

SORPTION BEHAVIOR OF Co^{2+} , Zn^{2+} AND Ba^{2+} IONS ON ALUMINA, KAOLINITE AND MAGNESITE

H. N. ERTEN, Z. GOKMENOGLU

Department of Chemistry, Bilkent University, 06533 Bilkent, Ankara (Turkey)

(Received January 24, 1994)

The sorption behavior of Ba^{2+} , Co^{2+} and Zn^{2+} ions on alumina, kaolinite and magnesite have been investigated using the batch method. ^{60}Co , ^{65}Zn and ^{133}Ba were used as radiotracers. The mineral samples were separated into different particle size fractions using an Andreasen Pipette. The particle sizes used in the sorption experiments were all less than $38\ \mu\text{m}$. Synthetic groundwaters were used which had compositions similar to those from the regions where the minerals were recovered. The samples were shaken with a lateral shaker at 190 rpm, the phases were separated by centrifuging and radioactivity counted using a NaI(Tl) detector. Kinetic studies indicated that sorption onto the minerals took place in two stages with the slower process dominating. The highest sorption was observed on alumina. Both Freundlich and Dubinin-Radushkevich type isotherms were found to describe the sorption process well. The distribution ratio, R_d , was found to be a function of the liquid volume to solid mass ratio. The R_d 's for sorption on binary mixtures of minerals were experimentally determined and compared with those predicted from R_d values of each individual mineral.

The need for ultimate disposal of nuclear wastes has stimulated a renewal of interest in the adsorption behavior of fission products as well as some activation product nuclides on minerals of the type found around the various types of proposed repositories. The typical repository is a chemical system with a stationary solid phase and a mobile groundwater phase. The composition of both phases influences the transport of radionuclides from their disposal sites. Other factors include pH, redox potential and temperature. Adsorption data are needed for the estimation of transport rates of these nuclides in the event of water penetration into the repository.

Most of the literature work on sorption was carried out using the batch method. Mainly cation sorption on various clay minerals were studied. The adsorbent was either a pure mineral, a mixture of minerals or natural soil. Comparisons were made in terms of the magnitude of the distribution ratio R_d . In some cases the effect of pH of the aqueous phase, and the cation concentration on the sorption process was examined.¹⁻¹⁵

The objective of the present work was to study the sorption behavior of Co^{2+} , Zn^{2+} and Ba^{2+} ions on kaolinite, magnesite and alumina. ^{60}Co (5.22 y), ^{65}Zn (244.10 d) and ^{133}Ba (10.5 y) were used as radiotracers. ^{140}Ba (12.79 d) is a fission product with a high yield and both ^{60}Co and ^{65}Zn are activation products. All are important in radioactive waste considerations.

Experimental

Minerals: The magnesite, alumina and kaolinite minerals used in the sorption experiments were obtained from the Mineral Research Institute (M.T.A.) in Ankara. The chemical composition of the minerals are given in Table 1. The particle size distributions of the minerals were determined using an Andreasen Pipette.¹⁶⁻¹⁷ Prior to each experiment the sample tubes were put into an ultrasonic bath for about five minutes. In this treatment the smaller sized particles attached onto the larger grains and the agglomerates were broken up. The particle sizes of solid samples used in our experiments were all less than 38 μm .

Synthetic groundwater: Experiments were carried out using synthetic groundwaters, prepared based on the composition of the groundwaters from the three regions Seydisehir, Mihalicik and Beysehir where the minerals alumina, kaolinite and magnesite were obtained, respectively. The composition of natural groundwaters from the three regions are given in Table 2. Bicarbonate was largely replaced by nitrate

Table 1
Chemical composition of the minerals used in the sorption experiments

Mineral component	Composition, %		
	Alumina	Magnesite	Kaolinite
SiO_2	–	8.2	72.79
Al_2O_3	99.99	0.34	17.48
Fe_2O_3	–	0.19	1.20
TiO_2	–	0.01	0.35
CaO	–	2.88	0.15
MgO	–	42.83	0.20
Na_2O	–	0.07	0.33
K_2O	–	–	0.32
Heat loss	–	45.19	6.58

because carbonate species in natural groundwaters are not in equilibrium with the atmospheric CO_2 .

