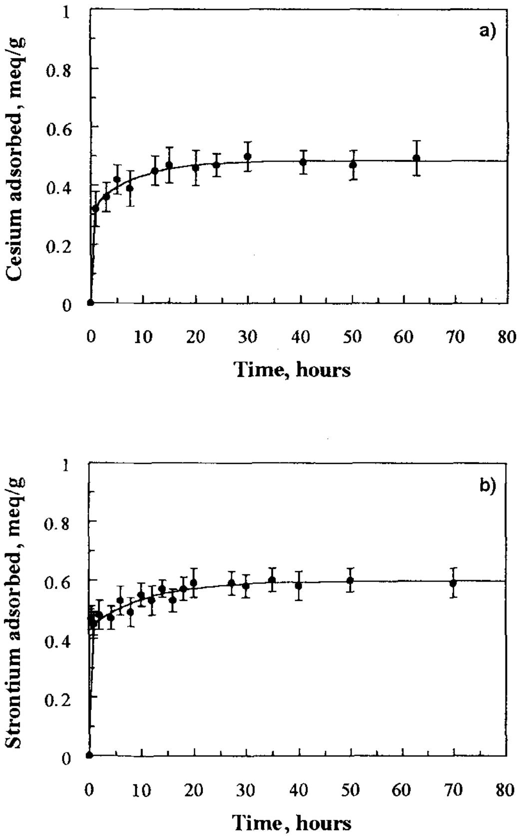

Fig. 3. Exchange kinetics on FRAZA-D of Cs^+ at a concentration of $1.0 \cdot 10^{-3}$M and pH ≈ 6.00 (a) and Sr^{2+} at a concentration of $0.5 \cdot 10^{-3}$M and pH ≈ 6.00 (b)

Results and discussion

The concentration of element *i* in the PIGE measurements was determined from the concentration in the reference material as:

$$C_i = C_{re}\frac{Y_i S_i}{Y_{re} S_{re}} \qquad (1)$$

where C_i and C_{re} are the concentrations of the sample and the reference pellet, Y_i and Y_{re} the yield of the sample and the reference pellet and S_i and S_{re} the corresponding stopping powers. The stopping power was calculated at the energy $E_{1/2}$ at which the yield of the nuclear reaction drops to one half. The energy $E_{1/2}$ for each element was determined from the work of SAVIDOU et al.[10] while the stopping powers used were calculated through the Ziegler-Biersack-Littmar coefficients.[11]

In the XRF method, a major difficulty is the presence of light elements as Al and Si in the bulk, which are "invisible" for X-ray measurements. To address this problem several techniques have been developed based on the monitoring of the coherent scattering of the incident radiation.[12–14] In the present case, the sum of Al and Si concentrations was determined from the intensity of the coherent scattering of the 60 keV X-ray from ^{241}Am. Because of their mass and concentrations, these elements contribute the most in the formation of the coherent peak. The contribution of heavier and thus observed elements was calculated and subtracted from the coherent scattering. The elements Al, Si, K, Ca, Ti and Fe were assumed to be present in the form of the corresponding oxides. The calculations of the composition were performed using the computer code XRF.[15] In this calculation, an iteration procedure was followed. An initial composition corresponding to the relative experimental counting rate was assumed and the absorption coefficients were calculated for the incoming and induced radiation. Then, a newer more correct composition was calculated leading to a different set of absorption coefficients and a more correct composition etc. The calculation ends when the results are stable at the level of 1%. The overall error due to the uncertainly of the absorption coefficient etc., is 5%.

The elemental analysis data of the starting clay, the pillared clay FRAZA and pillared clay with restored CEC (FRAZA-D) are shown in Table 2. Furthermore, the structural formulae of the samples can be estimated from the elemental composition according to the method described by VAN OLPHEN[16] and under the assumption that the amounts of tetrahedral silicon and aluminum as well as of octahedral iron* are the same in the three samples. In this way, the following structural formulae were derived:**

$$\begin{gathered}\text{Na-Zenith-N}: \langle Na_{0.81}K_{0.16}Ca_{0.019}\rangle \\ [Si_{7.75}Al_{0.25}]\{Al_{3.14}Mg_{0.75}Fe_{0.05}Ti_{0.06}\}O_{20}(OH)_4 + \\ + 0.14SiO_2 + 0.08Fe_2O_3 \text{ (outer oxides)}\end{gathered}$$

$$\begin{gathered}\text{FRAZA}: \approx \langle Na_{0.036}K_{0.18}Ca_{0.018}\rangle \\ [Si_{7.75}Al_{0.25}]\{Al_{3.22}Mg_{0.67}Fe_{0.05}Ti_{0.06}\}O_{22}+ \\ +2(H_2O) + 0.08Fe_2O_3 \text{ (outer oxides)} + \\ + \langle 0.49Al_2O_3 \rangle \text{ (pillars)}\end{gathered}$$

