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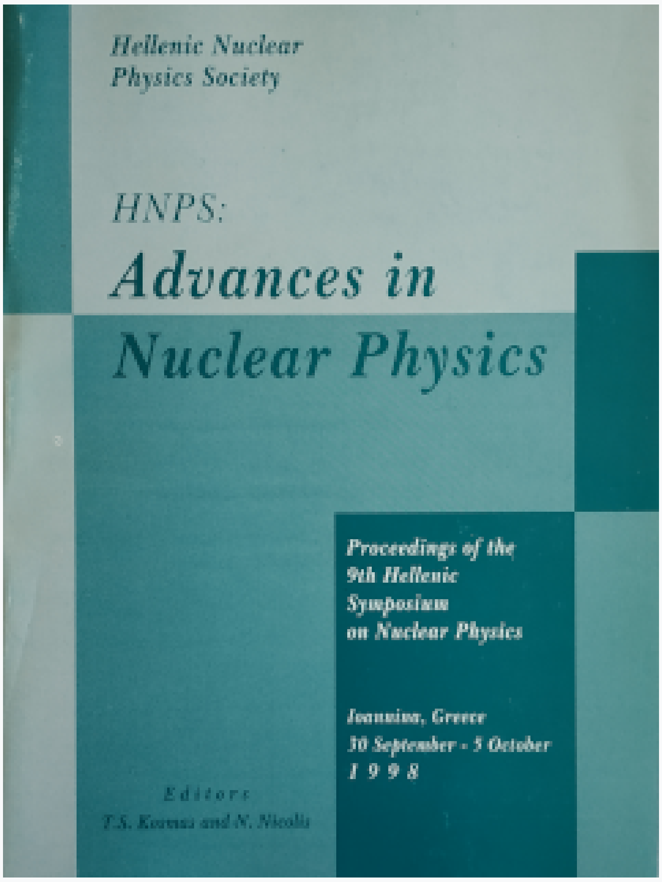

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Radioactive contaminants binding on pillared layered clays

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Abstract

The selective sorption of radioactive cesium and strontium on Pillared Layered Clays was investigated. Two reference samples were initially used in experiments, both *in vitro* and *in vivo*. An improved nanocomposite-pillared clay with different organization and structural evolution of its building blocks, was constructed, characterized by several methods and employed in exchange experiments. The results derived from the improved material administration in ruminants for strontium and cesium sorption were positive and further investigation is under way.

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1 Introduction

Nuclear weapons' tests, routine releases from nuclear installations and accidental releases as the Chernobyl accident, have in the past resulted in a considerable contamination of the environment by radioactive substances. Furthermore, the effective remediation of the large quantities of hazardous waste stored in underground tanks is of primary concern. The restoration of a radiocontaminated ecosystem and the management of nuclear wastes has been in the past the subject of extensive research [1]. Among the problems associated with this management is the isolation, separation and removal of some of the most hazardous radionuclides: radiocesium and radiostrontium [2]. To address this problem, several materials have been investigated with regard to their properties as effective trapping agents for this cations and a number of sorbents, ion exchangers and advanced extractants are currently being developed for removing Sr^{2+} and Cs^{+} from complex environments as the digestive tract of animals and highly alkaline tank wastes, acid wastes and groundwater [3]. Although some of these materials have proved effective in special circumstances, a general, efficient, low cost material for radio cation and especially radiostrontium binding is still elusive.

During the past six years, the Nuclear Physics Laboratory of the University of Ioannina has been conducting vigorous research with the aim to develop selective sorbents of radioactive cations. In this direction, a novel class of modified smectites, Aluminum Pillared Layered Clays (PILCs), were tested and their selective properties for cesium and strontium trapping in various liquid media were studied.

Pillared layered clays (PILCs) constitute a novel class of materials prepared by propping apart the clay lamellas with nano-size pillars of metal oxides and thus creating a permanent two dimensional zeolite-like network of pores. They are usually prepared from smectites by exchanging the charge-compensating cations between the clay lamellas with cationic complexes of metals as e.g. Al^{13+}. The good application prospect of PILCs is based on the combined properties they exhibit, such as the cation exchange capacity, the complementary zeolite like network of pores with adjustable size, high thermal stability, high specific surface area and high stability with respect to ionic concentration of complex environments, as e.g., the digestive tract of animals and humans or in the management of nuclear wastes.

