

## Radiochemical study of $\text{Co}^{2+}$ sorption on chlorite and kaolinite

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In this work, the sorption behavior of  $\text{Co}(\text{II})$  ions on natural chlorite and kaolinite as a function of time, concentration and temperature was studied.  $^{60}\text{Co}$  radiotracer method and the batch technique were used. The kinetic results indicated that about one day of contact time was enough to achieve equilibrium. The sorption process was described by Freundlich type isotherms. Sorption of  $\text{Co}(\text{II})$  ions on both clays was found to be endothermic with  $\Delta H^\circ$  (kJ/mol) and  $\Delta S^\circ$  (kJ/mol·K) being 33 and 0.14 for kaolinite and 17 and 0.102 for chlorite, respectively. The magnitudes of the corresponding  $\Delta G^\circ$  values suggest that sorption occur mainly via an ion exchange mechanism on both clays.

### Introduction

The radionuclide  $^{60}\text{Co}$  ( $T_{1/2} = 5.3$  y) is one of the most important activation products in nuclear reactors. It is among the major long-lived radionuclides released from nuclear facilities, that are potentially hazardous to the biosphere.

The adsorption of radionuclides on clay minerals is widely accepted to be an important process from the point of view of radioactive wastes. The natural availability of clays in large quantities, their relatively good sorption properties, their low permeability and their stability compared to organic exchangers are among the reasons that makes clays very useful in controlling radionuclide concentrations in industrial effluents or their use as backfill material in burial sites of radioactive wastes.

The sorption behavior of  $\text{Co}(\text{II})$  on alumina, kaolinite and magnesite was studied previously in our laboratories as a function of time of contact, loading and  $V/m$  ratio.<sup>1</sup> The objective of this work was mainly to examine the effects of loading and temperature on the sorption behavior of  $\text{Co}(\text{II})$  ions on chlorite and kaolinite clays utilizing the radiochemical method and using  $^{60}\text{Co}$  as the radiotracer.

Kaolinite is a typical example of the two-layered clays in which the unit structure is formed by a silica (tetrahedral) sheet and a brucite/gibbsite (octahedral) sheet stacked on one another and held by Van der Waals' forces. Kaolinite has little isomorphous substitutions and its structure is nonexpanding.

On the other hand, chlorite is an example of three-layered clays in which the unit structure is formed by alternating three layers (two tetrahedral and one octahedral) with a brucite sheet sandwiched in between. Chlorite can have large isomorphous substitutions leading to the development of a negative charge on the structure, and is a nonexpanding clay.

Both of the clays possess low cation exchange capacities (CEC). Typical values reported in literature for the CEC of chlorite and kaolinite are 15 and 6 meq/100 g, respectively.<sup>2</sup>

### Experimental

#### Characterization by X-ray diffraction

X-ray diffraction patterns for kaolinite and chlorite used in this work were recorded at the Hydrogeology Department Laboratories at Hacettepe University using a Philips DY 687 model diffractometer. The spectra given in Fig. 1 revealed that the kaolinite samples contained other geological fractions such as feldspars and quartz in appreciable amounts. Chlorite samples, however, contained appreciable amounts of illite and minor amounts of calcite, quartz and feldspars.

#### Pretreatment procedure

The chlorite and kaolinite samples used throughout these studies were obtained from the Turkish Mining Institute MTA. The particle size of the fractions used in all our experiments was  $< 38\mu\text{m}$ . Aliquots of 30 mg clays were put into pre-weighed tubes, and 3 ml portions of laboratory tapwater containing the cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (0.35, 0.12, 0.27, 0.44 meq/l, respectively) were added into each tube. The tapwater was taken as a substituent for groundwater. The samples were then shaken for 4 days with a lateral shaker at 125 rpm. They were then centrifuged at 6000 rpm for 30 minutes and the liquid phases were discarded. Each tube was then weighed to determine the amount of water remaining inside after discarding the decantate ( $\Delta W_{\text{pl}}$ ). This pretreatment step was intended to allow for the interaction of the clay samples with aqueous medium prior to sorption experiments.

