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A COMPARATIVE STUDY ON THE SORPTION AND DESORPTION OF Hg, Th AND U ON CLAY

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The sorption and desorption of uranium, thorium and mercury on a western Anatolian montmorillonite, obtained from the deposit located in Kula, were studied by application of a batch technique. The clay used is a tertiary clay originally found in a rather large geological formation of west Anatolia. It is nearly pure montmorillonite. Its cation exchange capacity (CEC) determination was performed for ammonium acetate by the Mehlich procedure. The mean CEC was found to be 83 meq/100 g, which, taking into account that CEC determinations were carried out on unfractionated material, is in good agreement with previously reported data. The concentration ranges were between 70-1500 ppm for mercury and 100-2000 ppm for thorium and uranium. The relative importance of test parameters, e.g., pH, clay particle size, groundwater composition, contact time and solid/water ratio, which determine the distribution coefficients was studied. The sorption coefficients varied between 2.7-6.4 ml/g for U, 0.22-1.59 ml/g for Th and 152.4-427.2 ml/g for Hg. The differences of distribution coefficients are discussed. The data could be fitted to Freundlich and Langmuir isotherms. The quantities of the sorbed and desorbed Th were much lower than its theoretical CEC's. This attitude was attributed to the blocking of montmorillonite by cation islands sorbed in the interlayer. Hg is

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sorbed most strongly. The experimental results indicate that the montmorillonites studied should be effective components of the buffer and backfill material and lead to eventual immobilization of these elements, which are environmentally dangerous.

INTRODUCTION

In the second half of the 20th century humanity has come face to face with two linked events: scientific and technological development, which causes an increasing pollution of the natural environment.

The nuclear waste problem, increasing in parallel to nuclear experiments, nuclear energy and applications of radioisotopes (medicine, agriculture, metallurgy, chemistry, etc.) and heavy metal derivatives, which can stay stable for long periods in natural environment all affect the life cycles of members of the ecosystem in a negative way. The effect of radioactive elements and heavy metals on the cycle of environment and food linkage on different steps has been the object of many studies. The mercury waste leads to high local mercury contaminations of the adjacent rivers and ground water. Methylmercury chloride was the main mercury species responsible for the poisoning. Mercury species dissolved in pore water are probably more toxic than compounds which are strongly attached to particles in the sediment. For this reason methods have frequently been reported to determine group parameters of mercury and not of individual species[1-5].

During last years world attention was exclusively directed towards the use of crystalline (especially granite), saline (mainly salt domes but also bed salt), and

argillaceous (clays and shales) formations for the long-term disposal of radioactive wastes. The ion-exchange processes with soil fines are of major importance for the retention of radionuclides and heavy metals in geological formations[6-9].

Clay is being examined as a candidate packing material for proposed radioactive waste repositories in hard rock and a primary geological medium. The interaction between clay mineral and aqueous solution plays an important role in controlling their level and in preventing their disposal into the terrestrial and marine environment. The environmental impact, cycle and cation-exchange process of different actinides, lanthanides and heavy metals in different geological media were studied[10-11].

Sorption is a general term used to cover all aspects of interaction between the mobile and the stationary phase. This may include ion-exchange, physical sorption and chemisorption, filtration and precipitation. It is important to understand the mechanisms of sorption if one is to predict radionuclide migration rates with any degree of confidence[12].

The chemical composition of liquid phase, the ground-water flow rate, CEC of soil and the temperature are the main factors which affect the transport of elements by the ground-water.

The aim of this study is to investigate the adsorption of uranium, thorium and mercury on a west Anatolian montmorillonite, for the purpose of removing and/or controlling environmental pollution in natural media.

TABLE 1

Approximate mineralogical composition of the clay

Component	%	Component	%
Heating loss	5.93	CaO	0.44
MgO	0.27	$Na_2O + K_2O$	4.78
SiO_2	66.08		
AlO_3	18.85		
Fe_2O_3	3.0	CEC (mean)	83
TiO_2	0.6	pH	7.25

EXPERIMENTAL

Support material

The support material used in this study was taken from Kula mines which is a tertiary clay originally found in a rather large geological formation in west Anatolia of Turkey. It is nearly pure montmorillonite. The formation is sedimentary and probably derived from volcanic ash.