The present work investigated the selective uptake of cesium and strontium ions from cationic aqueous solutions by a reference and a specially tailored pillared clay via exchange kinetic measurements and exchange isotherms. Furthermore the selective removal of strontium from the complex environment of rumen liquid taken from slaughtered sheep and PILCs efficacy in an *in vivo* experiment involving six lactating ewes, were also investigated.

2 Experimental Procedures

Three type of Al-PILCs coded ATHINA, AZA [4] and FRAZA were used. A detailed description of the preparation of FRAZA and the CEC restoration of ATHINA, AZA and FRAZA is given elsewhere [5]. The techniques of XRD, PIGE, XRF, N_2 adsorption-desorption, were used for the elemental characterization of FRAZA [5,6].

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 gamma 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 gamma 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.

Table 1
Structural data and characteristics of the PILC materials.

Material	d_{001} (nm)	BET S (m^2/g)	Pore Volume (cm^3/g)	Micro-pore (%)	Meso-pore (%)	Mean Radius r_o (μm)	CEC (meq/g)
ATHINA-A	13-18	130	-	-	-	80	0.41±0.03
AZA-A	18.2±0.05	220±110	0.06-0.08	100	-	150	0.43±0.02
AZA-D	18.2±0.05	220±110	0.06-0.08	100	-	150	0.630.05
FRAZA-D	≈1.76	110±10	0.11±0.01	≈25	≈75	-	0.63±0.04

3 Results and Discussion

3.1 In vitro strontium and caesium sorption experiments with PILCs

In an initial series of experiments the materials ATHINA and AZA, with characteristics shown in Table1, were used in exchange experiments. Typical kinetics of caesium sorption in different masses of ATHINA-A are shown in Figure 1. As seen in this figure, the adsorption process in PILCs was slow under static experimental conditions. The kinetics were analyzed through the laws of isotopic exchange with film diffusion as the rate-determining step [7]. The experimental data were fitted with a first order kinetic equation of the form

$$f(t) = f(\infty)[1 - \exp(-Rt)] \tag{1}$$

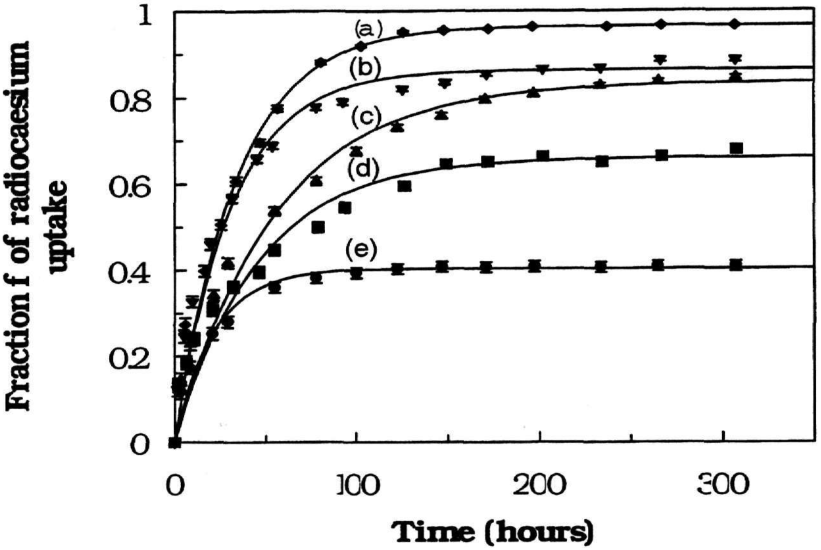

Fig. 1. Kinetics of radiocaesium uptake from aqueous solution ^{137}Cs: 1.7x10^{-11} M and H: 2x10^{-4} M by (a) 150 mg; (b) 100 mg; (c) 60 mg; (d) 30 mg and (e) 10 mg of ATHINA-A. (Curves represent the fit of the experimental data in eqn (1)).

where f is the fractional uptake defined by

$$f(t) = (\mathrm{Act_{INIT}} - \mathrm{Act_t})/\mathrm{Act_{INIT}} \tag{2}$$

and R the rate of uptake defined by

$$R = \frac{3D\,(\mathrm{Q_{MAT}} + \mathrm{Q_{SOL}})}{r_o\,\delta\,\mathrm{C_{MAT}}\,V} \tag{3}$$

in which D is the diffusion coefficient (cm^2 sec^{-1}) , Q_{MAT} the amount of ions in the material (mmol), Q_{SOL} the amount of ions in solution (mmol), r_o the mean grain radius (cm), C_{MAT} the ionic concentration in material (mmol cm^{-3}), δ the film thickness and V the solution volume (cm^3). Sorption rates of the order of hours were determined. Furthermore, the rate of adsorption was different for the two material studied and faster in ATHINA-A than AZA-A as a result of the smaller particle size of ATHINA-A. Strontium kinetics in the two materials were faster than caesium kinetics due to electro-selectivity and were both decreased in the presence of competitive ions. The rate of caesium or strontium exchange was increased with the increase of stable isotope's concentration or available exchange sites.

