



The Sorption of Cesium and Strontium Ions onto Red-Clay from Sivrihisar-Eskisehir (Turkey)

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Abstract. The sorption of Cs and Sr ions from aqueous solutions (concentration range: 20–400 mg/L) by red-clay from Sivrihisar-Eskisehir (Turkey) has been investigated using EDXRF spectrometry. The XRD pattern of the sample indicates that it contains montmorillonite, illite, albite, chlorite and quartz. The results indicate the presence of correlations between sorbed Cs ions and desorbed Na and K ions and sorbed Sr ions and desorbed Mg and Ca ions. Sorption processes are found to show a Freundlich-type behaviour. The Dubinin–Radushkevich (D–R) isotherm has been applied to the sorption data and the parameters of the D–R equation were calculated.

Key words: cesium, strontium, clay, adsorption

1. Introduction

In recent years, land burial of radioactive wastes has become a common practice. For this reason the interaction of radionuclide ions with various soil fractions plays an important role in the extent of contamination of underground waters. Clays are the most important components in such interactions, and together with zeolites and other microporous materials, are used as sealers or liners in waste landfills. Their main role is to limit the migration and transfer of the radionuclides through aquatic pathways [1–9]. Anatolian red clay, obtained from the well-known deposits of Sivrihisar-Eskisehir (Turkey), is a mixed clay. Its major component is montmorillonite and also contains illite, albite, chlorite and quartz, in lesser extents. This study is devoted to the possibility of using the abundant Anatolian red clay as sorbing material for Cs⁺ and Sr²⁺ ions. It is hoped that the sorption properties of the red clay for these ions may lead to the efficient usage of this mineral in the nuclear industry and the disposal of nuclear waste.

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2. Experimental

In this study red-clay obtained from Sivrihisar-Eskisehir (Turkey) has been used as sorbing material. The clay sample was ground to approximately 200-mesh size powder. The mean density of the clay was found to be 2.45 g cm^{-3} . The X-ray powder diffraction pattern of the natural clay was recorded on a Jeol JDX 19C diffractometer. The cation exchange capacity (CEC) of the red clay was measured after Na^+ saturation and further ion exchange with NH_4^+ . FT-IR spectra of the natural and ion treated clays were recorded by a Jasco 300 E FT-IR spectrometer. The chemical analysis of the major elements of the clay sample was performed on a KeveX 0700 EDXRF spectrometer.

Adsorption experiments were carried out by using radioisotope energy dispersive X-ray fluorescence (EDXRF) spectrometry. The samples were excited using an ^{241}Am source ($25 \mu\text{Ci}$) and a HPGe detector with resolution of approximately 350 eV FWHM at 5.89 keV was used. The quantitative analyses were performed by the fundamental parameter technique (FPT), in order to minimize the matrix effects in X-ray fluorescence analysis. The details of this technique were given in references [10–13].

In the case of FPT, the geometric factors, G_i , for each element i {that were related to the incident-exciting X-ray intensity, the geometric factor of the spectrometer and the detection efficiency for the fluorescence radiation from element i }, were first determined experimentally, by using uniform thin standard samples, according to [13] and then a calibration graph for the spectrometer was drawn. The geometric factors for the other elements of the sample investigated were calculated by using this graph. Finally, the absorption corrections of the elements and then the concentration of each element i of the sample was determined. The reliability of the FPT was checked by several measurements on the standard reference materials (NBS SRM 1633a and soil-5 standard of the International Atomic Energy Agency). The over all error in the FPT is estimated to be less than $\pm 10\%$. This error has been calculated as a square root of sum of variances of different parameters used.

AnalaR grade CsCl and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ from Merck were used for preparation of stock aqueous solutions of Cs and Sr in the concentration range 20–400 mg/L. Cation treated clays were prepared by immersing the natural red-clay samples (500 mg) in 50 mL of the stock solutions of Cs or Sr in bottles, at room temperature, for one day ($\text{pH} = 7$). They were then filtered and washed several times with deionised water and dried in an oven at 85°C .

The distribution coefficient, K_d (L/g), was calculated from the following equation:

$$K_d = \{(A_0 - A_1)/A_1\} \cdot \{V / m\}, \quad (1)$$

where A_0 is the initial concentration of Cs/Sr ion in solution (mg/L) and A_1 is the final concentration of Cs/Sr ion in solution after filtration of the clay (mg/L), V is the volume of the solution (L) and m is the mass of the clay (g).

