

SORPTION/DESORPTION OF Cs ON CLAY AND SOIL FRACTIONS FROM VARIOUS REGIONS OF TURKEY*

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ABSTRACT

The sorption desorption behaviour of Cs ion in the concentration region of 10^{-8} to 10^{-4} meqml⁻¹ have been studied using clay and soil fractions from various regions of Turkey. The sorption curves for all the material studied show similar behaviour indicating at least two different sorption processes. One with high and the other with low distribution coefficients. The results of desorption studies indicate that Cs cation is to a large extent attached to the solid material in a reversible manner. The adsorption isotherms were found to be nonlinear in all cases. The increase of R_D values with decreasing particle size in most cases, suggests that sorption and or exchange is primarily a surface phenomenon in the clay and soil fractions studied.

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1. INTRODUCTION

Sorption studies of various cations on soil material are quite important with respect to the effects of radioactive waste on the groundwater environment. In recent years, radioactive materials have been produced and used in ever increasing quantities. Some of these materials have been released to the environment mainly as a result of nuclear weapons testing and accidents occurring at nuclear power or reprocessing plants. Most recently the accident at the nuclear power plant at Chernobyl is an example of the environmental contamination with radioactive nuclides.

Water present in the environment contacts many substances during its movement on and beneath the surface of the earth. The most common and widespread of the various soil components are the clay minerals. The interaction between clay minerals and water plays an important role in controlling the concentrations of radioactive substances in water and in preventing their dispersal into the environment. The main factors which affect the transport of radionuclides by the groundwater include chemical composition of groundwater, the groundwater flow rate, the exchange capacity of soil, and temperature.

The effects of these factors on the sorption and transport properties of radionuclides has been the subject of many investigations. The general objective of these studies was to establish a basis for the prediction of radionuclide behaviour in

geologic environments.

The aim of this work was to study the sorption characteristics of some clays and soil fractions from various regions of Turkey.

2. EXPERIMENTAL

The first cation chosen for study was caesium. The behaviour of caesium in the soil is of considerable interest since the radio-nuclide ^{137}Cs due to its long half-life ($t_{1/2}=30.17$ y), is a principle radiocontaminant. Furthermore the chemistry of caesium is simple and ^{137}Cs is commercially available as a suitable tracer.

TABLE I
Caesium ion concentrations
used in adsorption/desorption studies.

[Cs] ^o (meq/ml)
1.19×10^{-8}
1.02×10^{-7}
1.02×10^{-6}
1.01×10^{-5}
1.01×10^{-4}

The sorption experiments were carried out at initial caesium concentrations as given in Table 1. The ^{137}Cs tracer was

obtained from the Radiochemical Centre, Amersham. According to the supplier's information the total activity was 5 mci, the volume 1 ml and the Cs ion concentration $210 \mu\text{g Cs/ml}$. 0.3 ml of this solution was evaporated over a water bath to dryness. The residue was dissolved in 10 ml bidistilled water. To four 2.5 ml portions of this solution nothing was added to the first, 1 ml of solution containing 1.693 mg CsCl/ml was added to the second, 1 ml of solution containing 16.93 mg CsCl/ml was added to the third and 1 ml of solution containing 169.3 mg CsCl/ml was added to the fourth portion. All the samples were then filled to the 100 ml mark with bidistilled water. The resulting stock solutions were kept in plastic bottles. The count rates of the stock solutions diluted 1:100 were about 80 cps.

The sorption, desorption experiments were carried out using the batch method. Weighed amounts of clay samples were kept in contact with known volumes of solution for certain times. After separation of the two phases the change in the concentration of the adsorbate in the solution was determined radiochemically. The phases were separated by centrifugation.

The clay minerals were obtained from the four regions indicated on the map given in Fig 1, where the distribution of some mineral occurrences in Turkey is shown. The clay samples were the following:

- 1- Resadiye bentonite (Na-bentonite); Region 1.
- 2- Giresun white bentonite (Ca-bentonite); Region 2.
- 3- Mihaliççik Ahirözü (Kaolinite); Region 3.

- 4- Sındırgı (Kaolinite-alunite); Region 4.
 5- Küre clay; Region 2.

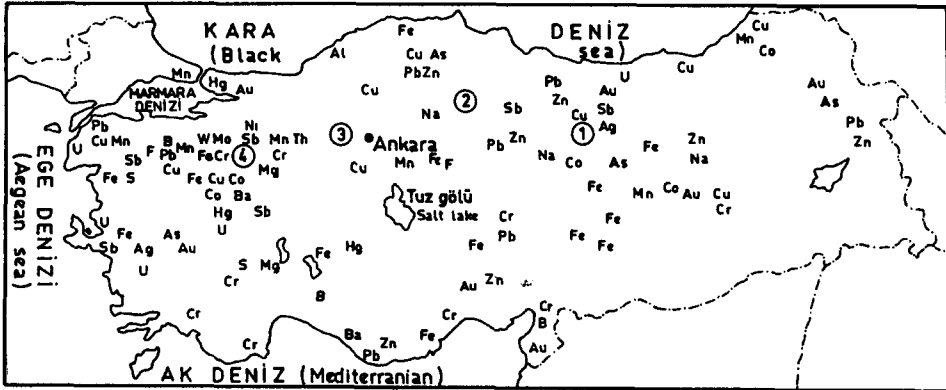


Fig 1 Distribution of some mineral occurrences in Turkey

The first two clay minerals are of montmorillonite type, the rest are of kaolinite type with the general formulas;
 $Al_4(Si_4O_{10})_2(OH)_4$ and $Al_4Si_4O_{10}(OH)_8$ respectively. Kaolinite is a two layer clay type whose layers consist of one tetrahedral and one octahedral sheet, whereas montmorillonite is a three-layer type clay which has an octahedral sheet between two tetrahedral sheets. In general, kaolinite clays have layers bound more tightly together than other clay types and they permit less substitution of other ions for Al and Si. These structural differences are reflected in low ion-exchange capacity for the kaolinite clays and low plasticity because of a low capacity to absorb water. In the montmorillonite type clays

the layers are bound less tightly, this leads to properties such as swelling in polar solvents and very large ion-exchange capacities.

In the experiments Resadiye bentonite and Mihaliççik kaolinite were used as representatives of montmorillonite and kaolinite type clays.

The soil fractions from Sarayköy about 30 kms northwest of Ankara where the Turkish Atomic Energy Authority laboratories will be situated; were separated into various size fractions by wet sieving followed by sedimentation. The particle size distribution of the clay samples and soil fractions of $<20 \mu\text{m}$ size were determined by using an Andreasen Pipette. The samples were first dried at 110°C for 24 hours. 10 grams of the dried samples were then shaken for 12 hours with bidistilled water and then introduced into the pipette. At various preset times 10 ml solutions were taken, dried and the amount of solid material determined. The size of the particles were calculated according to their rate of sedimentation using Stokes' Law.

Sorption experiments were carried out using groundwater from the Middle East Technical University (METU) water system. In the case of Sarayköy soil fractions, groundwater from Sarayköy was used. The water samples were filtered through $0.22 \mu\text{m}$ Seitz bacteriological filter before use.

