Sorption–Desorption Behaviour of Barium on Clays*

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ABSTRACT

*Batch experiments were performed to study the sorption behaviour of
Ba^{2+} ion on three different clay minerals determined to be predominantly
kaolinite, montmorillonite and mixed chlorite–illite. Synthetic ground-
water was used and the concentration of Ba^{2+} ion was in the range of 10^{-8}
to 10^{-4} N. Grain sizes of the solid particles were all $<38\ \mu m$. Cation
exchange capacities were obtained using the silver–thiourea (AgTU)
method. The variation of R_D values was studied as a function of contact
time, shaking rate, Ba^{2+} ion concentration, v/m ratio and pH. The
saturation time varied with each type of clay; about 6, 8 and 12 days of
shaking time were necessary for chlorite–illite mixed clay, kaolinite and
montmorillonite respectively. Shaking rate affected only the rate of sorp-
tion and not the saturaton R_D values. Sorption was found to be reversible
on kaolinite and partly reversible on montmorillonite and chlorite–illite
clays. The variation of R_D as a function of Ba^{2+} ion concentration
exhibited characteristic inverse S-shaped curves suggesting the presence of
at least two different types of exchange sites. Sorption of Ba^{2+} ion was
observed to depend on pH and v/m ratio. The sorption isotherms were
found to fit Freundlich and Dubinin–Radushkevich type isotherms well.*

INTRODUCTION

Disposal of nuclear wastes in geologic media is believed to be an adequate
way of providing the necessary protection for humans and the environ-

183

ment. Since sorption in geologic media is an important mechanism for the delay of radionuclide migration to the biosphere and the food chain, sorption and desorption characteristics of radionuclides should be investigated in order to estimate rates of transport of the nuclides in the event of water penetration into and through the waste repository. Possible mechanisms in rock–nuclide interactions are physical sorption, chemisorption, ion-exchange, precipitation, substitutions of ions in the crystal lattice and diffusion into the rock matrix followed by sorption in the solid. These mechanisms differ in kinetics, reversibility, pH-dependence, etc. Thus, various chemical and physical parameters would have a large influence on the sorption of a radionuclide on a solid. Because clays have been proposed as suitable backfill materials for the storage of radioactive waste, there has been an increasing interest in the studies of sorption behaviour of various radionuclides on clays (Torstenfelt et al., 1981; Grütter et al., 1986; Torstenfelt, 1986; Berry et al., 1988).

Our previous work on sorption has been concerned with the fission products cesium and strontium (Erten et al., 1988a; Erten et al., 1988b). Surveying the literature on the subject, it appears that the sorption of barium has not been extensively studied. We have therefore decided to investigate the sorption behaviour of barium on clays. ^{140}Ba ($t_{1/2}$ = 12·8 d) is a serious radiocontaminant during the first 100 days when fission products are discharged into the environment from sources such as nuclear power plants (routinely or accidentally) and from nuclear weapons testing. Furthermore, Ba^{2+} lies between Sr^{2+} and Ra^{2+} which are the most interesting nuclides of Group 2A with respect to radioactive waste considerations. Therefore, as a representative of the alkali-earth homologs, barium is a suitable element to study. ^{133}Ba was chosen as a tracer because of its long half-life (10·7 year) and well observable γ-ray 356 keV energy.

EXPERIMENTAL

Clay minerals

Clay minerals from three regions of Turkey, Sındırgı, Giresun and Afyon, were used in the Ba^{2+} ion sorption studies. X-ray diffraction analysis and infrared spectrometry were used for identification. The X-ray patterns as shown in Fig. 1 indicated that the clays were predominantly of kaolinite, montmorillonite and chlorite–illite types. Size fractionation of the minerals was accomplished by sieving and sedimentation (Loomis, 1938; Norton & Speil, 1938). Montmorillonite and kaolinite clays were separated into three different grain sizes, <5 μm, 5–10 μm and 10–30 μm. A natural
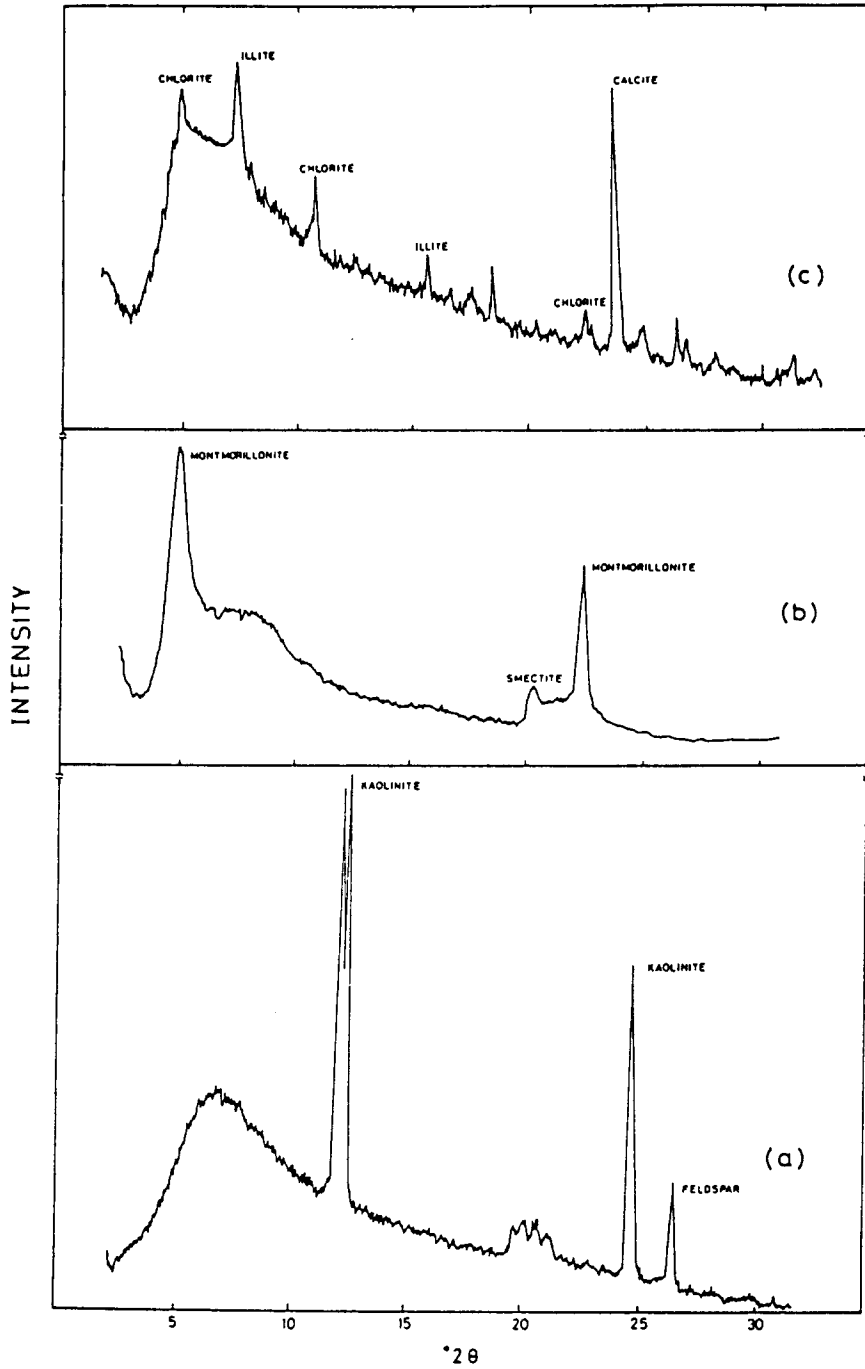
Fig. 1. X-ray diffraction spectra of clay samples (CuK$_\alpha$ radiation): (a) Sındırgı clay; (b) Giresun clay; (c) Afyon clay.