Sorption studies: The solid phase was pretreated with synthetic groundwater prior to sorption experiments. Sorption studies were then carried in polypropylene centrifuge tubes. A known weight of solid and 4 ml of the liquid phase containing a certain initial amount of the cation of interest and its radiotracer were shaken together. After shaking for about 6–8 days with a lateral shaker at 190 rpm the phases were separated by centrifuging at a speed of 12,000 rpm for 30 minutes. The distribution ratios were

determined by counting 1 ml of the aqueous phase before and after sorption with a well type NaI(Tl) detector. In the desorption studies, the liquid phase following adsorption was centrifuged and discarded. 4 ml of the synthetic groundwater was added to each tube and shaken for the desired sorption time. The samples were then centrifuged and

Table 2
Chemical composition of groundwaters from the three regions
where the mineral samples were taken

Component	Composition, meq/ml		
	Seydisehir	Mihaliccik	Beysehir
Na^+	2.17	1.15	0.48
K^+	0.24	0.08	0.15
$\text{Ca}^{2+} + \text{Mg}^{2+}$	7.00	7.73	6.80
HCO_3^-	7.06	7.52	6.10
Cl^-	0.60	0.48	0.33
SO_4^-	1.75	1.06	0.98
pH	7.50	7.70	7.90
Conductivity ($\text{EC} \times 10^9$)	840	758	720

1 ml of the liquid phase was counted. All batch experiments were carried out in duplicate.

The distribution ratios R_d for adsorption, desorption as well as percent adsorption were calculated according to the equations given earlier.¹⁰⁻¹⁵

Results and discussion

The sorption of a cation in solution onto the solid phase is assumed to be governed by first order kinetics. The logarithm of the remaining activity in the aqueous phase plotted against the time of sorption should give a straight line where the slope would be related to the rate constant and the intercept to the initial concentration of the cation. Such linear dependence was not observed in most of our studies. The observed curves were complex and they were assumed to be made up of a combination of first order sorptions. The various rate constants were obtained by resolving these curves just like resolving a complex radioactive decay curve with more than one half-life.¹⁸

The rate constants and the initial activities obtained by resolving complex decay curves in the sorption of Ba^{2+} , Co^{2+} and Zn^{2+} cations on alumina, kaolinite and magnesite

Table 3
Rate constants and initial activities obtained by resolving complex kinetic curves in the sorption of Co^{2+} , Zn^{2+} and Ba^{2+} ions on alumina, magnesite kaolinite

Species	Rate constant, h		Initial activity, cpm	
	k_1	k_2	A_1^0	A_2^0
Alumina				
Co^{2+}	$1.78 \cdot 10^{-3}$	$2.90 \cdot 10^{-2}$	86.48	2.72
Zn^{2+}	$6.00 \cdot 10^{-3}$	$4.00 \cdot 10^{-2}$	200.34	1.94
Ba^{2+}	$1.33 \cdot 10^{-3}$	-	1224.15	-
Magnesite				
Co^{2+}	$6.25 \cdot 10^{-4}$	$4.80 \cdot 10^{-3}$	3827.62	1.31
Zn^{2+}	$7.33 \cdot 10^{-4}$	$5.22 \cdot 10^{-3}$	2392.27	1.38
Kaolinite				
Co^{2+}	$4.00 \cdot 10^{-4}$	$3.20 \cdot 10^{-2}$	1380.22	2.12
Zn^{2+}	$6.94 \cdot 10^{-4}$	$3.10 \cdot 10^{-2}$	1652.40	1.95