The geological composition and size distribution of the clay have been determined and are summarized in Table 1 and Fig. 1. The mean density is 2.64 g/cm^3.

The CEC determination for this material was performed by the ammonium acetate and Mehlich procedures[13-15]. The clay powder was changed into the Ba-form and the mean CEC value was found to be 83 meq/100 g, which, taking into account that CEC determinations were carried out on unfractionized material, is in good agreement with previously reported data[16-19].

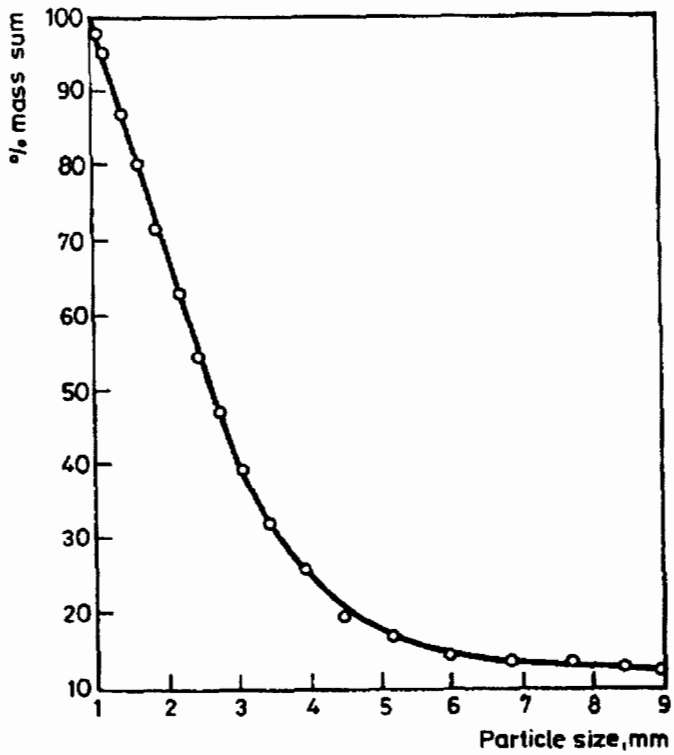

Fig. 1. Particle size distribution of montmorillonite

Solutions

All chemicals used in the analysis or process had GR purity, and were obtained from E. Merck Company, Riedel, Uparc or Fluka S.A.

Experimental

The clay samples were contacted with a synthetic ground-water which had the same composition as natural ground-water. The chemical and physical properties of ground-water are shown in Table 2.

TABLE 2

Properties of the synthetic groundwater

Appearance	: clear	Hardness (French)	: 3
pH	: 7.2	Color	: colorless
Fluoride (mg/l)	: 0.05	Smell	: no smell
Chloride (mg/l)	: 9.9	Taste	: normal
Nitrate (mg/l)	: 2.21	Deposit	: non-existent
Sulfate (mg/l)	: non-existent	Active chlorine	: non-existent
Ammonia	: non-existent		

The concentration range of uranium solutions was chosen according to uranium quantity in the nuclear waste solution. The clay samples equilibrated with ground-water were dried at 60 °C for 24 h. For the sorption and desorption experiments 2.0-10 g of montmorillonite samples were weighed in 100 ml Erlenmayer flasks. After the addition of 30 ml of standardized UO_2^{2+} solution and measurement of the pH of the solution, the sample was shaken in a reciprocating shaker between 30 min and 24 h in a thermostated water bath at 25 °C.

The pH was also measured after equilibrium. After the establishment of equilibrium the mixtures were centrifuged for 15 min at 10000 rpm. The UO_2^{2+} concentration was determined by a spectrophotometric method[16].