mineral sample containing mainly chlorite–illite mixed clay was not a pure sample. It was passed only through a 38 μm sieve and was used without further fractionation. Cation exchange capacities (CEC) of the clay minerals were determined by measuring the silver remaining in solution after silver–thiourea (AgTU) extraction (Searle, 1986).

TABLE 1

Chemical Composition of Synthetic Groundwater Samples Used in the Sorption Studies

Component (meq/l)	Sındırgı	Giresun	Afyon
Na^+	0.89^a	0.22	2.08
K^+	—	0.01	0.40
Ca^{2+}	4.70	2.28	5.46
Mg^{2+}	3.15	0.30	3.38
$CO_3^{2-\,b}$	0.17	0.28	0.90
NO_3^-	3.14	1.34	4.48
Cl^-	0.84	0.02	0.25
$SO_4^{2-\,b}$	0.18	0.10	0.82
pH	7.2	6.5	7.1

^{a}$Na^+ + K^+$ concentration.

^{b}Carbonate and sulphate were replaced by nitrate when sorption studies were carried out at higher initial Ba^{2+} ion concentration.

Synthetic groundwater

Synthetic groundwaters having similar compositions to the groundwaters of the three regions were used in sorption experiments. Bicarbonate ions, however, were largely replaced by nitrate ions in order to prevent carbonate precipitation. Table 1 gives the synthetic groundwater compositions used in the sorption studies.

Procedure

The sorption experiments were carried out using the batch technique. Weighed amounts of clay samples were kept in contact with known volumes of solution for certain times. Polypropylene centrifuge tubes with caps were used throughout. A typical sorption experiment employed approximately 50 mg clay (dry weight) and 4 ml solution resulting in a liquid–solid ratio of 80 ml/g. The samples were shaken at room temperature using a circular type shaker with a speed of 190 rpm. Phase separations were achieved by centrifuging at a speed of 12 000 rpm for about 30 minutes.

[133]Ba ($t_{1/2}$ = 10·7 year) purchased from the Radiochemical Center, Amersham was used as tracer. Activity measurements were made by means of a NaI(Tl) detector.

In the pretreatment step, clays were equilibrated with the synthetic groundwater. The concentrations of the major cations and the pH of the pretreatment solution changed only slightly during this step.

At the beginning of the sorption step, synthetic groundwater containing [133]Ba was added to the samples. Barium concentrations between $1·56 \times 10^{-8}$ N and $1·53 \times 10^{-3}$ N were used. The sorption time varied from 1 hour to 28 days. In the desorption studies, Ba-free synthetic groundwater was used following the adsorption step.

Concentration and distribution ratio calculations

The distribution ratio is defined as:

$$R_{D,ad} = \frac{[Ba]_{s,ad}}{[Ba]_{ad}} \tag{1}$$

where $[Ba]_{s,ad}$ = concentration of barium in the solid phase after sorption (meq/g) and $[Ba]_{ad}$ = concentration of barium in the solution after sorption (meq/ml).