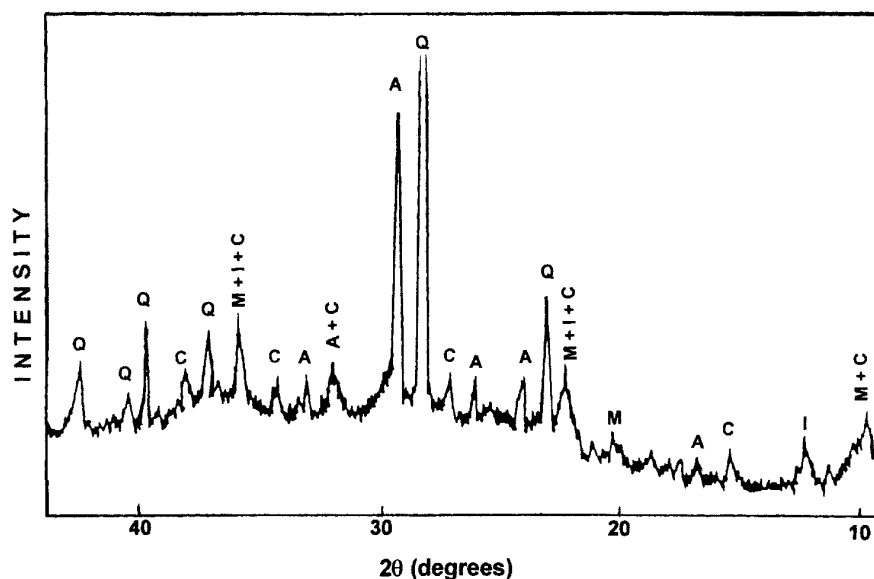


Figure 1. The XRD pattern of the natural red clay ($\text{CuK}\alpha$). Q = Quartz; C = Chlorite; M = Montmorillonite; I = Illite; A = Albite.

3. Results and Discussion

The XRD pattern of the natural red-clay indicates that it contains montmorillonite, illite, albite, chlorite and quartz. (See Figure 1). The mineralogical analysis of the red-clay indicated that the major component of the clay is montmorillonite. Chemical analysis of the natural sample is given in Table I. The CEC value of the clay was found to be 36 meq/100 g. The stability of the clay sample after the adsorption process was verified by IR spectroscopic investigation.

The amount of sorbed Cs and Sr cations on the Cs and Sr treated red clays in aqueous solution of 120 mg/L cation concentration are given in Table II. The decrease in the amount of Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions after the Cs/Sr adsorption process is also given in the table for comparison. The chemical analysis results indicate the presence of correlations between sorbed Cs^+ ions and desorbed Na^+ and K^+ ions and sorbed Sr^{2+} ions and desorbed Mg^{2+} and Ca^{2+} ions. Figure 2 presents the cesium or strontium uptake (mg/g) as a function of the final concentration of the solution.

The distribution coefficients K_d of Cs and Sr in the 20–400 mg/L concentration range have been determined. The K_d values are compatible with those found on clays [2]. The plot of K_d -values against the initial cation concentration in solution is shown in Figure 3. At low Cs or Sr concentrations (20 mg/L) high distribution coefficients results whereas the converse is the case at high starting Cs or Sr concentrations (400 mg/L). The inverse correlation between Cs/Sr cation concentration and the distribution coefficient (K_d) indicates the greater partitioning of Cs/Sr into

Table I. Chemical analysis of natural red-clay

Component ^a	%	Component ^b	$\mu\text{g/g}$
SiO ₂	59.10	Rb	87 ± 5
Al ₂ O ₃	19.05	Sr	218 ± 11
∑(FeO+Fe ₂ O ₃)	6.35	Y	55 ± 4
CaO	4.00	Zr	165 ± 8
TiO ₂	1.03	Nb	35 ± 3
MgO	1.50	Mo	30 ± 2
Na ₂ O	1.50	Sb	20 ± 2
K ₂ O	1.00	Ba	575 ± 25
MnO	0.11	Ce	140 ± 8
P ₂ O ₅	0.02	Nd	30 ± 2
L.O.I ^c	6.50	Cs	n.d ^d

^a Measured by Kevex 700 EDXRF, using X-ray fluorescence method with an accuracy of 1%.