The following experimental procedure was used in the adsorption studies; tubes were cleaned, dried at 60°C overnight, cooled and weighed. About 100 mg of soil or clay was added and weighed. 10 ml of groundwater was added into the tubes and they were shaken for four days. They were then centrifuged for 30 minutes at 6000 rpm and the liquid phases were discarded. This pretreatment step was aimed at equilibrating the clay samples with the groundwater prior to adsorption experiments. 10 ml of Cs solution was then added from the desired stock solutions after 1:100 dilution with groundwater. They were then shaken for the desired sorption time. The samples were then centrifuged again and the liquid phase was decanted into a clean tube. 5 ml of this liquid was counted using a 35 cm³ calibrated Ge(Li) detector connected to a multichannel analyser. The adsorption distribution ratio, $R_{D,ad}$, was calculated from the measured activities before and after shaking using the following relations;

The distribution ratio is defined by

$$R_{D,ad} = \frac{[Cs]_{s,ad}}{[Cs]_{ad}} \dots\dots\dots (1)$$

where $[Cs]_{s,ad}$ = concentration of Cs in the solid phase after sorption (meq/g)

$[Cs]_{ad}$ = concentration of Cs in the solution after sorption (meq/ml)

Since at the beginning of sorption V ml of solution with an initial caesium concentration $[Cs]^{\circ}$ was added and at the end of sorption step $(V + \Delta W_{pt})$ ml of solution with concentration $[Cs]_{ad}$ was present, here ΔW_{pt} is the amount of liquid remaining in the tube after pretreatment and decantation, the concentration of Cs in the solid after sorption is given by

$$[Cs]_{s,ad} = \frac{V \cdot [Cs]^{\circ} - [Cs]_{ad} \cdot (V + \Delta W_{pt})}{w_s} \dots\dots\dots (2)$$

and

$$[Cs]_{ad} = \frac{A_{1,ad}}{A^{\circ}} [Cs]^{\circ} \dots\dots\dots (3)$$

Substituting equations (2) and (3) into equation (1) leads to;

$$R_{D,ad} = \frac{V \cdot A^{\circ} - A_{1,ad} (V + \Delta W_{pt})}{A_{1,ad} \cdot w_s} \dots\dots\dots (4)$$

where A° = Initial count rate of 5 ml of solution added for sorption

$A_{1,ad}$ = count rate of 5 ml of solution after sorption

w_s = weight of solid material (g).

For desorption studies the following experimental procedure has been used;

Following the adsorption step, 10 ml of groundwater was added to the sample tube, shaken for the desired time, centrifuged and decanted. 5 ml of the liquid phase was counted.

The distribution ratio of desorption, $R_{D,de}$, was calculated from the following relation;

$$R_{D,de} = \frac{V \cdot A_{1,ad}^{(V + \Delta w_{pt} - \Delta w_{ad})} - A_{1,de}^{(V + \Delta w_{ad})}}{A_{1,de} \cdot w_s} \quad ..(5)$$

where;

ΔW_{ad} = the amount of liquid remaining in the tube after adsorption and decantation

$A_{1,de}$ = count rate of 5 ml of solution after desorption

The rest of the terms in equation (5) have been defined earlier.

3. RESULTS AND DISCUSSION

The size and distribution of clay and soil fractions are shown in Fig 2. Per cent Finer Than (FT) distribution is plotted against diameter of particles. It is seen that most of the particles were finer than $10 \mu m$ in diameter.

Chemical analysis of water samples used in the experiments as well as the solutions after pretreatment with various clay and soil fractions are given in Tables II and III for cations and anions respectively. The low concentrations of anions and cations in METU groundwater is striking. METU gets its water supply from a nearby lake. The water is treated in a treatment plant before distribution. The water used in the sorption studies was this tap water. Water treatment is probably responsible for low concentrations of anions and cations. The water compositions after pretreatment steps and the Sarayköy groundwater compositions are all similar and reasonable.

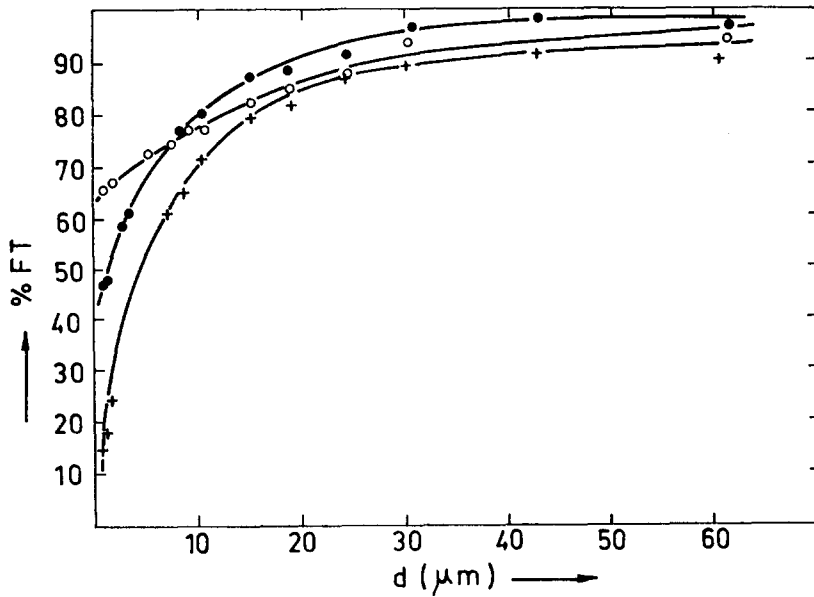


Fig 2 Size distribution of clay samples. % Finer Than (FT) distribution against diameter of particles.

- Sarayköy soil
- Resadiye clay
- + Mihaliççik clay

The pH of METU groundwater was measured as 7.4 and the conductance as 0.8 mho. After pretreatment the pH became 8.0.

Neutron activation analysis was used in the determination of thirteen element concentrations in clays from the four regions of Turkey shown in Fig 1. The clay samples were irradiated in the Küçükçekmece Nuclear Reactor at a thermal neutron flux of

TABLE II

**Chemical Analysis of Water Samples Used In
Adsorption/Desorption Studies.
Cation Concentrations**

Water Samples		Cation Concentrations (mg/l)					
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Sr ²⁺	Li ⁺
METU Ground- water	No pretreatment	1.10	1.11	0.80	0.34	<0.002	0.003
	Pretreatment with Mihaliççık clay ($\geq 10 \mu\text{m}$)	85.00	5.01	35.50	14.90	0.220	0.016
	Pretreatment with Mihaliççık clay ($\leq 10 \mu\text{m}$)	197.00	4.50	8.20	14.90	0.031	0.020
	Pretreatment with Reşadiye Clay ($\geq 10 \mu\text{m}$)	314.00	10.10	13.30	71.50	0.076	0.033
	Pretreatment with Reşadiye clay ($\leq 10 \mu\text{m}$)	336.00	13.40	13.90	81.40	0.115	0.037
Sarayköy ground- water	No pretreatment	102.00	4.61	23.30	39.00	0.991	0.051
	Pretreatment with soil fractions from 1-4 meters	103.00	7.20	46.00	27.00	0.830	0.052

TABLE III

**Chemical Analysis of Water Samples Used In
Adsorption/Desorption Studies.
Anion Concentrations**

Water Samples		Anion Concentrations (mg/l)			
		Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻
METU Ground- water	No pretreatment	0.60	< 0.30	0.60	35.00
	Pretreatment with Mihaliççık clay (≥ 10 μm)	10.40	52.80	1.30	227.00
	Pretreatment with Mihaliççık clay (≤ 10 μm)	19.20	56.90	0.50	393.00
	Pretreatment with Reşadiye Clay (≥ 10 μm)	8.40	90.00	-	412.00
	Pretreatment with Reşadiye clay (≤ 10 μm)	7.40	94.80	-	434.00
Sarayköy ground- water	No pretreatment	43.00	73.70	35.00	317.00
	Pretreatment with soil fractions from 1-4 meters	41.70	76.10	34.50	137.00

$1.5 \times 10^{-13} \text{ n.cm}^{-2}.\text{s}^{-1}$. The irradiation time was 2 hours and counting was started after a cooling period of about 7 days. The activities were measured on a $35 \text{ cm}^3 \text{ Ge(Li)}$ detector connected to a 4096 channel analyzer.