Since at the beginning of the sorption step V (ml) of solution with concentration $[Ba]^0$ is added and at the end of the sorption step ($V + \Delta W_{pt}$) ml of solution with concentration $[Ba]_{ad}$ are present, the concentration of Ba in the solid phase after sorption is given by:

$$[Ba]_{s,ad} = \frac{V[Ba]^0 - [Ba]_{ad}(V + \Delta W_{pt})}{W_s} \tag{2}$$

$[Ba]_{ad}$ may be defined in terms of activity as

$$[Ba]_{ad} = \frac{A_{1,ad}}{A^0}[Ba]^0 \tag{3}$$

From eqns (1), (2) and (3) the following equation is obtained:

$$R_{D,ad} = \frac{VA^0 - A_{1,ad}(V + \Delta W_{pt})}{A_{1,ad}W_s} \tag{4}$$

Here, A^0 = initial count rate of solution added for sorption (cps);

$A_{1,ad}$ = count rate of solution after sorption (cps); W_s = weight of solid material (g); V = volume of solution (ml); and ΔW_{pt} = amount of liquid remaining in the tube after pretreatment, before sorption (g).

For desorption studies, using similar equations as above, the following relation for the distribution ratio is derived;

$$R_{D,de} = \frac{VA^0 - A_{1,ad}(V + \Delta W_{pt} - \Delta W_{ad}) - A_{1,de}(V + \Delta W_{ad})}{A_{1,de}W_s} \qquad (5)$$

where, ΔW_{ad} = the amount of liquid remaining in the tube after sorption and decantation (g); and $A_{1,de}$ = count rate of solution after desorption (cps).

RESULTS AND DISCUSSION

The particle size distributions of the three clay minerals were obtained by the Andreasen pipette method (Loomis, 1938; Norton & Speil, 1938) and are shown in Fig. 2. Kaolinite type clay is seen to have the highest fraction of smaller size particles.

CEC values, determined experimentally via the AgTU complex, were also calculated from the Dubinin-Radushkevich isotherm model. The results are shown in Table 2 together with the literature values. The CEC values of kaolinite and chlorite–illite type clays are in very good agreement

TABLE 2
Cation Exchange Capacities of the Clay Minerals Used for Ba^{2+} Sorption Studies

Clay	CEC (meq/100 g)			
	d (μm)	Literature	Experimental[a]	Model[b]
Kaolinite	<5		5	4
	5–10	3–15	9	9
	10–30		5	4
Montmorillonite	<5		22	22
	5–10	70–100	21	21
	10–30		19	21
Chlorite–illite	<38	10–40	15	16

[a]Determined experimentally using the Silver–Thiourea method.
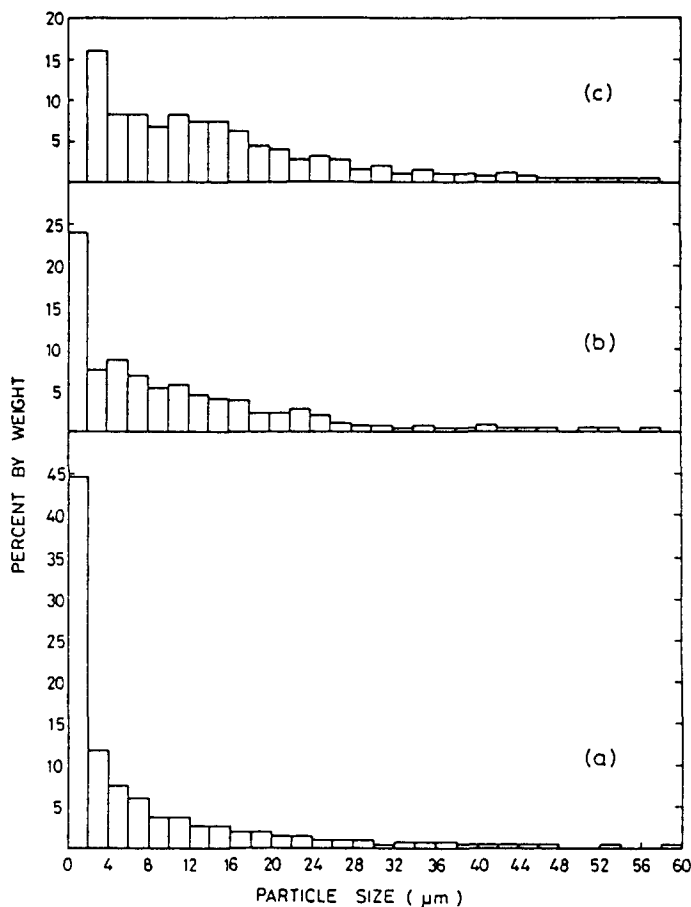[b]Calculated from the Dubinin–Radushkevich isotherm model.

Fig. 2. Size distributions of clay samples. Per cent by weight against particle size: (a) Sındırgı clay; (b) Giresun clay; (c) Afyon clay.