^b Measured by Radioisotope excited EDXRF, using FPT, uncertainties are sample standard deviations (1σ and $n = 7$).

^c Loss on ignition.

^d Not detected.

Table II. Sorption of Cs⁺ and Sr²⁺ ions (mg eq./g) from 120mg/L aqueous solution on red-clay and the decrease in the amount of Na⁺, K⁺, Mg²⁺ and Ca²⁺ ions after the Cs/Sr adsorption process*

	Sorption (mg eq./g)		Desorption (mg eq./g)			
	Cs ⁺	Sr ²⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Cs ⁺ treated clay	0.037	–	0.026	0.012	n.a.**	n.a.
Sr ²⁺ treated clay	–	0.020	n.a.	n.a.	0.008	0.012

* The uncertainty is found to be less than ±10%, which has been calculated as the standard deviation for ten measurements.

** n.a.= not altered.

the solid phase at lower concentrations of cation in solution. Thus, the sorption of Cs or Sr ions on red-clay is concentration dependent but non-linear. The result indicates that Cs and Sr uptake by red clay is mainly due to ion exchange.

The sorption processes are found to show Freundlich-type behaviour obeying the linear form of the equation (see Figure 4). The linearized Freundlich equation is given as [14, 15]:

$$\log q = \log K_F + n \log C, \quad (2)$$

where q is the amount of cation (Cs⁺ or Sr²⁺) adsorbed per unit weight of clay (mole/g), C is the cation (Cs⁺ or Sr²⁺) concentration in solution (mole/L), K_F and

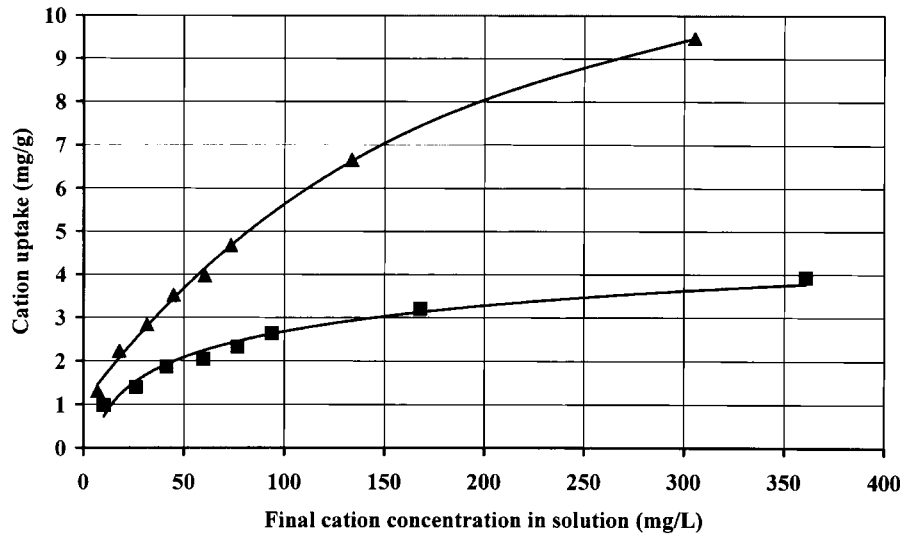


Figure 2. The amount of sorbed Cs⁺ (▲) or Sr²⁺ (■) by red-clay, as a function of the final cation (Cs/Sr) concentration in liquid.