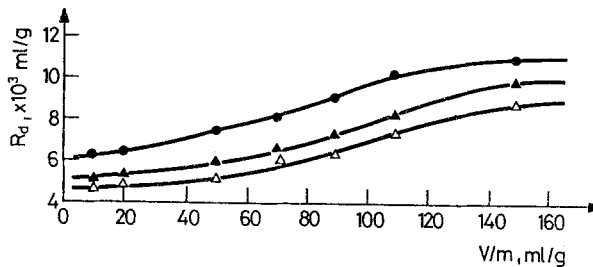


Fig. 1. Variation of the distribution ratio as a function of V/m in the sorption of Ba^{2+} ion on alumina. Initial Ba^{2+} ion concentration: ● $[\text{Ba}]_0 = 7.65 \cdot 10^{-7}$ meq/ml, ▲ $[\text{Ba}]_0 = 7.65 \cdot 10^{-6}$ meq/ml, Δ $[\text{Ba}]_0 = 7.65 \cdot 10^{-5}$ meq/ml

are given in Table 3. Except for the sorption of Ba^{2+} on alumina, two different first order rate constants are obtained for each cation. The magnitude of the corresponding intercepts indicate that the slower rate is the predominant mode of sorption in all cases.

A series of measurements showed that the sorption of Ba^{2+} , Co^{2+} and Zn^{2+} ions increased with increasing liquid volume to solid mass, (V/m), ratio of the sorption system. The behavior of R_d as a function of V/m is illustrated in Fig. 1 for the sorption of Ba^{2+} ion on alumina. As the V/m ratio increases the particles become more exposed, thus increasing the available area for sorption. Another general trend observed is the decrease of R_d with increasing initial cation concentration. This may be a result of the fact that at higher concentrations the loading of the sorbent approaches its saturation capacity and the available sorption sites decrease with increasing cation concentration.

Table 4
Parameters n and K (ml/g) obtained from fits to Freundlich
type isotherms for the various sorption systems

V/m , ml/g	Co^{2+}		Zn^{2+}	
	n	K	n	K
Magnesite				
10	1.06	164.20	0.91	4.44
20	1.03	104.5	0.90	4.47
50	0.98	46.53	0.90	5.40
70	0.94	28.26	0.91	7.75
90	0.92	21.29	0.91	9.08
110	0.87	13.71	0.91	10.74
150	–	–	0.91	10.71
Ba^{2+}-alumina				
10	0.96	2383.65		
20	0.94	1802.34		
50	0.93	1851.37		
70	0.94	2558.48		
90	0.92	2022.19		
110	0.93	2773.07		
150	0.95	4214.54		
Co^{2+}-kaolinite				
10	0.98	101.90		
20	0.99	123.61		
50	1.01	191.35		
70	0.97	115.66		
90	0.96	120.84		
110	0.96	128.97		

The results of the treatment of the experimental data according to Freundlich and Dubinin–Radushkevich type isotherms are given in Tables 4 and 5, respectively. Fits to both type of isotherms were quite good. The parameter K in the Dubinin–Radushkevich isotherm is related to the mean energy of adsorption, E , by the relationship:¹⁹

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

The results for various adsorbing systems of this work are given in Table 6. It is interesting to observe that all values are lower than the energy range for ion-exchange type reactions (8–16 kJ/mol). The concentration of a radionuclide sorbed on the solid phase (meq/g) is found to decrease with increasing mass of the adsorbing solid. This

Table 5
Parameters $C_{s,m}$ (meq/g) and K (meq^2/kJ^2) $\times 10^{-9}$ obtained from fits to Dubinin-Radushkevich type isotherm for various adsorption system

V/m , ml/g	Co^{2+}		Zn^{2+}	
	$C_{s,m}$	K	$C_{s,m}$	K
Magnesite				
10	0.06	5.38	0.01	5.50
20	0.08	5.46	0.02	5.50
50	0.07	5.49	0.02	5.67
70	0.06	5.33	0.03	5.71
90	0.02	4.69	0.03	5.71
110	0.05	4.98	0.04	5.76
150	-	-	0.04	5.76
Ba^{2+}-alumina				
10	0.19	3.88		
20	0.19	3.81		
50	0.38	4.07		
70	0.93	4.31		
90	0.54	4.11		
110	0.70	4.18		
150	0.36	3.55		
Co^{2+}-kaolinite				
10	0.01	4.31		
20	0.02	4.46		
50	0.03	4.62		
70	0.04	4.64		
90	0.04	4.63		
110	0.04	4.46		

Table 6
Mean energy of adsorption for various adsorbing systems studied in this work

Sorption system	Adsorption energy, kJ/mol
Alumina- Ba^{2+}	5.6
Kaolinite- Co^{2+}	5.3
Magnesite- Co^{2+}	4.9
Magnesite- Zn^{2+}	4.7

relation may be expressed by the equation,

$$C_s = C_s^0 \cdot m^\gamma \quad (2)$$

where C_s – is the sorbed concentration (meq/g),
 C_s^0 – is the specific sorbed concentration (meq/g),
 m – is the mass of the sorbing solid (g),
 γ – is the sorption exponent (< 0).