$$\begin{gathered}\text{FRAZA-D}: \approx \langle Na_{0.66}K_{0.18}Ca_{0.018}\rangle \\ [Si_{7.75}Al_{0.25}]\{Al_{3.26}Mg_{0.63}Fe_{0.05}Ti_{0.06}\}O_{22} + \\ + 2(H_2O) + 0.08Fe_2O_3 \text{ (outer oxides)} + \\ + \langle 0.49Al_2O_3 \rangle \text{(pillars)}\end{gathered}$$

In order to trail in some detail the changes in the elemental composition during the PILC preparation, the data of Table 2 were transformed into the number of atoms of each element per 100 atomic mass units, i.e., as atom % (Table 3). As shown in Table 3, the percentage of silicon was practically constant in the three samples.

---

* The amount of iron in the structure of Na-ZENITH-N was taken constant according to the value reported at the Final Report for Contract No. BRE2-063 where the authors had performed Mössbauer Spectroscopy. The rest was attributed to clay impurities.

** Symbols: < > denote the exchangeable cations, [ ] the tetrahedra and { } the octahedra.

Table 2. Elemental composition (in wt.%) of the starting clay (Na-Zenith-N), the pillared clay FRAZA and the pillared clay with restored CEC (FRAZA-D)

Element	Na-Zenith-N	FRAZA	FRAZA-D
Si[1]	25.89 ± 0.26	24.06 ± 0.24	24.04 ± 0.24
Al[1]	10.42 ± 0.10	14.43 ± 0.14	14.07 ± 0.14
Fe[2]	1.84 ± 0.09	2.01 ± 0.10	2.12 ± 0.11
Ca[2]	0.080 ± 0.003	0.080 ± 0.004	0.080 ± 0.004
Mg[1]	2.02 ± 0.20	1.80 ± 0.18	1.63 ± 0.16
K[2]	0.47 ± 0.02	0.78 ± 0.04	0.78 ± 0.04
Na[1]	2.05 ± 0.04	0.090 ± 0.002	1.68 ± 0.03
Ti[2]	0.29 ± 0.01	0.33 ± 0.02	0.33 ± 0.02

[1] PIGE.
[2] XRF.

Table 3. Elemental composition (in atom%) of the starting clay (Na-Zenith-N), the pillared clay FRAZA and the pillared clay with restored CEC (FRAZA-D)

Element	Na-Zenith-N	FRAZA	FRAZA-D
Si	0.922 ± 0.009	0.857 ± 0.008	0.856 ± 0.008
Al	0.371 ± 0.004	0.514 ± 0.005	0.501 ± 0.005
Fe	0.033 ± 0.001	0.036 ± 0.002	0.038 ± 0.002
Ca	0.0020 ± 0.0001	0.0020 ± 0.0001	0.0021 ± 0.0001
Mg	0.083 ± 0.008	0.074 ± 0.007	0.067 ± 0.003
K	0.012 ± 0.001	0.020 ± 0.001	0.020 ± 0.001
Na	0.089 ± 0.002	0.0039 ± 0.0001	0.073 ± 0.001
Ti	0.0063 ± 0.0002	0.0068 ± 0.0004	0.0067 ± 0.0004

This finding is consistent with the fact that silicon is a major clay constituent and its composition is not influenced by the intercalation process. The amount of Al increased after pillaring due to the intercalation of aluminium pillars in the interlamellar space. In contrast, iron, titanium and calcium were practically constant in all the samples. The amount of Mg in Na-Zenith-N diminished in FRAZA and FRAZA-D although its measurement had an error of about 10% due to the low cross section of the reaction $^{25}\mathrm{Mg}(p,p'\gamma)^{25}\mathrm{Mg}$ and the large background underneath the $E_\gamma = 585$ keV line. Table 3 shows an increase in the amount of potassium between clay FRAZA to FRAZA-D. This increase can be explained by the presence of potassium impurities in the sodium compounds and water used in the preparation and treatment of this PILC. A concomitant explanation is that potassium is not easily exchanged because of its known locking in 2:1 clay structures.[17] Therefore, the CEC practically available for Sr^{2+} or Cs^{+} uptake is only related to exchangeable sodium interlayer ions. The amount of the interlayer Na^{+} is dramatically reduced up to 95% in FRAZA as a result of its exchange by the poly-oxocations of the pillaring solution. Furthermore, the amount of sodium ions is restored up to 80% in FRAZA-D. This restoration is schematically depicted in Fig. 4 through the variation of the 440 keV peak of $^{23}\mathrm{Na}$ in the three samples. The deficit of 20% in the CEC after restoration may be due to the presence of hydronium ions still remaining in the pillared structure. Another explanation is that all or part of this CEC deficit is due to the charge carried by the pillars. Indeed, by assuming that Na^{+}, K^{+} and Ca^{2+} are the only exchangeable cations and by converting the weight percentages to equivalent concentrations (meq·g^{-1} of material), one finds that the sum for the equivalent concentrations of Na^{+}, K^{+} and Ca^{2+} is 1.05 meq·g^{-1} for the starting clay Na-Zenith-N, while the corresponding sum for FRAZA-D is only 0.96 meq·g^{-1}. This means that the pillars in FRAZA-D might still carry a positive charge of up to 0.09 meq·g^{-1}.