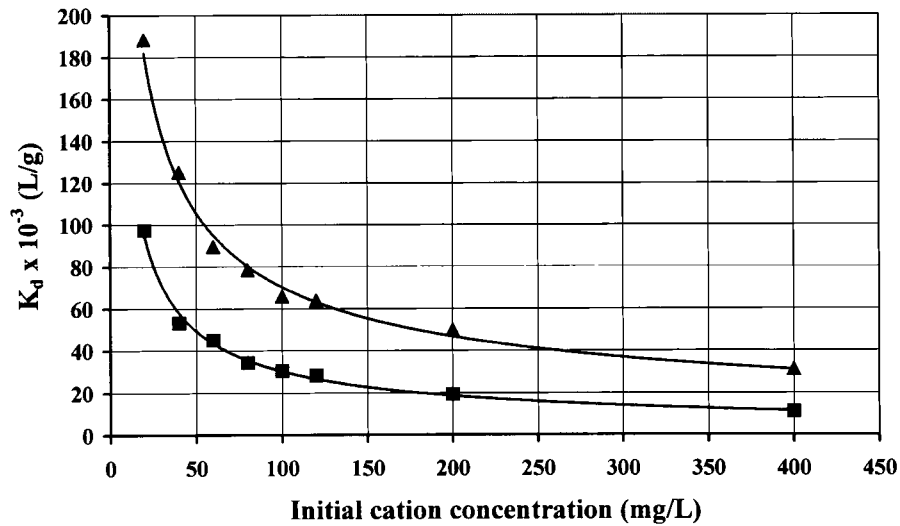


Figure 3. Variation of the distribution coefficient K_d (L/g) as a function of initial Cs⁺ (▲) or Sr²⁺ (■) concentration (mg/g) in solution.

n are constants. In Figure 4 the graphs of $\log q$ versus $\log C$ for Cs⁺ and Sr²⁺ are given. The linear dependence of $\log q$ on $\log C$ indicates the applicability of a Freundlich isotherm for sorption of Cs⁺ and Sr²⁺ cations of the red-clay. The parameters of the sorption isotherm, estimated using the plot presented in Figure 4, are given in Table III. The sorption data of this work are well described by the Freundlich equation with slopes less than one. This indicates that the sorption of

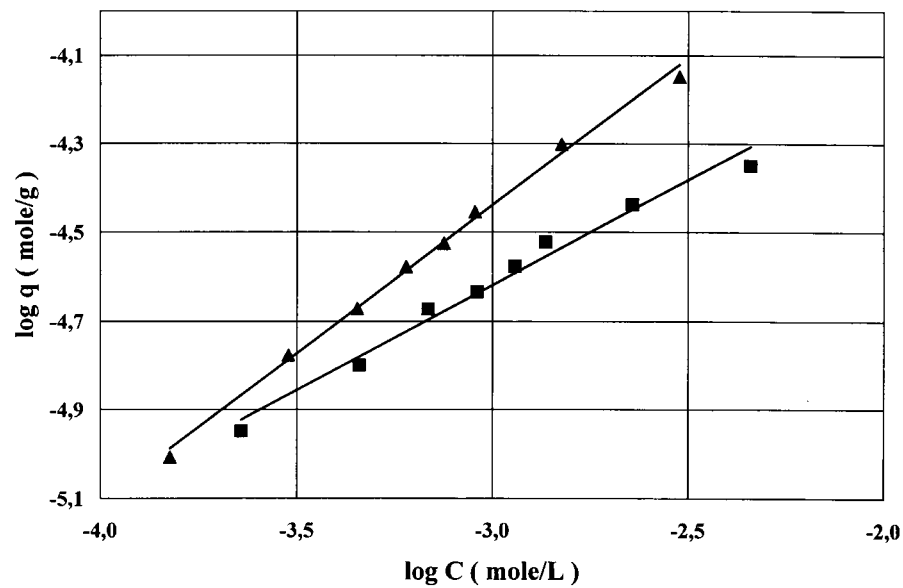


Figure 4. Freundlich-type plots for sorption of Cs⁺ (▲) and Sr²⁺ (■) by the red-clay.

Table III. Parameters of sorption isotherms

Isotherm	K_F	n	K	X_m	r
Freundlich, Cs ⁺ sorption	3.64×10^{-3}	0.67			0.9981
Freundlich, Sr ²⁺ sorption	0.64×10^{-3}	0.47			0.9906
D-R, Cs ⁺ sorption			-0.0072	3.04×10^{-4}	0.9974
D-R, Sr ²⁺ sorption			-0.0056	1.27×10^{-4}	0.9964

Cs or Sr on red clay is concentration dependent i.e. non linear. The Freundlich isotherm has also been used to model the sorption of lanthanides on clay minerals [16–17].