For the sorption/desorption experiments of thorium about 3.0 g of montmorillonite sample was weighed in a 100 ml Erlenmayer. After the addition of 30 ml of the appropriate thorium nitrate solution, the sample was shaken in a reciprocating shaker between 30 min and 2 h in a thermostated water bath at 25 °C. After the establishment of equilibrium the clay samples equilibrated with ground-water were centrifuged for 15 min at 10000

rpm and the thorium concentration was determined in the supernatant solution titrimetrically (EDTA titration) and photometrically (TOPO method)[20-21]. The amount of thorium sorbed on the clay was calculated from the difference between the initial and final concentrations in the aqueous phase. All sorption/desorption experiments were duplicated.

The sorption/desorption studies for mercury were carried out as described below. About 10 ml mercury(I) nitrate solution was used with the liquid/solid ratio of more than 3, and it was shaken in a reciprocating shaker for 2 h. The change in adsorption and desorption depending on pH value was also examined. After measuring the pH of the mercury(I) nitrate solutions they are added to weighed clay samples. All experiments were done in a thermostated water bath at 25 °C. The Hg_2^{2+} concentration was determined by a spectrophotometric method[16].

Only samples from the solution phase were taken and the distribution coefficient was calculated from:

$$K_d = \{ [(C_o - C)/m]/[C/V] \}$$

where C_o is the initial element concentration in solution (mol/l), C is the final element concentration in solution (the concentration after certain contact time, mol/l), m is the mass of sorbent (g), and V is the volume of the solution phase (ml).

Thoroughly sieved and washed montmorillonite sorbent and water were contacted and to adjust the pH, an acidic stock solution was added. The distribution coefficients of element concentrations in solution phase were determined as a function of following parameters: contact-time, clay size, concentration and pH. The data obtained from sorption/desorption experiments were fitted with

Freundlich and Langmuir isotherms[22-23]. The linearized Freundlich equation is

$$\lg x = \lg k + N \lg C$$

where x is the amount of solute adsorbed per unit weight of solid ($meq.g^{-1}$), C is the equilibrium solute solution concentration ($meq.ml^{-1}$) and k and N are constants. The Langmuir equation is

$$C/X = 1/k_a . 1/X_m + C/X_m$$

where X and C are defined as above for the Freundlich equation, k_a is the affinity constant and X_m is the maximum amount of the element that can be adsorbed in a monolayer.

RESULTS AND DISCUSSION

The experimental data for the sorption and desorption of uranium, thorium and mercury by the montmorillonite depending on contact time, element concentration, clay size and pH are shown in Figures 2-5.

The influence of contact time can be explained by various processes which control the mechanisms of uptake and rate of diffusion into the matrix of the soil. The order of uptake for this montmorillonite type can be recognized from the intersection of graphs and it is independent of contact time at values greater than 10 h for uranium and 2 h for both thorium and mercury (Fig. 2, 2a).

The effect of clay size or particle diameter on the adsorption of uranium is examined between 0.05 and 0.4 mm. The results show that the +0.1 - 0.2 mm dimension

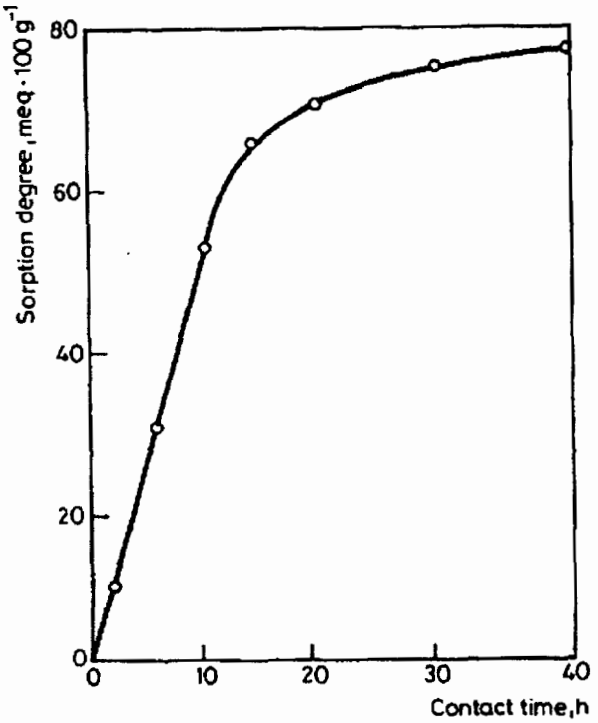

Fig. 2. Variation of uranium sorption depending on contact time

range is the most suitable for the adsorption process (Fig. 3).