The results of elemental abundances in clays are given in Table IV. Besides neutron activation analysis, x-ray diffraction and fourier transform infrared (FTIR) spectrometry were used to study the structure of the various clay samples. In Fig 3 FTIR-spectra of standard kaolinite type clay and Mihaliççik clay are shown. It is seen that Mihaliççik clay is of kaolinite type. Fig 4 shows FTIR-spectra of standard montmorillonite type clay and Resadiye clay. It is seen that Resadiye clay is clearly of montmorillonite type. The x-ray diffraction spectra of glycolated and air dried samples of Mihaliççik and Resadiye clays are shown in Figs 5 and 6 respectively. No shift in peak positions are observed between glycolated and unglycolated samples of Mihaliççik clay. Whereas Resadiye clay samples showed shifts in peak positions. These observations confirm the identification of these samples as kaolinite and montmorillonite type clays respectively.

The evolution of R_D values with time for the experiments with $[\text{Cs}]^0 = 1.19 \times 10^{-8} \text{ meq/ml}$ and $1.01 \times 10^{-5} \text{ meq/ml}$ and particle size fractions $< 10 \mu\text{m}$ and $> 10 \mu\text{m}$ is shown in Fig 7 for Mihaliççik clay samples. It is observed that in about four days of shaking time saturation is reached. For both Cs ion concentrations, the R_D values for the smaller size fractions are much higher than those of

the larger sizes. These observations suggest that the adsorption is primarily a surface phenomenon.

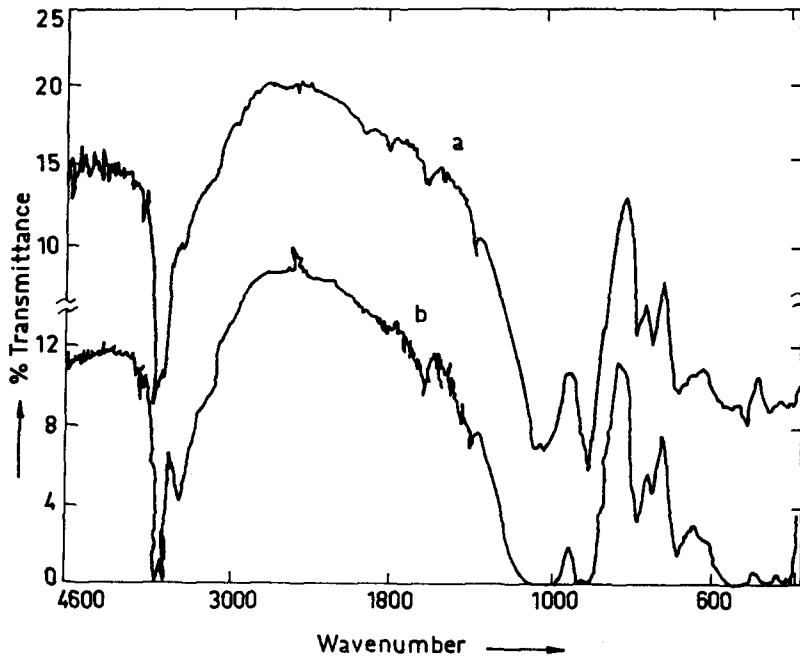


Fig 3 Fourier Transform Infra-Red Spectra of
a) Standard Montmorillonite type clay
b) Resadiye clay

TABLE IV

**Abundances (in ppm) of some Elements
in Turkish Clays**

Element	Region 1	Region 2	Region 3	Region 4
	Reşadiye clay	Küre clay	Mihalıççık clay	Sındırgı clay
Na	16320	247038	-	26706
Ba	4216	4525	-	3349
Ce	174	125	48.10	136.00
Co	15	35.7	10.90	2.80
Cr	35	14.5	13.00	20.30
Cs	0.6	0.6	2.10	0.70
Hf	3.4	2.6	4.70	2.90
La	20.5	42.4	6.90	43.60
Ta	0.5	1.8	0.20	0.80
Sb	2.3	-	36.00	14.00
Sc	5.9	10.4	12.70	7.70
Sm	4.1	7.30	3.60	4.80
Fe	47250	6300	4865	5600