with the literature data, whereas those for montmorillonite differ considerably. This probably reflects the CEC method used, silver–thiourea being a bulky complex and hence unable to exchange with the cations present between the layers in montmorillonite-like clays, for which the ion exchange capacity is mostly determined by the cations present at the sites located along the interlattice layers. Cremers *et al.* (1988) used the AgTU complex method in order to analyse quantitatively the number and selectivity pattern of different sites in various clay minerals, by masking these sites on the crystal edges using AgTU and letting ion exchange take place only at the sites located between layers.
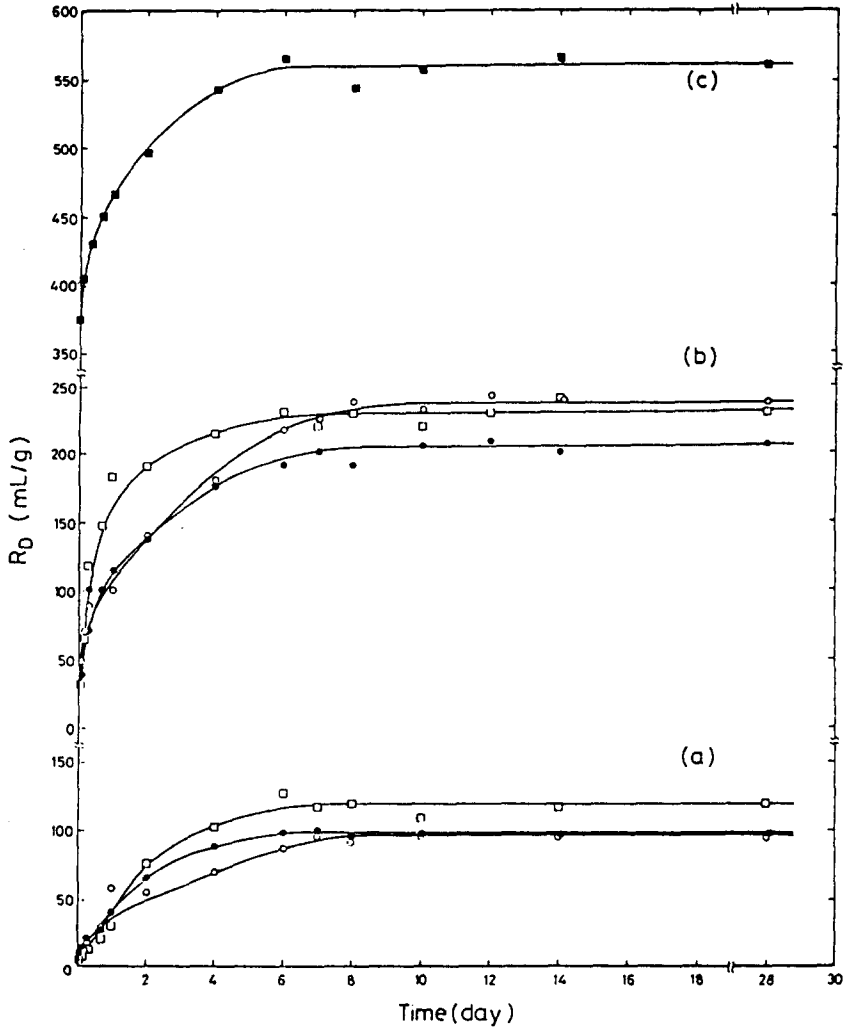
Fig. 3. Sorption kinetics. Change of R_D with contact time (initial Ba^{2+} ion concentration = 1.56×10^{-8} meq/ml). (a) Kaolinite particle size: O, $<5 \times 10^{-6}$ m; □, $5-10 \times 10^{-6}$ m; ●, $10-30 \times 10^{-6}$ m. (b) Montmorillonite particle size: O, $<5 \times 10^{-6}$ m; □, $5-10 \times 10^{-6}$ m; ●, $10-30 \times 10^{-6}$ m. (c) Chlorite–illite mixed clay particle size: ■, $<38 \times 10^{-6}$ m.

Kinetic studies

Kinetic studies were performed using two Ba^{2+} concentrations, 1.56×10^{-8} N and 1.53×10^{-5} N and various grain sizes. The results are shown in Fig. 3. It is observed that saturation is achieved at 6, 8 and 10 days of shaking for chlorite–illite mixed clay, kaolinite and montmorillonite
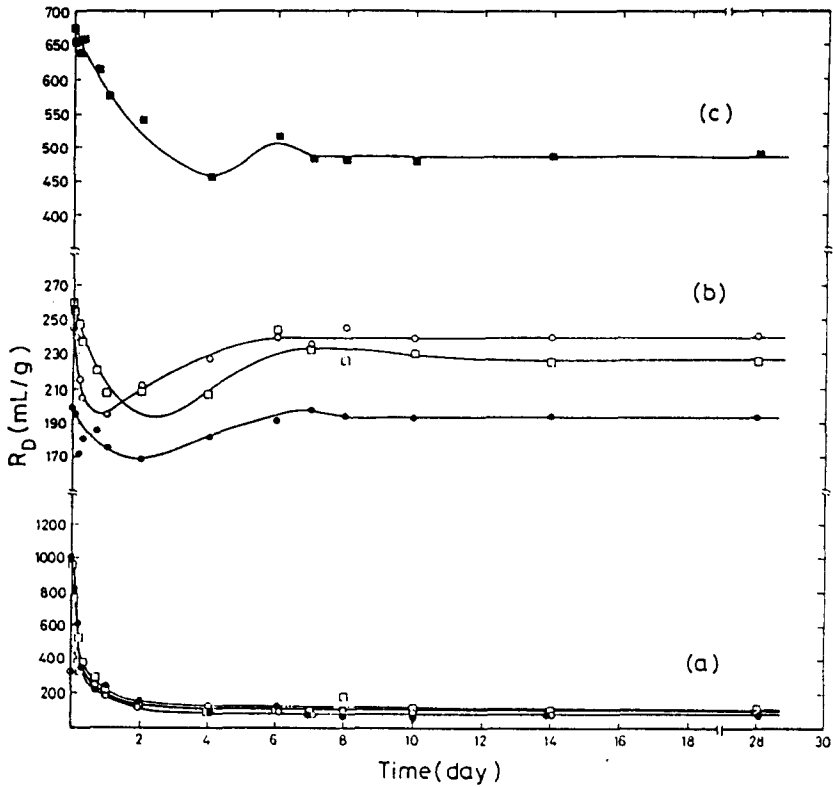
Fig. 4. Desorption kinetics. Change of R_D with contact time (initial Ba^{2+} ion concentration = 1.56×10^{-8} meq/ml). (a) Kaolinite particle size: ●, $<5 \times 10^{-6}$ m; □, $5–10 \times 10^{-6}$ m; ○, $10–30 \times 10^{-6}$ m. (b) Montmorillonite particle size: ○, $<5 \times 10^{-6}$ m; □, $5–10 \times 10^{-6}$ m; ●, $10–30 \times 10^{-6}$ m. (c) Chlorite–illite mixed clay particle size: ■, $<38 \times 10^{-6}$ m.