In all the following experimental work this size range of montmorillonite is taken as the main adsorbent material.

The influence of concentration on the sorption and desorption is summarized in Fig. 4. The experimental data show that the corresponding charges for montmorillonite were 77, 48 and 85 meq/100 g clay for uranium, thorium and mercury, respectively.

The experiments to determine the pH effect on sorption were studied for pH 13 < pH < 11 for uranium and 1 < pH < 3.2 for mercury (Fig. 5, Fig. 5a).

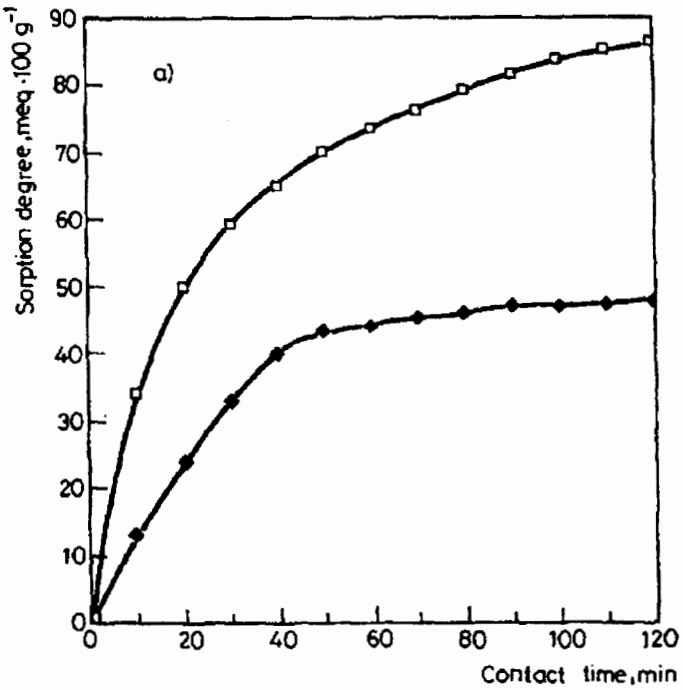

Fig. 2a. Thorium and mercury sorption vs. contact time

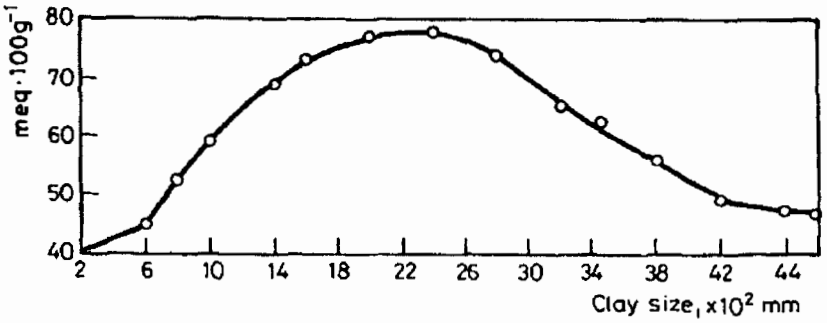

Fig. 3. The effect of clay particle size on uranium adsorption

The results indicate that the sorption and desorption of uranium is high at lower (pH < 6) and higher (pH > 8) pH regions. The sorption values decrease when the pH increases from 3 to 7 and afterwards both of them increase.