The two PILC materials were tested for selectivity in several aqueous solutions of competitive cations. The application of a phenomenological model developed for the results obtained in these experiments (NPL model [8]), determined the selectivity coefficients of Cs or Sr over competitive of Na, K, H and Ca. The selectivity sequence of cations in materials ATHINA-A and AZA-A was determined as $Cs^+ > K^+ > Na^+$ and $Sr^{2+} > Ca^{2+} > K^+ > Na^+$. The high PILCs' selectivity for Cs or Sr sorption over monovalent or divalent competitive cations was interpreted through the electrostatic interaction of the cations and the negative clay layers. Furthermore, the reduction of the potential energy of cation-PILC binding (mainly Coulomb energy) because of the cation hydration energy was considered. The later is inversely proportional with the ionic radius. Thus, the smaller ionic radius of Cs^+ (0.169 nm) than Na^+ (0.095 nm) or K^+ (0.133 nm) resulted in a higher electrostatic binding energy between the cation and the negatively-charged aluminosilicate sheets. The above interpretation was also used in the observed selectivity of Sr^{2+} (0.113 nm) over Ca^{2+} (0.095 nm). In the case of Sr^{2+} selectivity over Na^+, the valence electro-selectivity was also added. The above electrostatic interaction was also used in the explanation of the higher selectivity coefficients observed in AZA-A than ATHINA-A. This difference was attributed to the different d_{001} spacing of the two materials.

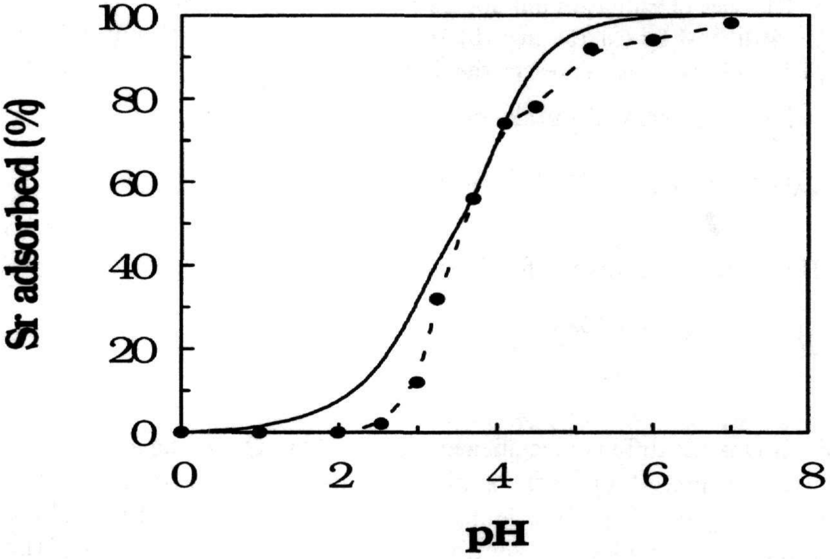

Fig. 2. Influence of pH in strontium sorption on 30 mg of ATHINA-A. The solid line represents the values that the NPL model predicts with k(Sr/H)=9 (pH=3.7). (Strontium concentration 1.7×10^{-11} M).

The study of strontium sorption dependence on pH revealed the disagreement of the observed sorption percentages with the one predicted by the NPL model in the region of low acidity (Figure 2). This result was due to CEC's reduction from the trapping of hydronium ions inside the clay structure. The temperature variation up to 40 C had no effect in strontium exchange which must be considered as a physical process and not a chemical. Finally, the observed influence of volume increase in strontium sorption was coincided with the predictions of the NPL model. With the help of this model and two further experiments in simulating rumen liquid an *in vivo* experiment was performed in the Agricultural University of Norway to study the sorption properties of PILCs in goats. It was observed that the administration of PILCs had no effect on the activity level in the milk of the animals. Possible reasons for this failure could be the saturation of PILCs with competitive cations and especially Ca, saturation with hydronium ions in the acid part of the digestive tract or the limited time of contact between the material and strontium in the digestive tract. This last reason was thought to be the most important and thus further efforts were concentrated towards improving the material in order to increase its CEC and speed up the process.