respectively. The ion exchange properties of kaolinite are generally believed to reflect broken bonds and possibly OH bonds on the surface of the clay particles (Carroll, 1959). It was thus expected that distribution ratios for kaolinite would exhibit a dependence on the particle size, as was previously observed with Cs^+ and Si^{2+} cations in our studies (Erten *et al.*, 1988a; Erten *et al.*, 1988b). However, such a strong dependence was not observed. On the other hand, montmorillonite had higher R_D values at smaller grain sizes, indicating surface area dependence. In the case of chlorite–illite mixed clay, since the percentage of small particles was markedly low (Fig. 2), sorption experiments were performed using unseparated grains. The desorption kinetic studies, as illustrated in Fig. 4, indicate rapid initial desorption for all clay types, followed by readsorption until saturation for montmorillonite.
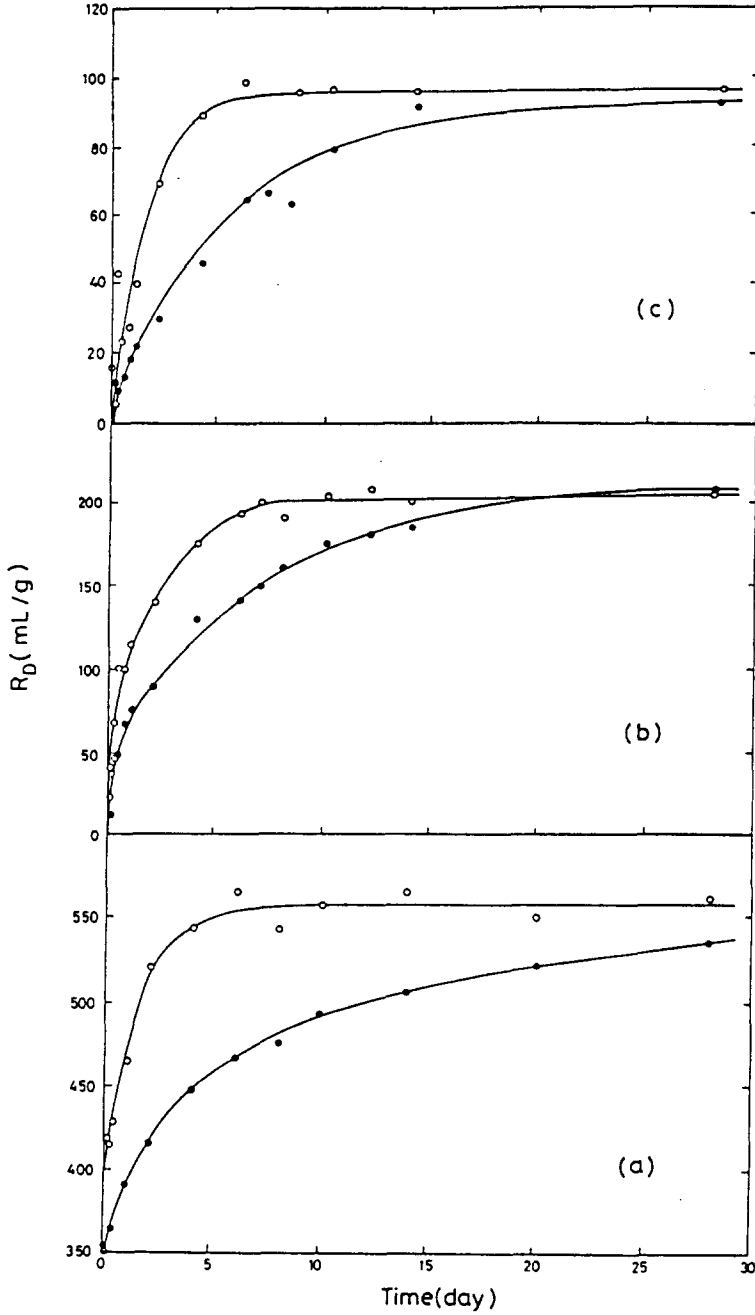
Fig. 5. Sorption kinetics. Variation of R_D as a function of time (initial Ba^{2+} ion concentration $= 1.56 \times 10^{-8}$ meq/ml): (a) chlorite–illite mixed clay; (b) montmorillonite; (c) kaolinite. $\bigcirc$, Samples were shaken at a rate of 190 rpm; $\bullet$, samples were not shaken.

In order to investigate the effect of water composition on sorption, pretreatment water was used in studying the sorption kinetics of kaolinite. Almost the same R_D values were obtained with pretreatment water as with synthetic water. Equilibrium was attained in a shorter time, however, when pretreatment water was used.

It is sometimes argued that shaking may lead to the creation of fresh fracture surfaces, thus increasing the surface area in contact with the solution and hence perhaps causing an increase in the distribution ratio. It was therefore decided to investigate the effect of shaking rate by carrying out sorption experiments without shaking of the samples as well as shaking at a rate of 190 rpm. The results are shown in Fig. 5. It is seen that the rate of sorption is strongly affected by shaking. Saturation was reached after longer times for unshaken samples. The saturation R_D values, however, do not differ significantly from one another. Thus no significant abrasion effect was observed, reflecting itself in higher R_D values for samples that were shaken during sorption.