The magnitudes of C_s^0 and γ can be obtained from a logarithmic plot of C_s vs. m as the intercept and slope for a constant initial radionuclide concentration. The relation given in Eq. (2) was used to analyze our sorption data. The results are given in Table 7 and illustrated in Fig. 2. Good fits are obtained in all cases with a correlation coefficient close to 1.

Table 7
 Sorption parameters obtained in the sorption of Ba^{2+} , Co^{2+}
 and Zn^{2+} ions on alumina, kaolinite and magnesite according
 to the relation $C_s = C_{s0} \cdot m^\gamma$

Initial concentration of cation, meq/ml	$C_{s,0}$, meq/g	γ
Alumina- Ba^{2+}		
$7.65 \cdot 10^{-5}$	$2.34 \cdot 10^{-4}$	-0.99
$7.65 \cdot 10^{-6}$	$2.34 \cdot 10^{-5}$	-0.99
$7.65 \cdot 10^{-7}$	$2.34 \cdot 10^{-6}$	-0.99
$7.65 \cdot 10^{-8}$	$2.34 \cdot 10^{-7}$	-0.99
Kaolinite- Co^{2+}		
$1.04 \cdot 10^{-5}$	$3.62 \cdot 10^{-5}$	-0.84
$1.04 \cdot 10^{-6}$	$3.46 \cdot 10^{-6}$	-0.86
$1.04 \cdot 10^{-7}$	$3.40 \cdot 10^{-7}$	-0.87
$1.04 \cdot 10^{-8}$	$3.38 \cdot 10^{-8}$	-0.88
Magnesite- Co^{2+}		
$1.04 \cdot 10^{-3}$	$7.30 \cdot 10^{-3}$	-0.39
$1.04 \cdot 10^{-4}$	$5.04 \cdot 10^{-4}$	-0.54
$1.04 \cdot 10^{-5}$	$3.57 \cdot 10^{-5}$	-0.71
$1.04 \cdot 10^{-7}$	$3.24 \cdot 10^{-7}$	-0.74
$1.04 \cdot 10^{-8}$	$2.46 \cdot 10^{-8}$	-0.81
Magnesite- Zn^{2+}		
$7.67 \cdot 10^{-4}$	$1.70 \cdot 10^{-3}$	-0.53
$7.67 \cdot 10^{-5}$	$1.73 \cdot 10^{-4}$	-0.61
$7.67 \cdot 10^{-6}$	$2.39 \cdot 10^{-5}$	-0.51
$7.67 \cdot 10^{-7}$	$2.30 \cdot 10^{-6}$	-0.58
$7.67 \cdot 10^{-8}$	$1.63 \cdot 10^{-7}$	-0.66

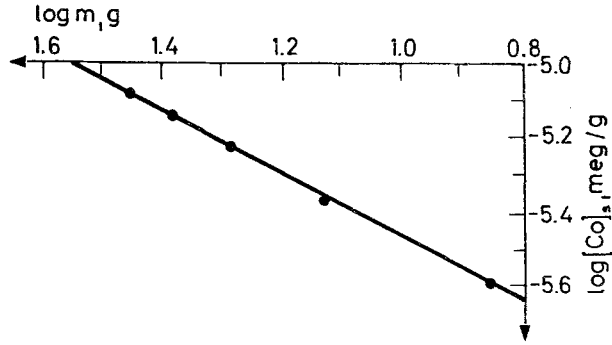


Fig. 2. Dependence of loading on mass m of the sorbing material according to $C_s = C_s^0 \cdot m^\gamma$, for the sorption of Co^{2+} ion on kaolinite. The initial Co^{2+} concentration $[\text{Co}^{2+}]_0$ was $1.04 \cdot 10^{-6}$ meq/ml