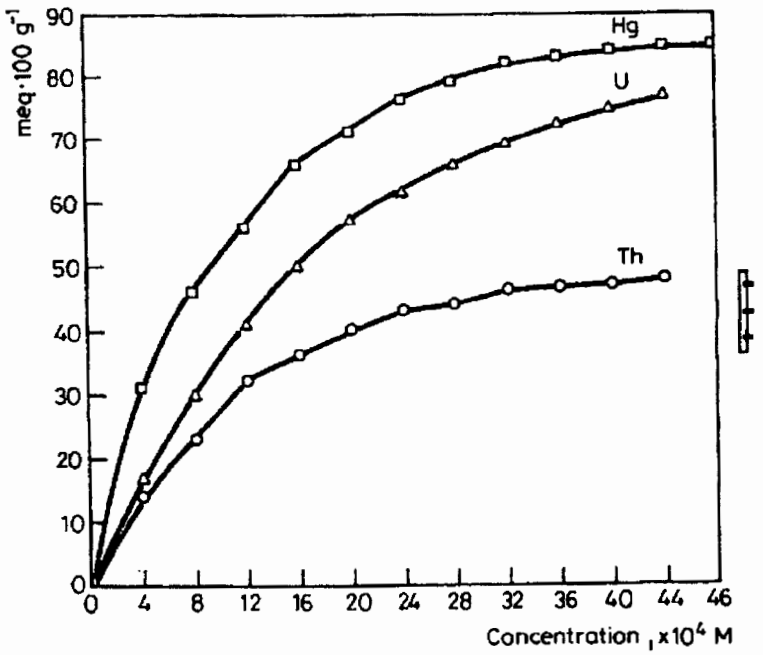

Fig. 4. Variation of uranium, thorium and mercury sorption depending on equilibrium concentration

Freundlich and Langmuir parameters for uranium, thorium and mercury are given in Fig. 6.

The results as a function of concentration suggest the existence of two types of cation-exchange phenomena. The first one is the increase of sorption below 1000 ppm and the second one occurs over 1000 ppm for all of the three cations. The data obtained indicate a relatively reversible behavior for sorption and desorption processes. It should be noted that mercury is sorbed most and desorbed least when thorium is sorbed least and desorbed most. This fact can be explained by their different ionic characters. It may be attributed to tightly bound layers in the case of montmorillonite structure which does not permit deep penetration of the solution into the clay

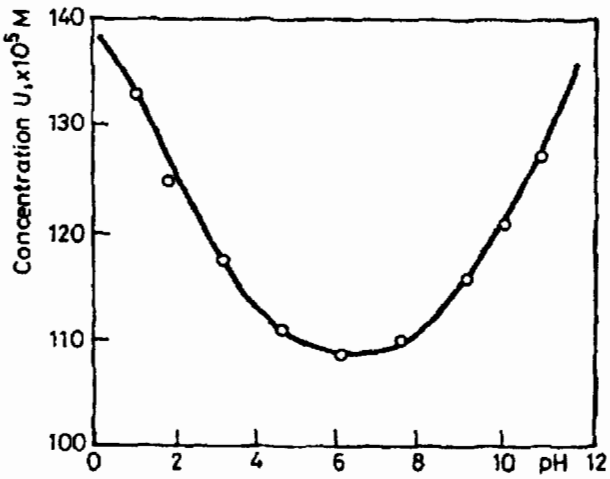

Fig. 5. The pH effect on uranium sorption

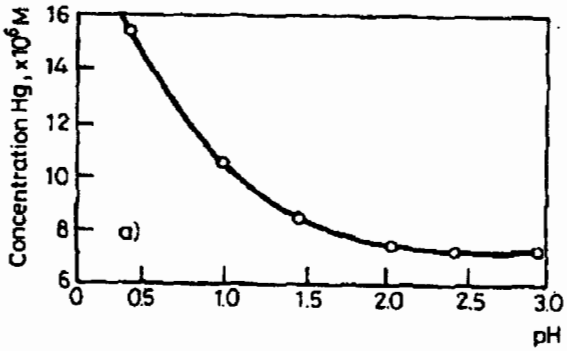

Fig. 5a. The pH effect on mercury sorption

lattice. The ion exchange properties of montmorillonite are generally believed to reflect broken bonds and possibly OH bonds on the surface of the clay particle.