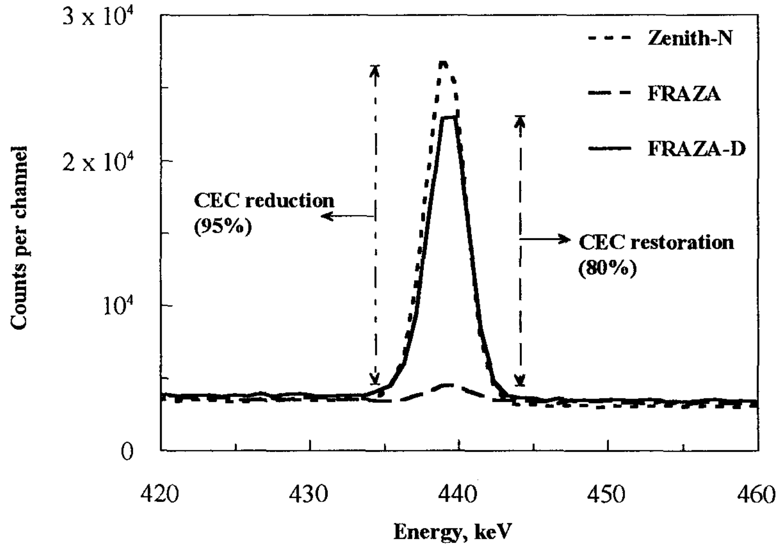

Fig. 4. Characteristic peak of $^{23}\mathrm{Na}$ by PIGE in the starting clay (Na-Zenith-N), the pillared FRAZA and the sample with restored CEC (FRAZA-D)

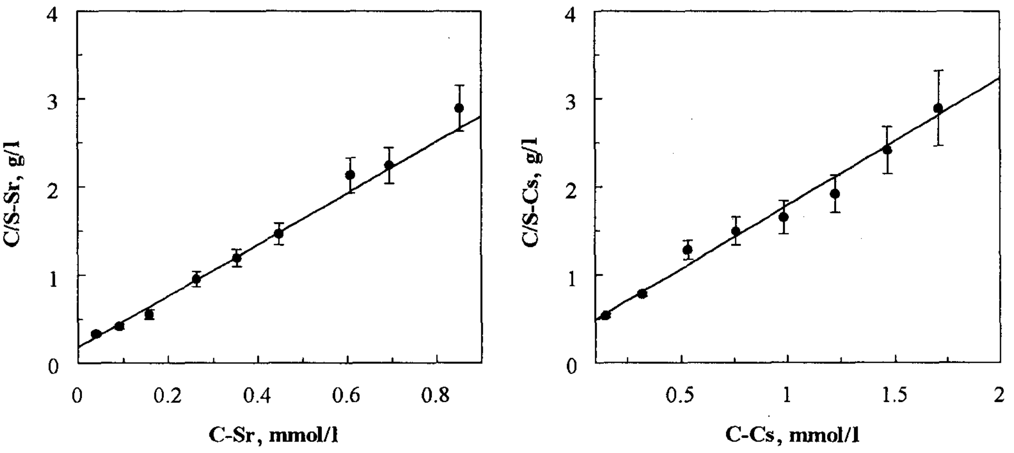

Fig. 5. Langmuir type isotherms of Sr^{2+} and Cs^{+} in material FRAZA-D

Table 4. Langmuir parameters for Sr or Cs uptake in FRAZA-D or AZA-D

Parameter	Sr-FRAZA-D	Cs-FRAZA-D
Q, mmol·g^{-1}	0.34 ± 0.02	0.69 ± 0.03
K_L, l·mmol^{-1}	16.1 ± 2.7	4.2 ± 0.3

The above CEC deficit was further investigated through Sr^{2+} or Cs^{+} exchange isotherms. These isotherms were of the Langmuir type and an equation of the form