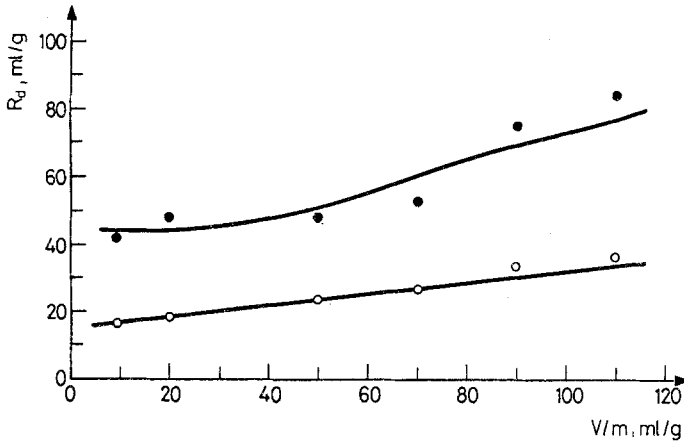


Fig. 3. Comparison of the experimental and calculated R_d values for the sorption of Co^{2+} and Zn^{2+} ions on magnesite. Initial concentrations: $[\text{Co}^{2+}]_0 = 1.04 \cdot 10^{-5}$ meq/ml, $[\text{Zn}^{2+}] = 7.67 \cdot 10^{-5}$ meq/ml; ● experimental points for sorption of Co^{2+} on magnesite, ○ experimental points for sorption of Zn^{2+} on magnesite, - calculated curves according to Eq. (3)

At low cation concentrations where the Freundlich constant n is close to unity as in our work, it was found that²⁰ the distribution ratio R_d was related to V/m and the parameters C_s^0 and γ by the relation

$$R_d = V/m \left(\frac{C_s^0 \cdot m^{\gamma+1}}{m_c - C_s \cdot m^{\gamma+1}} \right) \quad (3)$$

Here m_c is the total cation mass (meq).

Using Eq. (3) it is possible to calculate the distribution ratio for any specific cation-mineral sorption system. The results of such calculations are illustrated in Fig. 3 for the sorption of Co^{2+} and Zn^{2+} ions on magnesite. It is seen that there is a good agreement between experimental data and the corresponding calculated values.

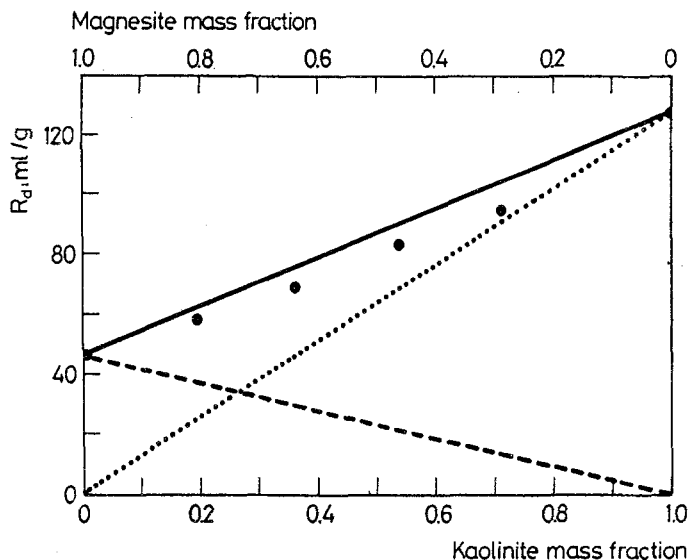


Fig. 4. Experimental and calculated distribution ratios for the sorption of Co^{2+} ion on kaolinite–magnesite mixture; ● experimental $R_{d,mix}$ values, — calculated $R_{d,mix}$ values, --- magnesite component of $R_{d,mix}$, ····· kaolinite component of $R_{d,mix}$

Another series of measurements were carried out, where the adsorbing solid species was a mixture of two different minerals. In such cases the distribution ratio $R_{d,mix}$ is expected to be related to the distribution ratios of the individual components when they are present alone. The equation relating them may be written as:

$$R_{d,mix} = (m_A/(m_A + m_B))R_{d,A} + (m_B/(m_A + m_B))R_{d,B} \quad (4)$$

where m_A – is the mass of mineral species A in mixture (g),
 m_B – is the mass of mineral species B in mixture (g),
 $R_{d,A}$ – distribution ratio of only species A (ml/g),
 $R_{d,B}$ – distribution ratio of only species B (ml/g).