3.2 Exchange experiments of improved PILC (FRAZA) for Sr and Cs binding

An improved nanocomposite-pillared clay with different organization and structural evolution of its building blocks, was used in exchange experiments. The structural data of FRAZA-D in comparison with AZA-D are presented in Table 1.

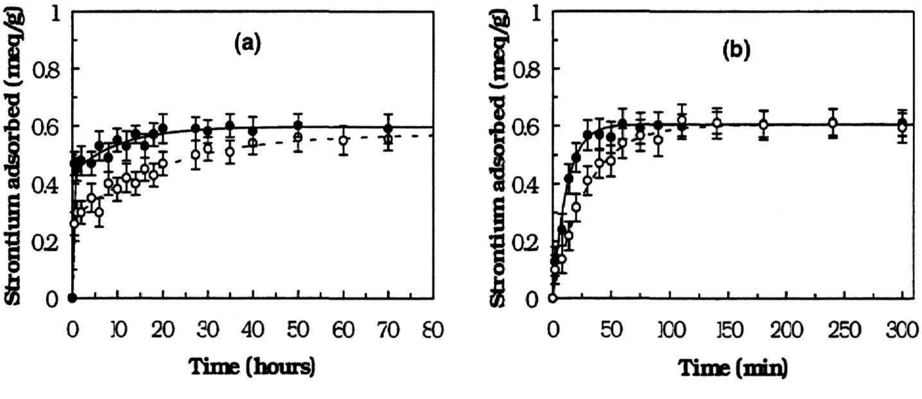

Fig. 3. Sr^{2+} exchange kinetics on AZA-D (open circles, dashed line) and FRAZA-D (black circle, solid lines) under (a) static and (b) dynamic experimental conditions. (Strontium concentration was $0.5x10^{-3}$ M and pH≈6.00. Grain sizes <45 μm were used for both the materials in the dynamic conditions).

Strontium or caesium exchange kinetic measurements were conducted for materials AZA-D and FRAZA-D under both static and dynamic experimental conditions with or without the presence of competitive cations. Typical strontium exchange kinetics are presented in Figures 3 for static and dynamic conditions. The strontium exchange kinetics were faster in FRAZA-D than 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 AZA-D as a result of the different microscopic arrangement of tactoids. The kinetic isotherms for caesium were similar to those of strontium, but the rate was even higher than in the case of the latter cation for both the materials. This behaviour was attributed to the smaller hydrated radius of caesium ion, a fact leading 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.

Following the exchange kinetics, the preference of FRAZA-D for Sr^{2+} over Na^+ or Ca^{2+} was investigated by equilibrating constant amounts of FRAZA-D, saturated with Na^+ or Ca^{2+}, in 200 ml of mixed Sr-Na or Sr-Ca chloride solutions at various ratios of the salts, constant total normality (0.01 N) and 25 C. The exchange isotherms are presented in Figures 4, 5 and confirm the strong preference of FRAZA-D for Sr over Na and its selectivity for Sr uptake than Ca [9].

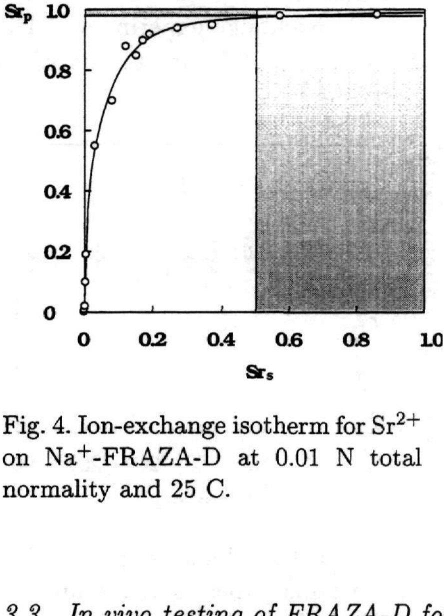

Fig. 4. Ion-exchange isotherm for Sr^{2+} on Na^+-FRAZA-D at 0.01 N total normality and 25 C.