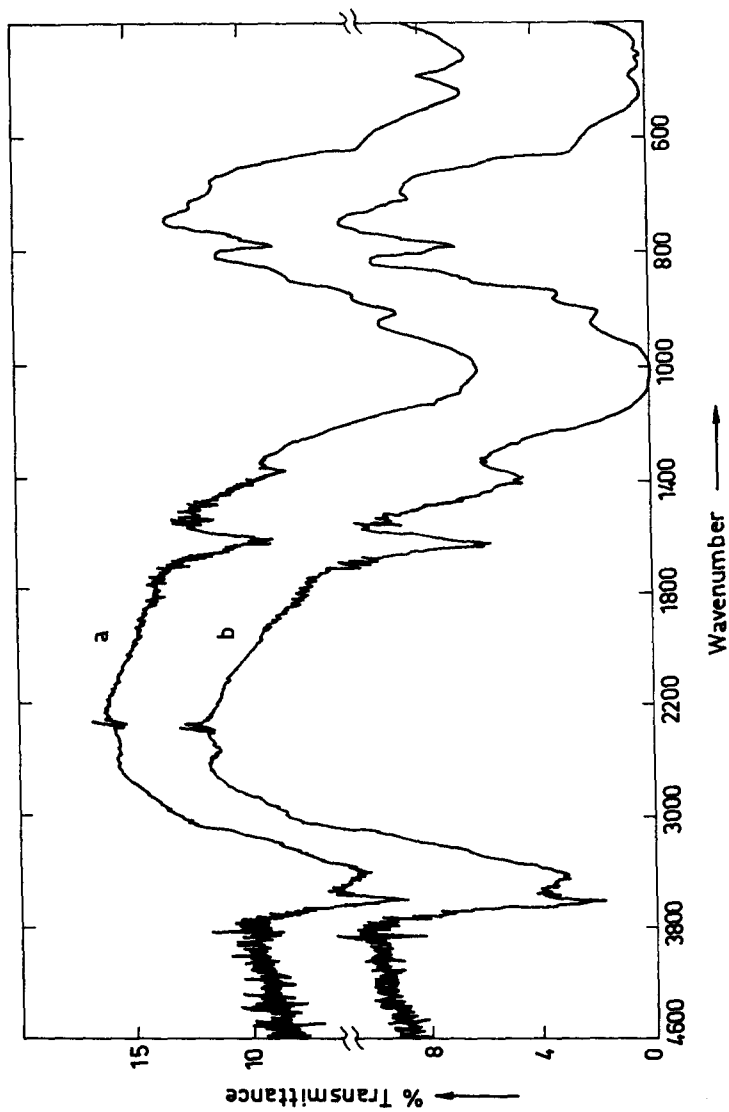


Fig 4 Fourier Transform Infra Red spectra of

- a) Standard Montmorillonite type clay
- b) Resadiye clay

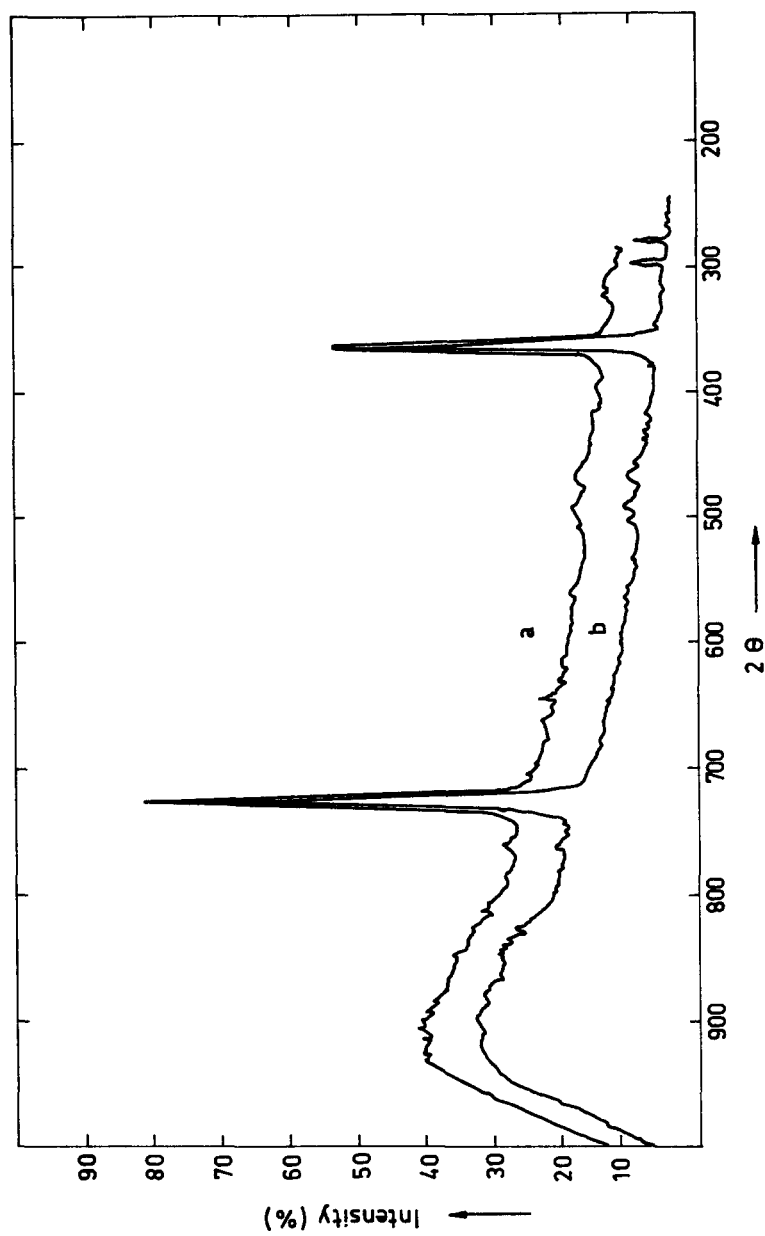


Fig 5 X-Ray Diffraction spectrum of Mihaliççik clay

- a) Glycolated clay samples
- b) Air dried clay samples

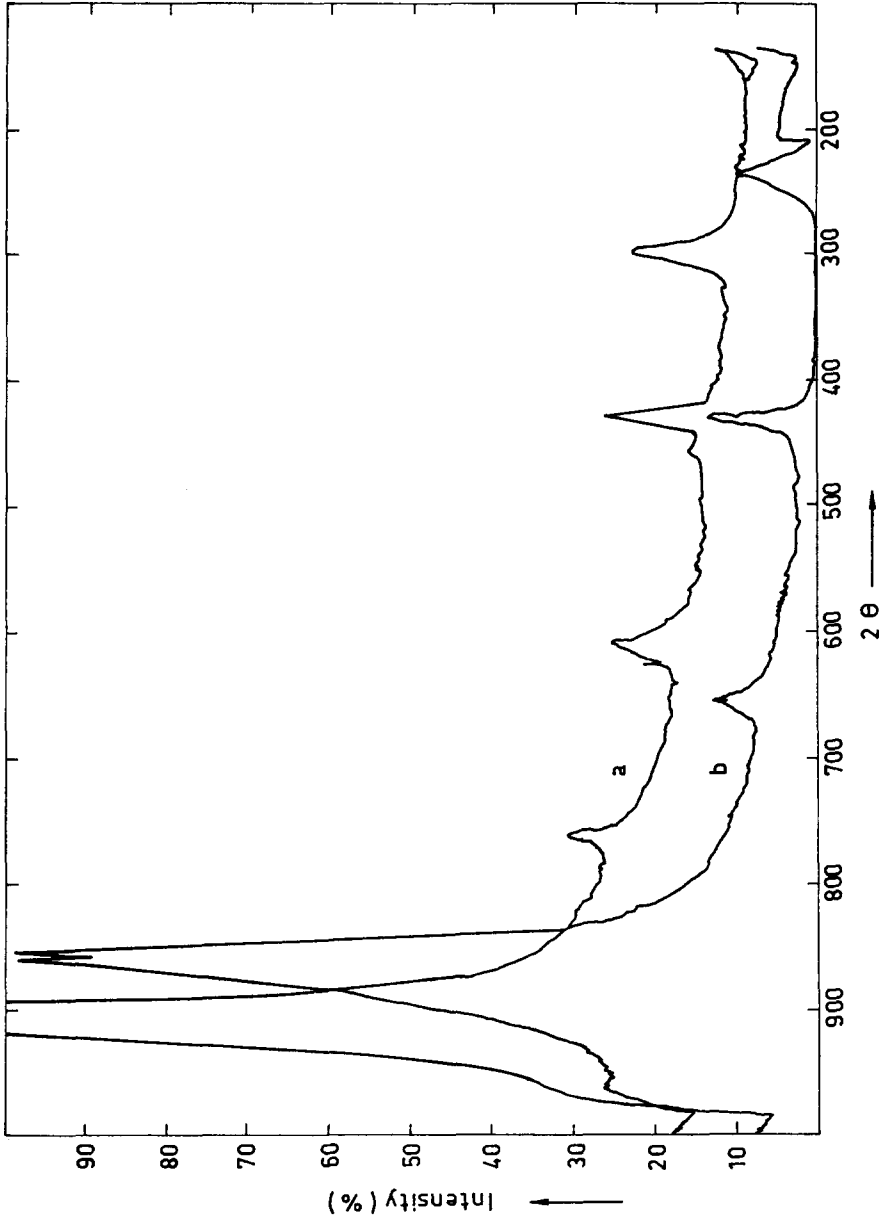


Fig 6 X-Ray Diffraction spectrum of Resadiye clay

- a) Glycolated clay samples
- b) Air dried clay samples

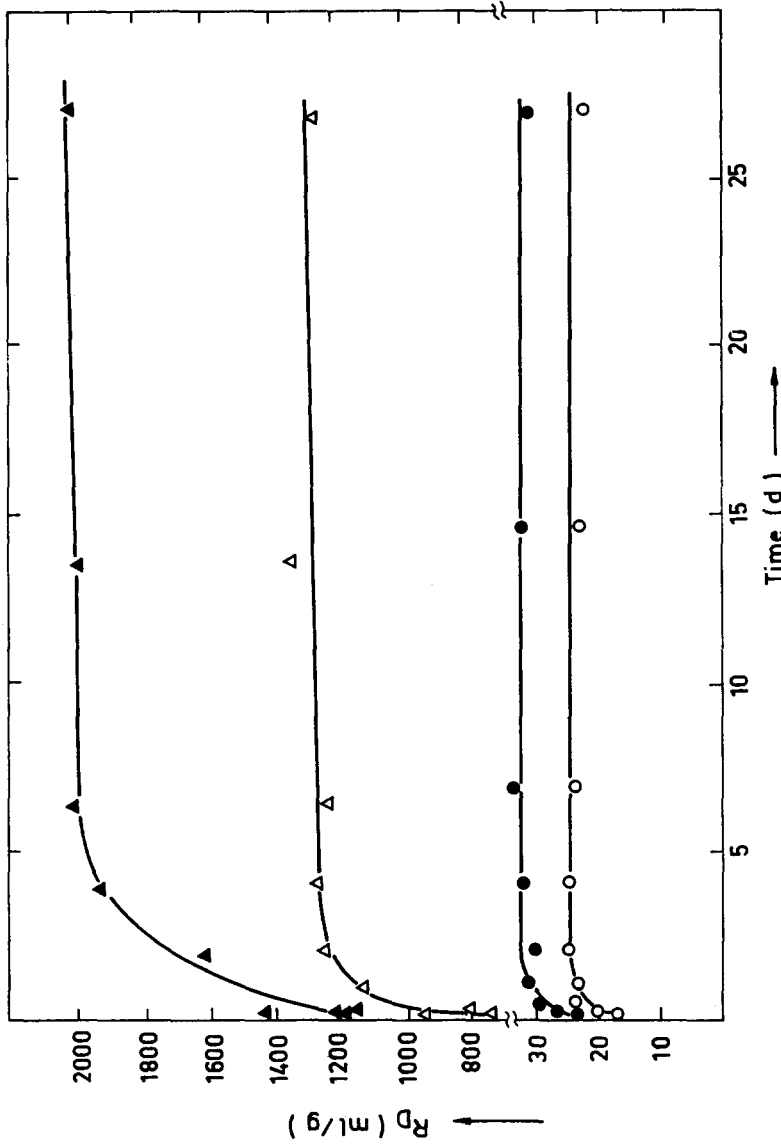


Fig 7 Sorption Kinetics. Change of R_d with time for Mihaliççik clay.

- Particle size $< 10 \mu\text{m}$, $[Cs] = 1.01 \times 10^{-5}$ meq/ml
- Particle size $> 10 \mu\text{m}$, $[Cs] = 1.01 \times 10^{-5}$ meq/ml
- ▲ Particle size $< 10 \mu\text{m}$, $[Cs] = 1.19 \times 10^{-8}$ meq/ml
- △ Particle size $> 10 \mu\text{m}$, $[Cs] = 1.19 \times 10^{-8}$ meq/ml

The adsorption as well as desorption results of distribution ratio, R_D , measurements as a function of Cs-ion concentration in the solid phase for two different size fractions ($<10 \mu\text{m}$ and $>10 \mu\text{m}$) of Mihaliççik clay are shown in Figs 8 and 9 respectively. It is observed that in both cases the adsorption-desorption phenomenon is reversible. Furthermore the curves exhibit a characteristic inverse S-shape. If the R_D values are taken to be true