Rate of sorption

If sorption follows first order kinetics, plots of the logarithm of the activity remaining in the aqueous phase against time are expected to be linear in the pre-equilibrium region. Such linear dependence was not observed in our sorption studies (Fig. 6). In order to resolve two or more overlapping mechanisms and/or rate constants, the analogy with a mixture of independently decaying readioactive species was used (Tunalı *et al.*, 1974). The results are shown in Fig. 6. Two different first order rate constants, with corresponding initial activities, were obtained for all clay samples. The results of the analysis are given in Table 3. In kaolinite, sorption was observed to take place predominantly with the slow mechanism. Since sorption in kaolinite takes place mostly on the surfaces and at the edges and with little sorption between the layers, the two mechanisms found can be ascribed to the sorption of Ba^{2+} ion on the surfaces and at the edges of kaolinite respectively. In the case of montmorillonite, the two mechanisms reflected by the two different rate constants probably represent adsorption on the surface and between layers respectively. The percentage of the two types of sorption are about equal as may be seen from the magnitudes of the A^0 values in Table 3. The chlorite–illite mixed clay was observed to sorb Ba^{2+} ion predominantly via the fast mechanism. The two rate constants observed in the sorption kinetic studies may also reflect the exchange of the Ba^{2+} ion with different bound cations such as Na^+, K^+, Ca^{2+}, etc., rather than different mechanisms of sorption. In order to study this kind of sorption, experiments were carried out to measure the extent
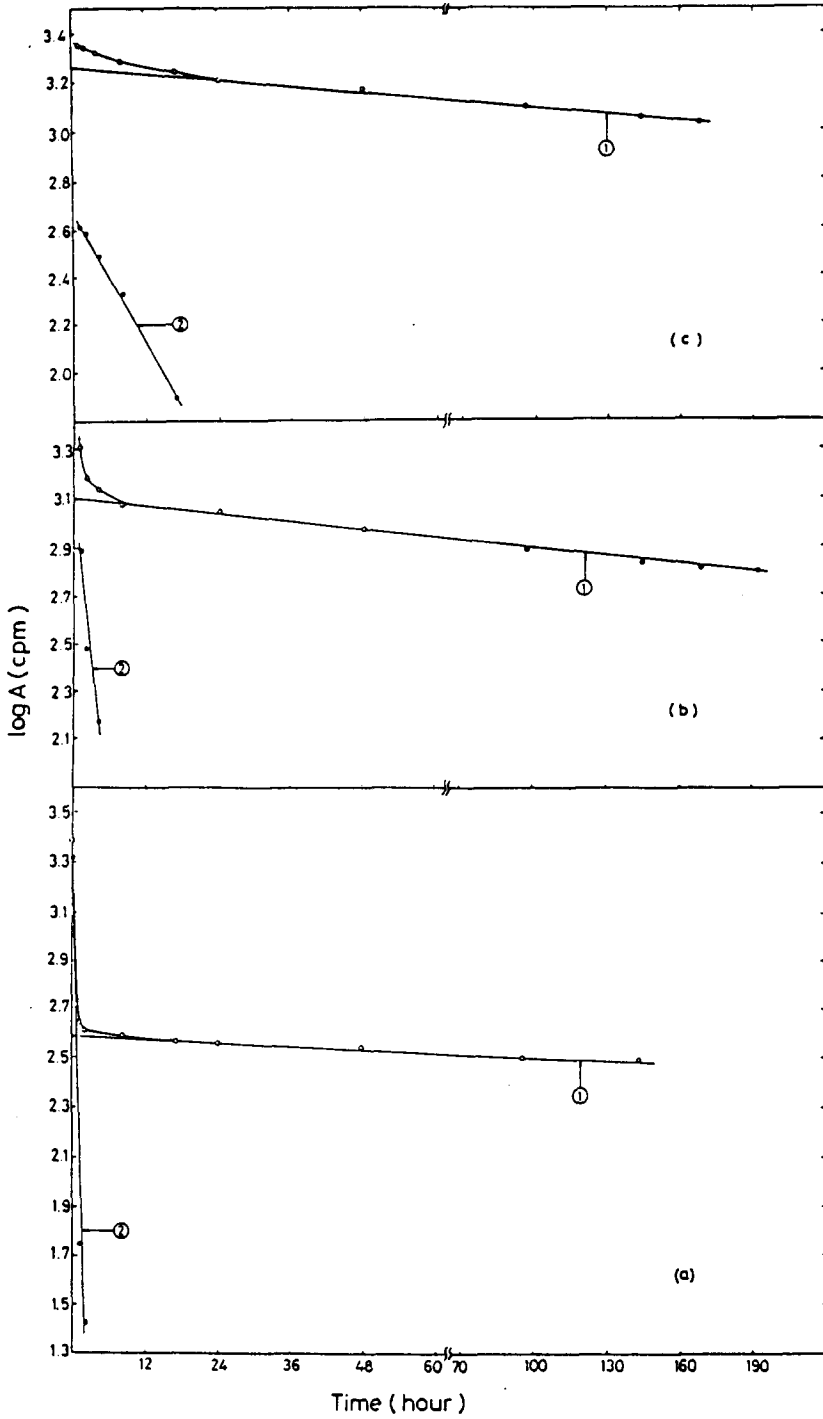
Fig. 6. Sorption kinetics. Plots of the logarithm of the activity remaining in the liquid phase as a function of time: (a) chlorite–illite mixed clay; (b) montmorillonite; (c) kaolinite.