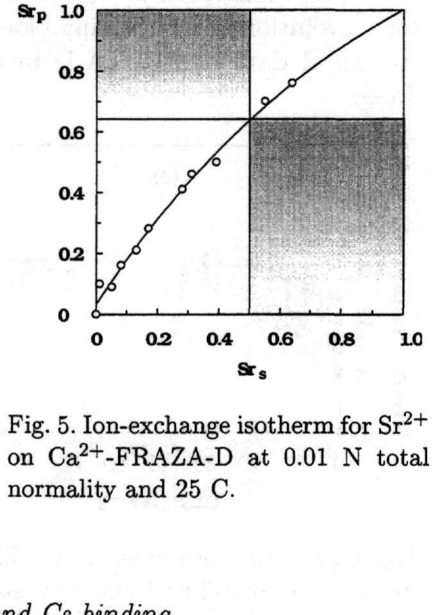

Fig. 5. Ion-exchange isotherm for Sr^{2+} on Ca^{2+}-FRAZA-D at 0.01 N total normality and 25 C.

3.3 In vivo testing of FRAZA-D for Sr and Cs binding

Following the *in vitro* experiments, the material FRAZA-D was tested *in vivo* at the Agricultural Research Station of Ioannina. The experiment involved six lactating ewes, separated into two groups of three each and kept in separate pens. For a period of 22 days a daily dose of 8000 Bq d^{-1} of ^{137}Cs, in the form of ionic solution, was administered to the animals in the first group (group A). During the same period a daily dose of 40000 Bq d^{-1} of ^{85}Sr was administered to the animals of the second group (group B). The animals were milked twice

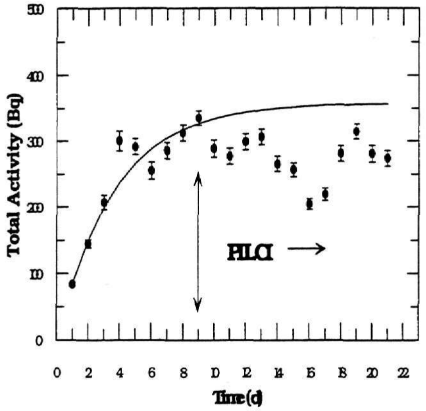

Fig. 6. Daily ^{137}Cs activity secreted in ewe's milk; 30 g of FRAZA-D daily administration started on day 9.

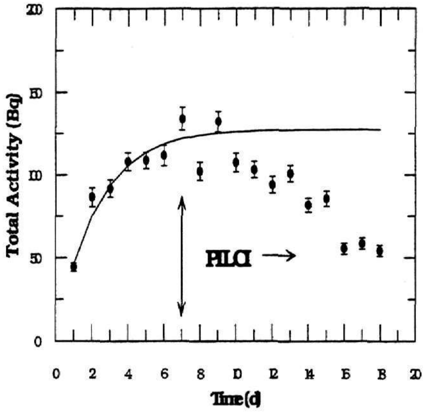

Fig. 7. Daily ^{85}Sr activity secreted in ewe's milk; 30 g of FRAZA-D daily administration started on day 7.

a day and daily milk production and activity concentration in the animals' milk were monitored.

Nine days into the ^{137}Cs experiment and seven days into the ^{85}Sr experiment, a constant daily dose of PILCI was also administered to two animals in each group. Although radioactivity levels in the milk of the remaining monitor animals stayed essentially constant (for the ^{137}Cs it slightly increased) during this latter period of the experiment, the total activity secreted daily in the milk of the ewes receiving the PILCI dose showed progressive reduction. This is shown in the data of Figures 6 and 7, in which the continuous curve represents the prediction for the equilibrium level in total daily activity secreted in milk, as derived from data points of the initial contamination period [10].

4 Conclusions

In spite of the positive results derived from the *in vivo* experiment, it is evident that further research is needed before PILCs can be developed into an effective prophylactic means against ingestion of radiocontaminated food for animals, animal products and eventually man. In particular, the *in vivo* experiment presented above suffers from many shortcomings, the most crucial of which is that the animals used were at the end of their lactation period. It is well known that at that stage the animals are physiologically unstable, with a continuous change in the feed-to-milk transfer factor [11]. In addition, the animals were not adequately segregated and isolated from environmental factors which can affect their behaviour. Indeed, it was observed that a severe thunderstorm in the Ioannina area in the beginning of the experiment, markedly reduced milk production for three days. Finally, the sample size was minimal. It is thus essential that the experiment is repeated under improved conditions which will exclude extraneous factors.

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