equilibrium constants, then they are not expected to show a variation with Cs-ion concentration. The results shown in Figs 8 and 9 suggest the existence of at least two types of adsorption and/or exchange phenomena. One taking place at low Cs-ion concentrations (till about $[\text{Cs}]_g = 0.5 \times 10^{-5}$ meq/g) and the other type starting at about $[\text{Cs}]_g = 1.0 \times 10^{-4}$ meq/g and continuing at higher concentrations. A transition from one type into the other takes place between Cs ion concentrations of 10^{-5} meq/g to 10^{-4} meq/g. At high Cs ion concentrations one may probably better describe the phenomenon as an exchange rather than an adsorption.

The reversible behaviour may be attributed to the tightly bound layers in the case of kaolinite structure which does not permit the deep penetration of the solution into the clay structure. Thus, the adsorption process takes place primarily at the surface which leads to an easy and effective release of the ions in desorption.

The adsorption isotherm for Mihaliççik clay is shown in Fig 10. It is seen that the isotherm is not linear and it reflects the characteristic shapes shown in Figs 8 and 9.

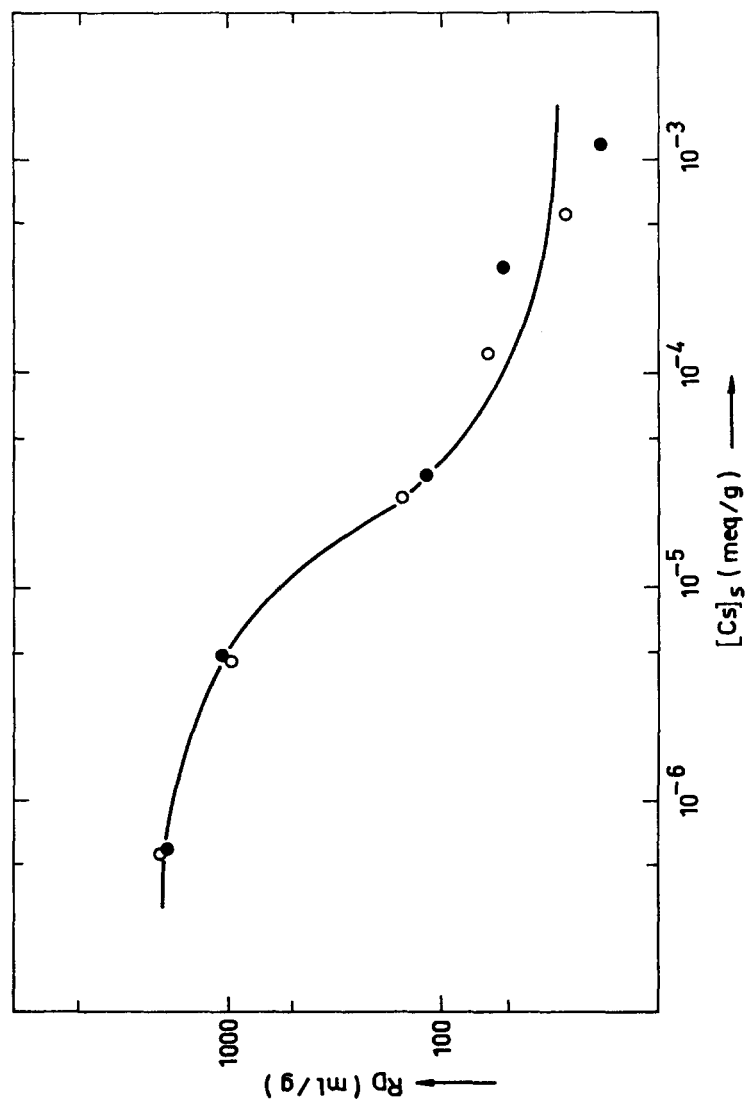


Fig 8 The changes of R_d values with cesium ion loading for Mihaliççik clay.
Particle size $10 \mu\text{m}$.