TABLE 3
Parameters Obtained from Curve Resolution

Type of clay	A_1^0 (cpm)	A_2^0 (cpm)	k_1 (h⁻¹)	k_2 (h⁻¹)
Kaolinite	1 819·7	467·7	$1·7 \times 10^{-3}$	$4·5 \times 10^{-2}$
Montmorillonite	1 258·9	1 120·0	$1·9 \times 10^{-3}$	$2·3 \times 10^{-1}$
Chlorite–illite	380·2	2 089·3	$6·0 \times 10^{-4}$	$9·5 \times 10^{-1}$
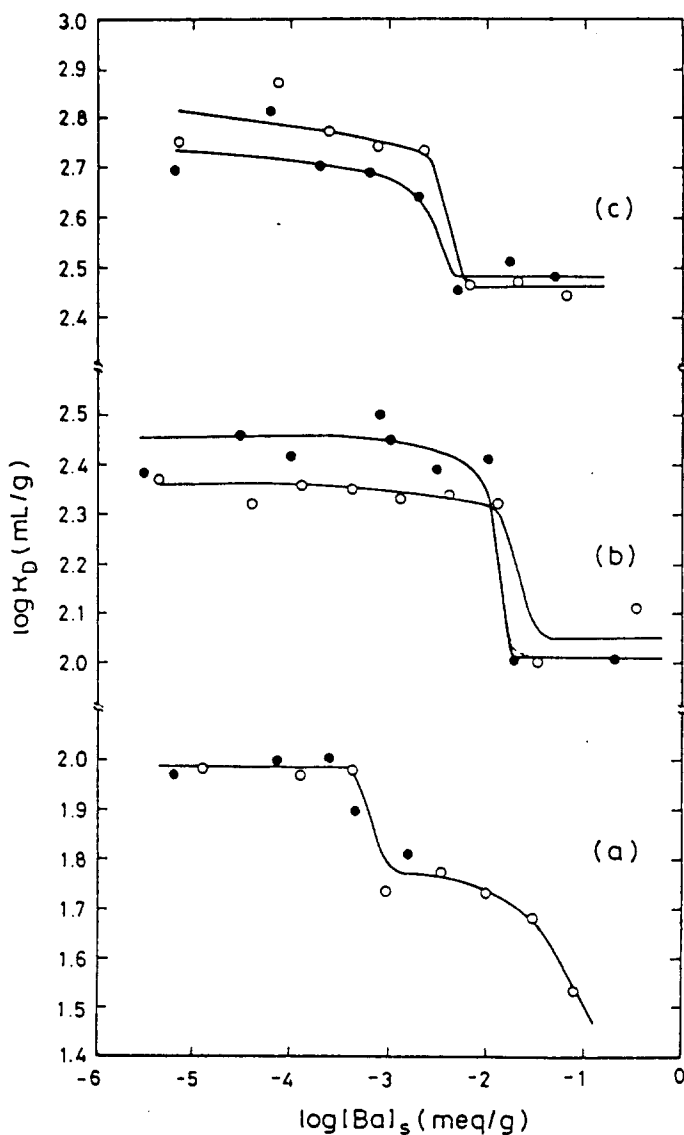
Fig. 7. Variation of R_D as a function of Ba²⁺ ion loading. (a) kaolinite; (b) montmorillonite; (c) chlorite–illite. ○, Sorption; ●, desorption.

of exchange of Ba^{2+} ion with K^+, Ca^{2+}, Sr^{2+} and Al^{3+} ions. The clay samples were first saturated with the respective cations given above and then sorption experiments with Ba^{2+} ion were carried out. The results indicate that Ba^{2+} exchanges most easily with K^+ followed by Ca^{2+}, Sr^{2+} and Al^{3+} ions respectively.

Influence of cation concentration on sorption

The variation of the distribution ratio as a function of Ba^{2+} ion loading for three clay types is shown in Fig. 7. The standard deviation of R_D values was less than 10% in all measurements. R_D values are not expected to show any concentration dependence if they are true equilibrium constants. They were, however, found to vary with the Ba^{2+} ion concentration and to exhibit typical inverse S-shape curves suggesting the presence of different exchange sites, as was found in the kinetic studies. These exchange sites may be divided into three types (Sawhney, 1972; Brouwer *et al.*, 1983; Evans *et al.*, 1983): (1) sites on the planar surfaces. Sorption on kaolinite probably takes place at these sites where sorption is usually reversible; (2) sites at the edges of clay interlayers. These sites would be accessible only to cations having the same size and charge as the bound cations; (3) sites along the interlattice layers of collapsed or non-expanding clay minerals. Sorption of cations on these positions is mostly irreversible. Sorption of Ba^{2+} ion on montmorillonite and chlorite–illite mixture which was observed to be partly reversible seems to take place at type (1), (2) and (3) sites.

Sorption isotherms

The sorption isotherms are shown in Fig. 8. The isotherms were fitted to three different types of isotherm equations (NEA, 1983), namely Langmuir, Freundlich and Dubinin-Radushkevich. The parameters obtained in these fittings are given in Table 4. The sorption isotherms are described well by Freundlich and Dubinin-Radushkevich equations. The corresponding empirical relation has been obtained as

$$R_D = K[Ba^{2+}]^{N-1} \tag{6}$$

from the Freundlich isotherm. Here, K and N are constants and $[Ba^{2+}]$ = concentration of Ba^{2+} ion in the solution after sorption (meq/ml). From the Dubinin-Radushkevich isotherm the equation