The Dubinin–Radushkevich (D–R) equation [18] relates pore filling to the free energy of the adsorption. Therefore the D–R isotherm has been applied to the sorption data and the parameters of this equation were calculated. The linear form of the D–R equation is given as:

$$\ln X = \ln X_m - K\epsilon^2, \quad (3)$$

where X is the amount of cation (Cs or Sr) adsorbed on the clay in mole/g, X_m is the maximum amount of cation (Cs or Sr) on the clay in mole/g, K is a constant and ϵ is given by the following equation:

$$\epsilon = RT \ln(1 + 1/C), \quad (4)$$

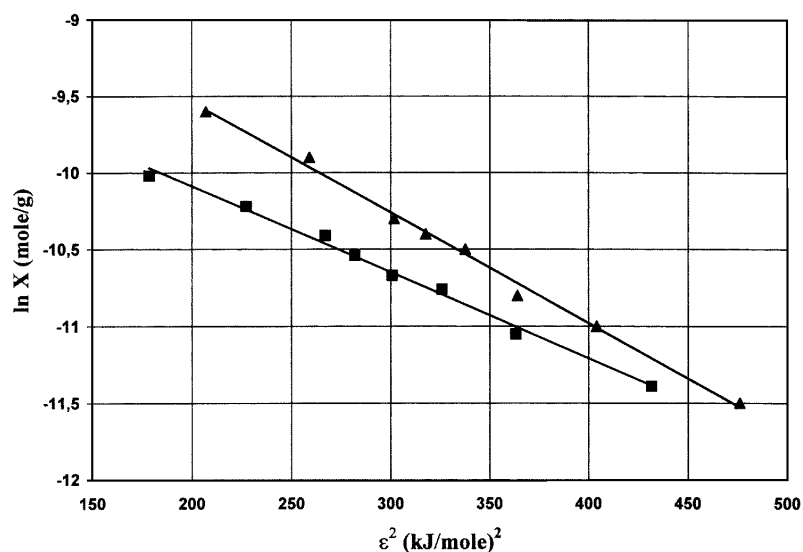


Figure 5. Dubinin–Radushkevich type plots for sorption of Cs⁺ (■) and Sr²⁺ (▲) by the red-clay.

where R is the gas constant ($8.13 \cdot 10^{-3} \text{ kJ mole}^{-1} \text{ K}^{-1}$), T is the temperature (288 K), and C is the equilibrium cation concentration of the solution (mole/L).

The plot of $\ln X$ versus ϵ^2 is given in Figure 5. The D–R parameters (K and X_m), estimated using the plot presented in Figure 5, are given in Table III. The mean energy of sorption is the free energy change of the clay when one mole of cation is transferred to the surface of the clay from infinity in solution. The constant K is related to the mean energy of sorption (E) as [19–20]:

$$E = 1/(-2K)^{1/2}. \quad (5)$$

The value of E is useful for estimating the type of sorption reaction occurring. It was found to be around 8.33 kJ/mole for Cs⁺ sorption and 9.45 kJ/mole for Sr²⁺ sorption, which are within the energy range of ion-exchange reactions, 8–16 kJ/mole [21]. The maximum sorption capacities for Cs and Sr, found using the D–R equation, are 30.4 and 25.4 meq/100 g, respectively. These correspond to about 84% and 71% of the total cation exchange capacity (36 meq/100 g) of the red clay, suggesting that Cs/Sr sorption has mainly an ion-exchange character.

4. Conclusion

In this study the sorption behaviour of Cs and Sr ions on red clay obtained from Sivrihisar-Eskisehir (Turkey) has been investigated. Cs and Sr sorptions on red-clay from aqueous solutions (20–400 mg/L) were found to be concentration dependent but non-linear. The chemical analyses of untreated and Cs/Sr treated samples indicated the presence of correlations between sorbed Cs ions and desorbed Na and

K ions and sorbed Sr ions and desorbed Mg and Ca ions. The Freundlich equation was used to illustrate the relationship between the amount of Cs or Sr adsorbed by the red-clay and its equilibrium concentration in solution. The mechanism involved in the Cs/Sr sorption process is found to be mainly an ion-exchange character. As a final conclusion, one could say that red-clay has high affinity for Cs and Sr and may be utilized for nuclear waste repositories, for constructing natural barriers around shallow-land burial sites of low-level radioactive wastes and heavy metal containing products.

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