- Adsorption
- Desorption

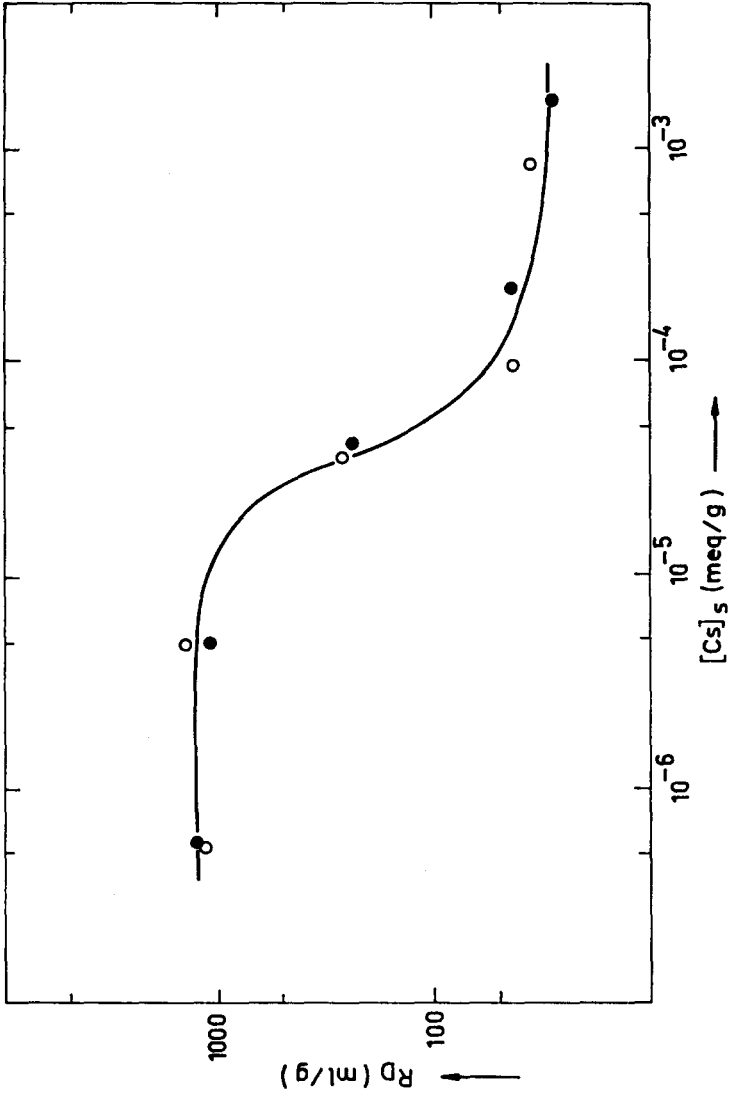


Fig 9 The changes of R_d values with cesium ion loading for Mihaliççik clay.
 Particle size $< 10 \mu\text{m}$.