$$R_D = [Ba^{2+}]^{-1} X \exp\{- K[RT \ln(1 + [Ba^{2+}]^{-1})^2]\} \tag{7}$$

is obtained. Here, X = cation exchange capacity per unit weight; R = gas constant; T = temperature (K); and K = constant.
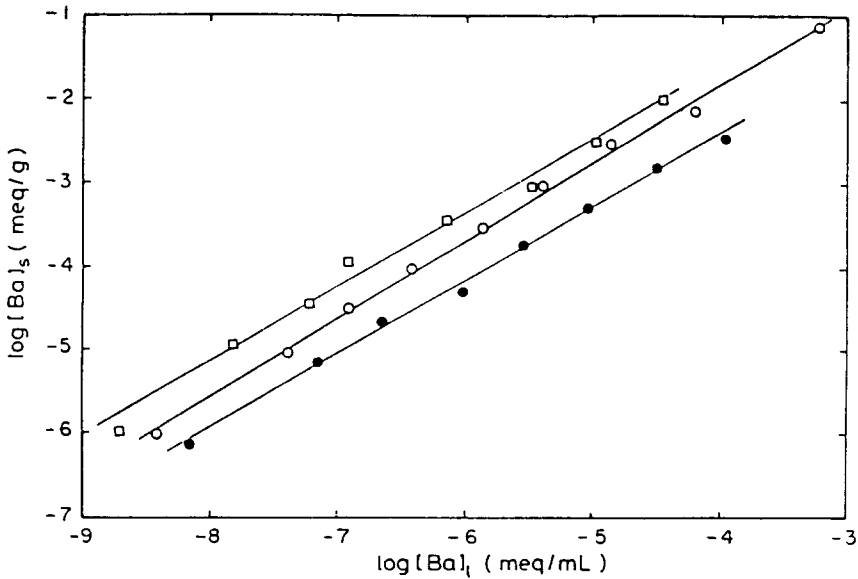
Fig. 8. Sorption isotherms of Ba^{2+} ion for the three clay samples: ●, kaolinite; ○, montmorillonite; □, chlorite–illite mixed clay.

TABLE 4

Empirical Parameters Obtained from Fits to Various Isotherm Models

Isotherm model	Parameters	Kaolinite	Montmorillonite	Chlorite–illite
Langmuir	X_m	0·002 1	0·076	0·006 1
	$1/b$	$2·25 \times 10^{-5}$	$3·51 \times 10^{-4}$	$8·32 \times 10^{-6}$
	C^a	0·75	0·65	0·59
Freundlich	K	7·5	86·0	98·5
	N	0·84	0·94	0·89
	C^a	1·00	1·00	1·00
Dubinin-Radushkevich	X	0·054	0·22	0·16
	K	$6·7 \times 10^{-5}$	$6·0 \times 10^{-5}$	$5·0 \times 10^{-5}$
	C^a	1·00	0·99	0·99

[a] Linear correlation coefficient.

Experimental R_D values were found to be in good agreement with those calculated using the empirical R_D equations.

Differences in sorptivities of various size particles may be attributed to their different cation exchange capacities. If the sorption curves of different grain sizes are normalized with respect to their CECs, this difference is expected to decrease. For kaolinite, normalization removed the differences at low Ba^{2+} loadings, whereas in the high Ba^{2+} region, the curves were still different, indicating the presence of other factors. In the case of montmorillonite, normalization removed the differences at all Ba^{2+} loadings.

The effect of pH and volume–mass ratio on sorption

The influence of pH on Ba^{2+} ion sorption was studied in the pH range 3–11. The pH adjustment of the SGW was carried out using NaOH and HNO_3. Sorption was observed to increase slightly with increase in pH for

TABLE 5
Steady State R_D Values for Ba^{2+} Ion Sorption on Clays

Clay	R_D (ml/g)
Kaolinite	127
Montmorillonite	238
Chlorite–illite	745

kaolinite and chlorite–illite. For montmorillonite, Ba^{2+} sorption passed through a minimum around pH 8 and increased considerably beyond that.

The influence of v/m ratio on the sorption of Ba^{2+} ion on chlorite–illite was investigated in the range of 10/1 to 200/1 ml/g. The R_D values slightly increased with increase in the volume–mass ratio within the range studied.

The highest observed steady state R_D values for the sorption of Ba^{2+} ion on the three different clays are given in Table 5. The chlorite–illite mixed clay is apparently the best sorbent for Ba^{2+} ion, despite the higher CEC of montmorillonite. This is probably due to the organic content of chlorite–illite mixed clay, which was determined (Jackson, 1958) to be about 5%, and to other structural characteristics. Tamura & Jacobs (1960), Jacobs & Tamura (1961) and Sawhney (1964), observed similar behaviour for Cs^+ ion sorption; non-expanding layer silicates, illite and micas sorbed more Cs from solution than did the expanding layer silicates, montmorillonite and vermiculite.

CONCLUSIONS

There are significant differences in the sorption behaviour of the three clays studied. The highest R_D values were obtained with chlorite–illite mixed clay followed by montmorillonite and kaolinite.

The distribution ratios tend to reach equilibrium in several days. Montmorillonite type clay reached equilibrium in the longest time. Generally, the distribution ratios were found to increase with decreasing particle size, reflecting mainly surface sorption processes.

Sorption was observed to take place in two stages each with a different rate constant in all clay types studied. In kaolinite, Ba^{2+} ion sorption occurred mainly on the surfaces and at the edges. In the case of chlorite–illite mixed clay and montmorillonite, appreciable amounts of Ba^{2+} ion were sorbed between the layers. Sorption was reversible in kaolinite and partially reversible in chlorite–illite and montmorillonite.

Distribution ratios varied with the initial Ba^{2+} ion concentration, giving characteristic inverse S-shape curves. Sorption isotherms were best described by Freundlich and Dubinin-Radushkevich type equations.

Volume to mass ratio did not influence sorption of Ba^{2+} ion strongly. Increase in the v/m ratio resulted in a slight increase in R_D values.

Sorption of Ba^{2+} on chlorite–illite and kaolinite was observed to increase slightly with increase in pH, whereas sorption of Ba^{2+} on montmorillonite depended strongly on pH; increase in both acidity and basicity of the solution led to increase in Ba^{2+} ion sorption.

ACKNOWLEDGMENT

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