Equation (4) is expected to be valid for cases where there are no interactions between the various components of the mixture. Such interactions would result in deviations of the experimental $R_{d,mix}$ values from those calculated using Eq. (4).

The experimental and calculated results for the sorption of Co^{2+} ion on various mixtures of kaolinite and magnesite are shown in Fig. 4. It is seen that although some deviation is observed the experimental points lie close to the line calculated from Eq. (4). This method of treatment of the mixtures seems to be satisfactory and can be extended to systems with more than two components.

If the distribution ratio of one of the species in the mixture is much larger, i.e., $R_{d,A} \gg R_{d,B}$, then that particular species will be the one that will determine the $R_{d,\text{mix}}$ values. In such cases the approximate relationship

$$R_{d,\text{mix}} = (m_A/(m_A + m_B))R_{d,A} \quad (5)$$

may be used to calculate the distribution ratio of such mixtures. Experimental results for the sorption of Co^{2+} on mixtures of kaolinite and alumina minerals confirmed the validity of Eq. (5). The R_d of 3445 ml/g for sorption on alumina was much greater than that of 129 ml/g for the sorption on kaolinite.

References

1. I. I. BAYAT, M. A. MALATI, J. Radioanal. Chem., 54 (1979) 399.
2. L. CARLSEN, P. BO, Sorption of Radionuclides on Clay Minerals, I.A.E.A. Sm-257/82, 1982, p. 97.
3. J. S. WAHLBERG, M. J. FISHMAN, Geolog. Surv. Bull., 1140 (1962) 1.
4. S.-Y. SHIAO, Y. EGOZY, R. E. MEYER, J. Inorg. Nucl. Chem., 43 (1981) 3309.
5. P. RAFFERTY, S.-Y. SHIAO, C. M. BINZ, R. E. MEYER, J. Inorg. Nucl. Chem., 43 (1981) 797.
6. S.-Y. SHIAO, R. E. MEYER, J. Inorg. Nucl. Chem., 43 (1981) 3301.
7. D. A. PALMER, R. E. MEYER, J. Inorg. Nucl. Chem., 43 (1981) 2979.
8. S. WINGEFORS, Radioact. Waste Manag. Nucl. Fuel Cycle, 5 (1984) 327.
9. K. AKIBA, H. HIROYUKI, J. Nucl. Sci. Tech., 27 (1990) 275.
10. S. HATIPOGLU, C. EYLEM, H. GOKTURK, H. N. ERTEN, Sci. Geol. Mem., 86 (1990) 79.
11. C. EYLEM, H. GOKTURK, H. N. ERTEN, J. Environ. Radioactivity, 11 (1990) 183.
12. S. AKSOYOGLU, H. GOKTURK, H. N. ERTEN, Turk. J. Nucl. Sci., 12 (1985) 13.
13. H. N. ERTEN, S. AKSOYOGLU, S. HATIPOGLU, H. GOKTURK, Radiochim. Acta, 44/45 (1988) 147.
14. H. N. ERTEN, S. AKSOYOGLU, S. HATIPOGLU, H. GOKTURK, The Sci. of Tot. Envir., 69 (1988) 269.
15. C. EYLEM, H. N. ERTEN, H. GOKTURK, Analyst, 114 (1989) 351.
16. A. G. LOOMIS, Am. Cer. Soc. J., 21 (1938) 393.
17. F. H. NORTON, S. SPEIL, Am. Cer. Soc. J., 21 (1938) 89.
18. N. K. TUNALI, H. N. ERTEN, S. KINIKOGLU, S. GUMUS, J. Radioanal. Chem., 49 (1979) 225.
19. L. L. AMES, J. E. McGRARRAH, B. A. WALKER, P. F. SALTER, Chem. Geol., 35 (1982) 205.
20. Z. GOKMENOGLU, M.Sc. Thesis, Department of Chemistry, Bilkent University, Ankara, 1991 (Unpublished).