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

was fitted to the experimental data (Fig. 5). In Eq. (2), C is the cation concentration in the solution at equilibrium (mmol·l^{-1}), S is the concentration in the material (mmol·g^{-1}), Q is the material capacity and K_L is the distribution coefficient that characterises the binding strength of the adsorbed cations. The results of the fits are given in Table 4. The values of parameters Q were around 0.70 meq·g^{-1} and confirmed the results of the elemental analysis. Furthermore, the post-exchange capacity of the pillared samples was less than the exchange capacity of the original clay (0.90 meq·g^{-1}). This capacity can be attributed entirely to the interlayer sodium ions. The higher values of parameter K_L for Sr^{2+} uptake on FRAZA-D over Cs^{+} indicated a stronger binding of strontium in material FRAZA-D. This finding can be attributed to the electro-selectivity of the bivalent strontium in the special geometrical constraints of the PILC.

Conclusions

This work provided direct evidence that the methods of PIGE and XRF can be used as an analytical tool for the elemental analysis of the abovementioned clays. Furthermore, the application of the above techniques in a specially tailored pillared montmorillonite determined the elemental composition and the CEC variation during the steps of its preparation. It was found that the CEC of the pillared sample after restoration is less than the exchange capacity of the starting clay. In this way, the post-exchange capacity of the pillared clay is directly related with the negative charge of the clay sheets since the pillars may still carry a positive charge. Radiotracer studies confirmed the above results and provided an indication for stronger binding of strontium than cesium. Therefore, several other aspects of the cation exchange process in PILCs as e.g., their selectivity for strontium uptake in the presence of competitive cations and their performance in a complex environment, are currently under investigation.

*

The research presented here was funded in part by the European Commission Radiation Protection Programme (Contract No. F13P-CT92).

References

1. R. A. SCHOONHEYDT, Introduction to Zeolite Science and Practice, H. VAN BEKKUM, E. M. FLANIGEN and J. C. JANSEN (Eds), Elsevier, Amsterdam, 1991, p. 201.
2. K. SUZUKI, T. MORI, US Patent 5,369,069 (1994) 8p.
3. D. T. KARAMANIS, X. A. ASLANOGLOU, P. A. ASSIMAKOPOULOS, N. H. GANGAS, A. A. PAKOU, N. G. PAPAYANAKOS, Clays Clay Minerals, 45 (1997) 709.

4a. G. DECONNINCK, J. Radioanal. Chem., 12 (1972) 157.
4b. J. A. COOPER, Nucl. Instr. Meth., 106 (1973) 525.
4c. D. GIHWALA, M. PEISACH, J. Radioanal. Chem., 70 (1982) 287.
4d. A. L. HANSON, K. W. JONES, Nucl. Instr. Meth., B9 (1985) 301.
4e. H. SALAH, B. TOUCHRIFT, Nucl. Instr. Meth., B129 (1997) 261.

5. G. DECONNINCK, G. DEMORTIER, J. Radioanal. Chem., 12 (1972) 189; 24 (1975) 437.
6. G. DEMORTIER, F. BODART, J. Radioanal. Chem., 12 (1972) 209.
7. M. J. KENNY, J. R. BIRD, E. CLAYTON, Nucl. Instr. Meth., 168 (1980) 115.
8. A. ANTTILA, R. HANNINEN, J. RAISANEN, J. Radioanal. Chem., 62 (1981) 293.
9. A. Z. KISS, E. KOLTAY, B. NYAKO, I. S. SOMORIAL, A. ANTTILA, J. RAISANEN, J. Radioanal. Nucl. Chem., 89 (1985) 123.
10. A. SAVIDOU, X. ASLANOGLOU, T. PARADELLIS, M. PILAKOUTA, Nucl. Instr. Meth., B (in press).
11. J. F. ZIEGLER, J. P. BIERSACK, U. LITTMARK, The Stopping and Range of Ions in Matter, Vol. 1, Pergamon Press, New York, 1980.
12. K. K. NIELSON, Anal. Chem., 49 (1977) 641.
13. T. O' REILLY, B. S. W. KING, Adv. X-ray Anal., 30 (1987) 165.
14. I. BOGDANOVIC, S. FAZINIC, S. ITSKOS, M. JAKSIC, A. KARYDAS, V. KATSELIS, T. PARADELLIS, T. TABIC, O. VALKOVIC, V. VALKOVIC, NIM B99, 1995, p. 402.
15. A. KARYDAS, Private communication.
16. H. VAN OLPHEN, Clay Colloid Chemistry, Interscience Publishers, New York, 1963, p. 248.
17. V. SUCHA, V. SIRANOVA, Clays Clay Minerals, 39 (1991) 556.