- Adsorption
- Desorption

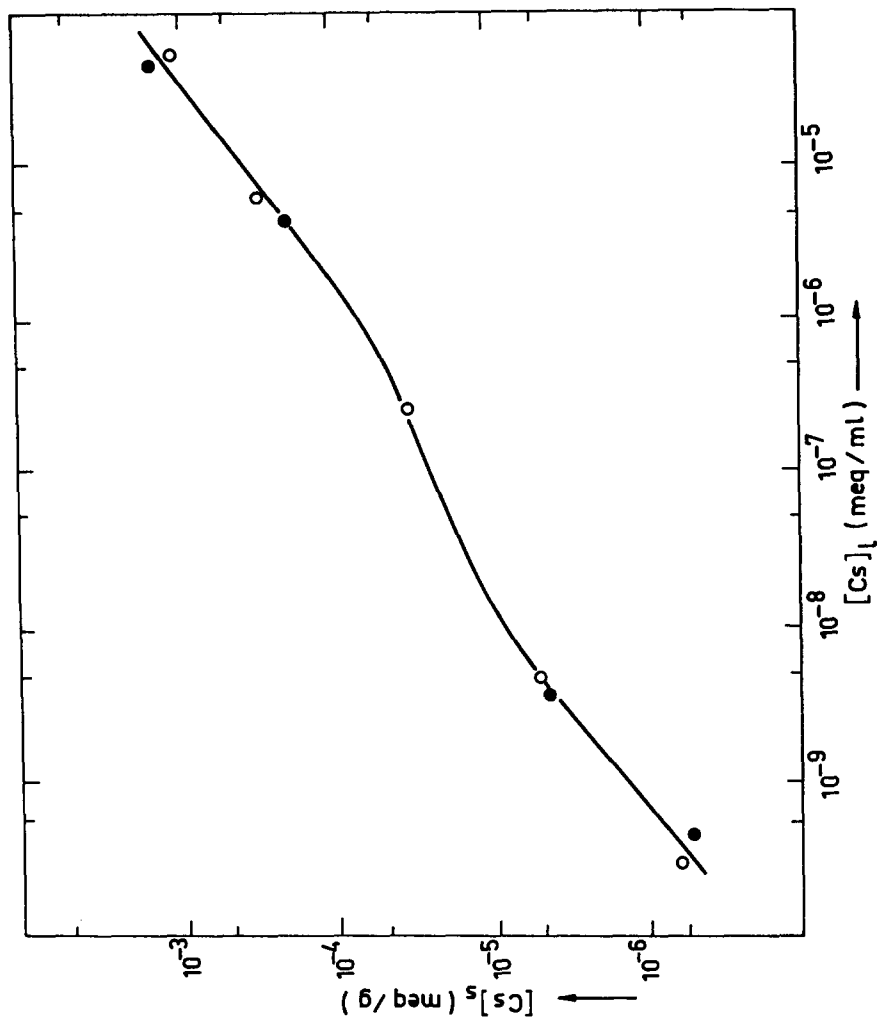


Fig 10 Sorption Isotherm of Mihaliççik clay

- Particle size $>10 \mu\text{m}$
- Particle size $<10 \mu\text{m}$

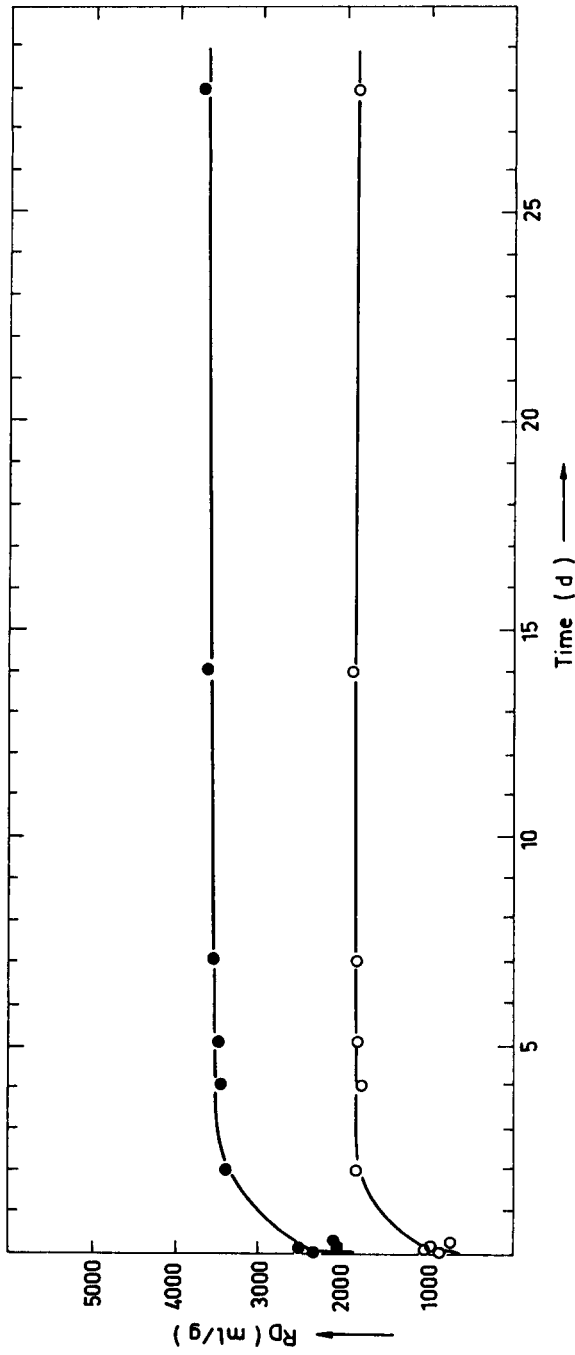


Fig 11 Sorption Kinetics. Change of R_d values with time for Resadiye clay.
[Cs]⁺ = 1.02×10^{-8} meq/ml

- Particle size $\approx 10 \mu\text{m}$
- Particle size $\approx 10 \mu\text{m}$

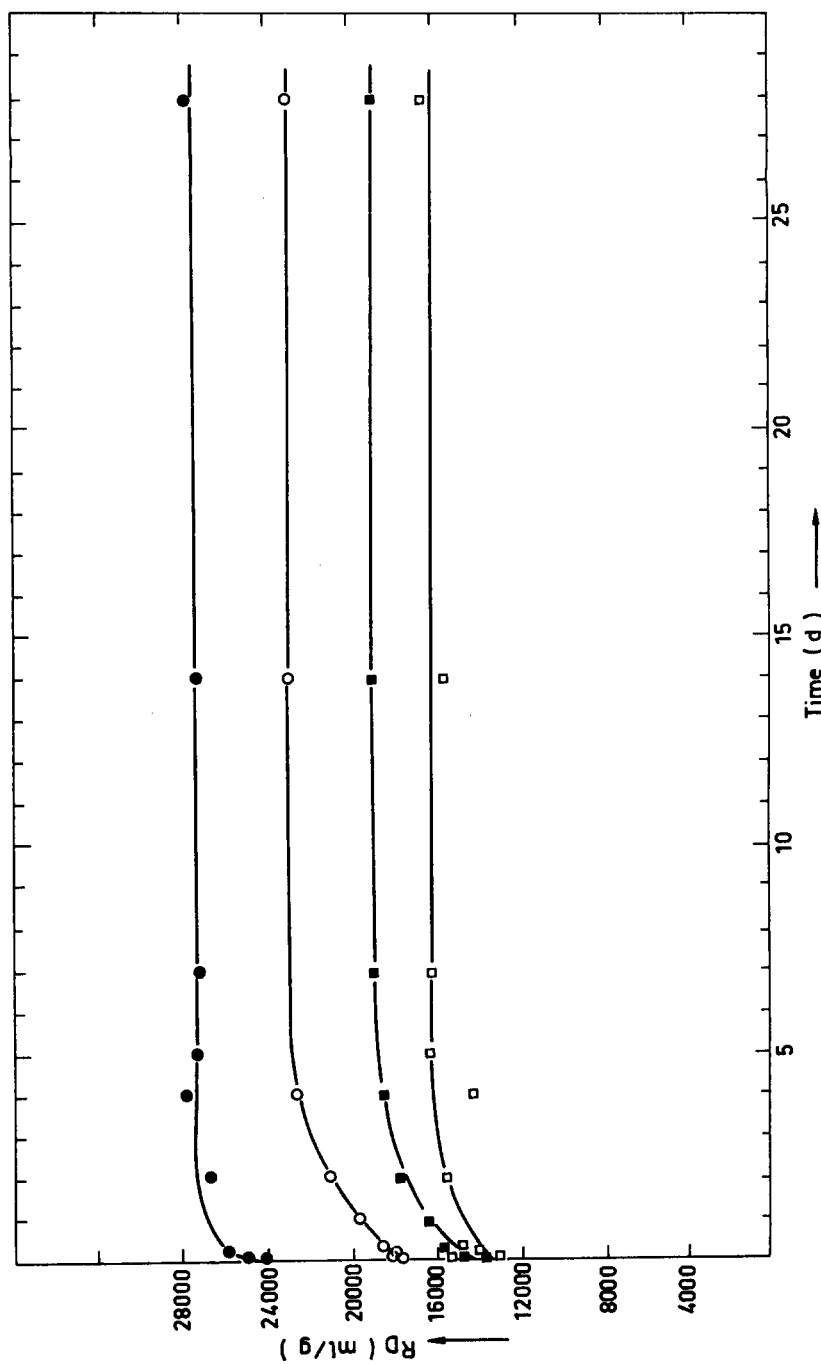


Fig 12 Sorption Kinetics. Change of R_d values with time for Sarayk6y soil fractions.
 $[\text{Cs}]^0 = 1.02 \times 10^{-8}$ meq/ml

- Particle size $< 5 \mu\text{m}$
- Particle size $5-10 \mu\text{m}$
- Particle size $10-20 \mu\text{m}$
- Particle size $> 20 \mu\text{m}$