When the slope values are less than unity for uranium and thorium, in the case of mercury it is greater than one. This is because mercury is a II B group element but thorium and uranium are IV A and VI A group elements,

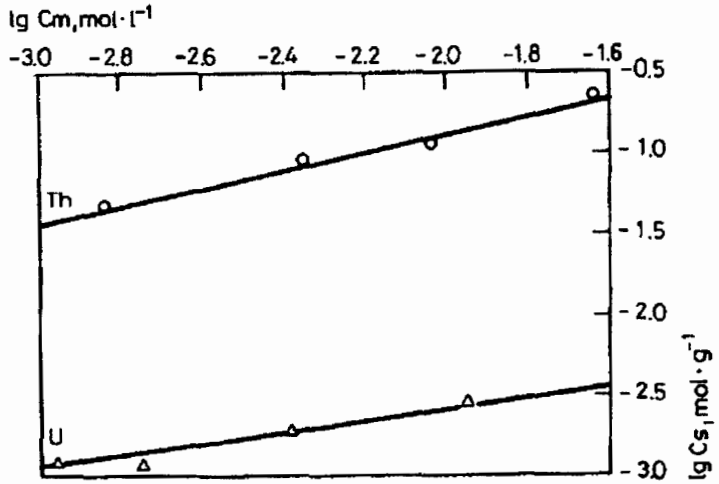

Fig. 6. Freundlich plot of uranium and thorium sorption

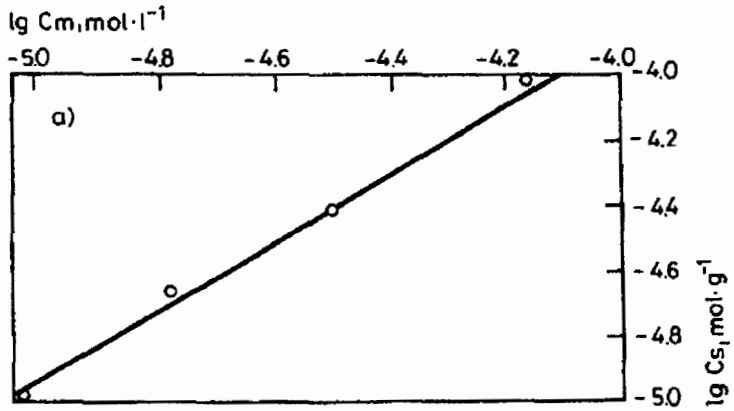

Fig. 6a. Freundlich plot of mercury sorption

respectively. The values of Freundlich and Langmuir parameters and the form of adsorption isotherms clearly indicate the establishment of equilibrium corresponding to an adsorption of each element around the theoretical charge of support material. In the case of thorium the fact that the sum of exchangeable cations is smaller than the mea-

sured CEC values, indicate that some dissolution of soluble salts occurred during determination of the exchange process. The relatively lower adsorption capacity against thorium could be attributed to the presence of some other different species of thorium existing under the experimental conditions. The sorption capacity for mercury does not change in the experimental pH range, however, its sorption is greater than that of the other elements examined.

CONCLUSION

The sorption and desorption behavior of uranium, thorium and mercury on montmorillonite have been studied. The results obtained reveal that the sorption of the elements studied on montmorillonite approximately obey the additivity rule without any corrections, except for the equilibrium ion concentration. Their sorption and desorption abilities are described by the distribution coefficients, Freundlich's parameters and Langmuir's affinity constant, which encompasses surface retention.

The sorption process for actinides can largely be taken as physical adsorption. The exchange processes would be less significant, except for non-complexed and non-hydrolyzed species at lower and higher pHs, and also for thorium the migration can be reduced due to the formation of hydrolyzed and polymerized species. The high degree of mercury sorption can be attributed to its low degree of hydrolysis.

In the light of the results discussed above, it is obvious that the test parameters have a marked effect on sorption and it is possible to retain thorium, uranium

and mercury on montmorillonite, which may be an effective support material for immobilization of the elements in question[24-25].

*

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