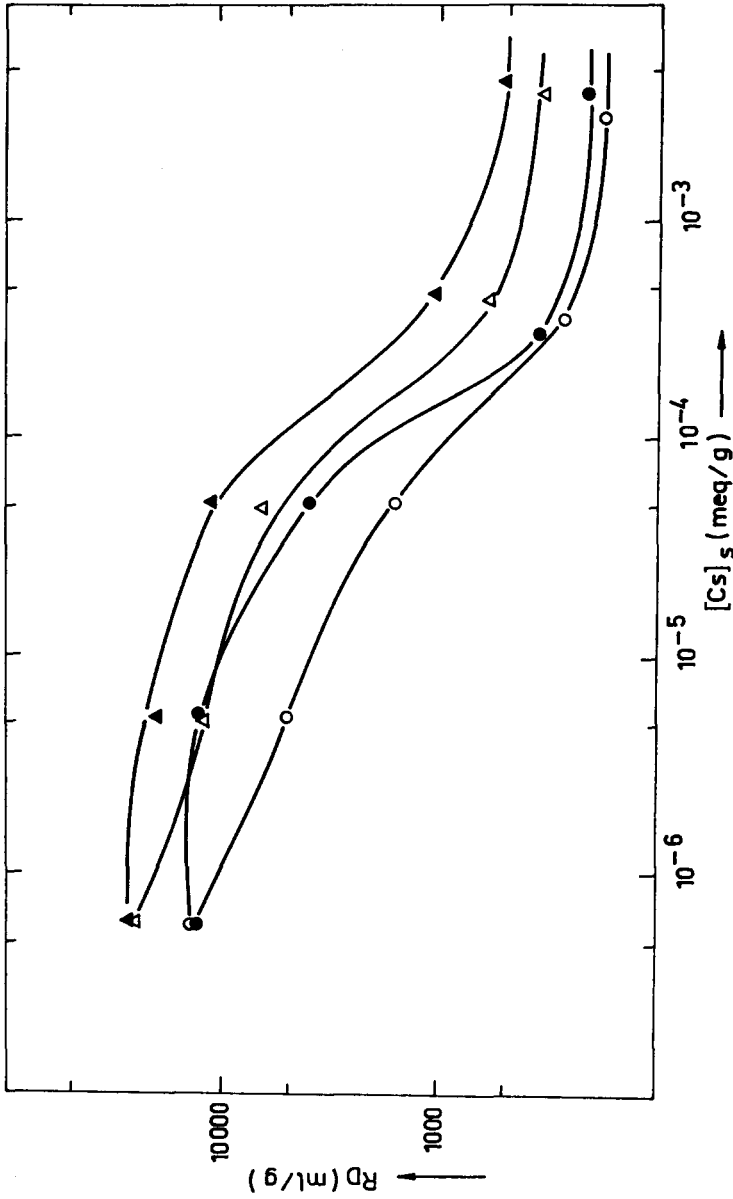


Fig 13 The change of R_d values with cesium ion loading for Sarayköy soil fractions.

- ▲ Adsorption, particle size $< 5 \mu\text{m}$
- △ Desorption, particle size $< 5 \mu\text{m}$
- Adsorption, particle size $< 20 \mu\text{m}$
- Desorption, particle size $> 20 \mu\text{m}$

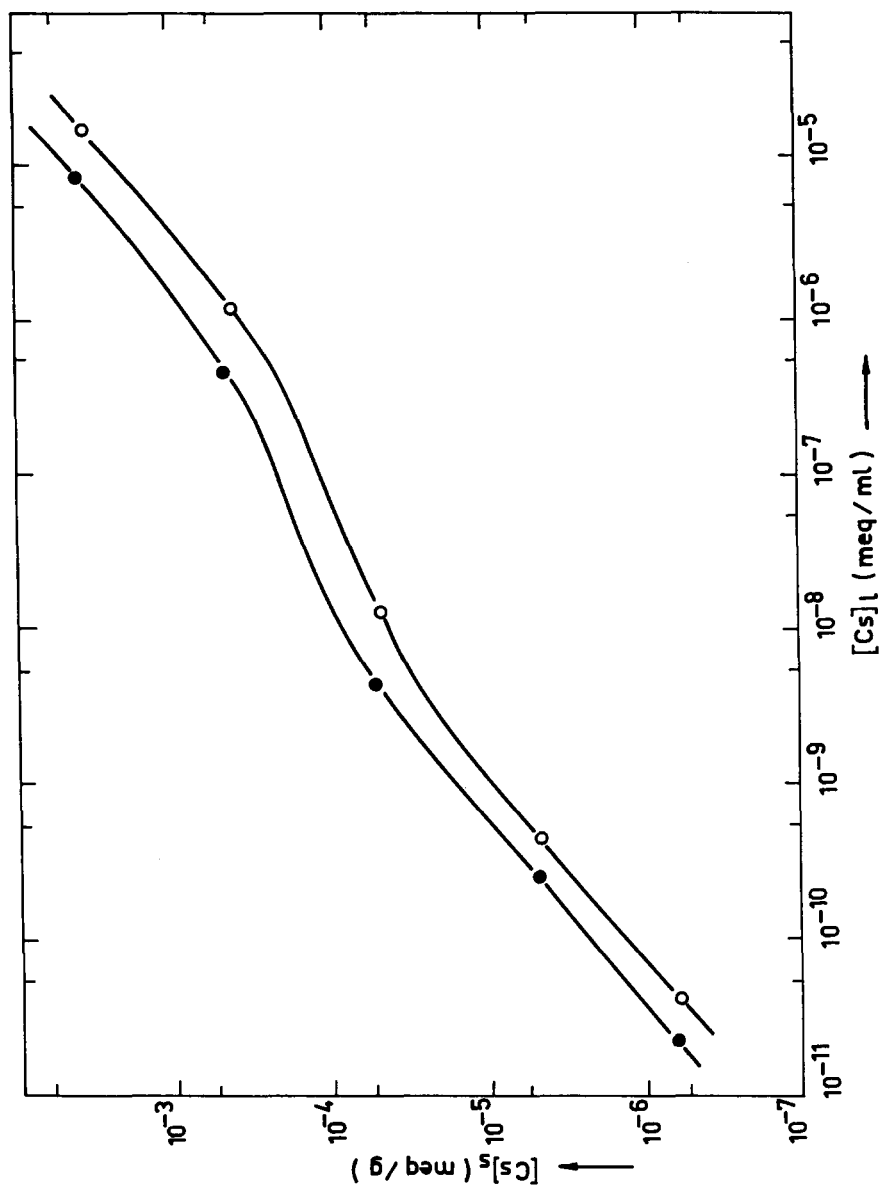


Fig 14 Sorption Isotherms of Saraykőy soil fractions.

- Particle size $< 5 \mu m$
- Particle size $> 5 \mu m$

The sorption behaviour of Cs cation with Resadiye clay was found to be similar to Mihaliççik clay with somewhat higher R_D values. As an illustration, the sorption kinetics are shown in Fig 11 for $[Cs]^\circ = 1.02 \times 10^{-8}$ meq/ml. The greater R_D values for larger particle size is not well understood.

The results of sorption studies using Sarayköy soil fractions are shown in Figs 12, 13 and 14. Fig 12 shows the change of R_D values with time for various particle size fractions. The large values of R_D as compared to those using pure clay fractions is striking. This may be due to the presence of organic components, particularly humic acid in the soil fractions. Increase in R_D values with decrease in particle size suggests primarily a surface phenomenon as in the case of Mihaliççik clay. The change of R_D values with Cs ion loading is shown in Fig 13. Similar characteristic curves as in the case of pure clay samples is observed. Fig 14 shows the adsorption isotherm. Again it is nonlinear.

It may be concluded that various clay and soil fractions adsorb or desorb caesium cation in a similar way. The differences observed are only in the magnitudes of R_D values which may be a reflection of their different cation exchange capacities.