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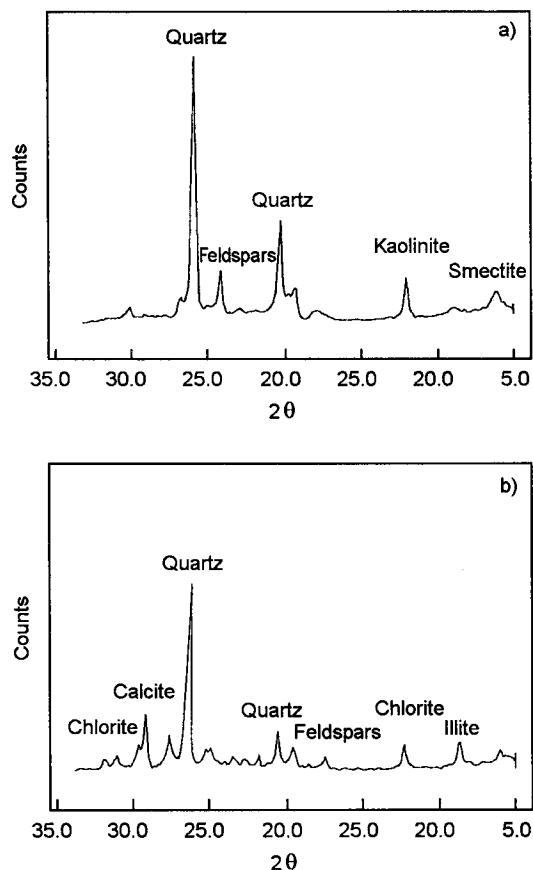


Fig. 1. X-ray diffraction spectrum of kaolinite (a) and of chlorite (b)

### Kinetic studies

To each of the 30 mg pretreated chlorite and kaolinite samples, 3 ml of solutions containing  $1 \cdot 10^{-3}$  meq/ml of  $\text{Co}^{2+}$  spiked with appropriate amounts of  $^{60}\text{Co}$  radiotracer were added. Sample tubes were shaken at room temperature for periods ranging from one to seven days. Samples were then centrifuged and 2 ml portions of the liquid phases were counted using a  $35 \text{ cm}^3$  calibrated Ge detector connected to a multichannel analyzer. Duplicate samples were measured for each point.

### Effect of loading and temperature

The effect of temperature on sorption was studied for three sets of cobalt solutions of initial concentrations  $3.7 \cdot 10^{-2}$ ,  $3.7 \cdot 10^{-3}$ ,  $3.7 \cdot 10^{-4}$  meq/ml. Experiments were carried out at four different temperatures: 30, 40, 50 and 60 °C. Temperature was kept constant during each experiment by means of an adjustable thermostat connected to the water bath. Three ml of the cation solution of interest containing an appropriate amount of radiotracer was added to each sample tube containing 30 mg of chlorite or kaolinite at the desired temperature.

The samples were shaken for one day, centrifuged and 2 ml portions of the liquid phase were counted.

The starting pH for all experiments ranged between 5.4–6.6 and the pH of distilled water was 6.7.

### Mathematical relationships

#### The distribution coefficient

The distribution coefficient of adsorption is defined as:

$$R_d = \frac{[C]_s}{[C]_l} \quad (1)$$

where  $[C]_s$  (meq/g) and  $[C]_l$  (meq/ml) are the concentrations of species  $C$  in the solid and liquid phases, respectively. At the beginning of the sorption step,  $V$  (ml) of solution with initial concentration  $[C]^\circ$  (meq/ml) was used, and at the end of sorption step  $V + \Delta W_{pt}$  (ml) of solution with concentration  $[C]_l$  was present, hence the concentration of  $C$  in the solid phase after sorption can be expressed as:

$$[C]_s = \frac{V[C]^\circ - (V + \Delta W_{pt})[C]_l}{W_s} \quad (2)$$

In terms of radioactivity,  $[C]_l$  can be written as:

$$[C]_l = \frac{A_1}{A^\circ} [C]^\circ \quad (3)$$

From Eqs (1), (2) and (3), the following equation can be obtained:

$$R_d = \frac{VA^\circ - (V + \Delta W_{pt})A_1}{A_1 W_s} \quad (4)$$

where  $A^\circ$  – initial count rate of solution added for sorption, cps/ml,  $A_1$  – count rate of solution after sorption, cps/ml,  $W_s$  – weight of solid material, g,  $\Delta W_{pt}$  – amount of liquid remaining in the tube after pretreatment, before sorption, g.

#### Thermodynamic relations

In a batch adsorption process, the adsorption reaction can be written as:



where  $C_1$  stands for the solute particles in solution,  $\underline{s}$  for the sorption sites on the surface of the adsorbent and  $C_s$  for the solute particles adsorbed on the adsorbent. The equilibrium constant for the reaction above can be written in terms of the activities as:

$$K = \frac{a_{C_s}}{a_{\underline{s}} \cdot a_{C_1}} \quad (6)$$

The activity of the solid phase can be taken as unity at the reference state, then the above expression can be written in terms of the concentrations and the activity coefficients 'γ' as:

$$K = \frac{[C]_s \cdot \gamma_{C_s}}{[C]_l \cdot \gamma_{C_l}} \quad (7)$$

for dilute solutions the activity coefficients can be approximated to unity, so that the equilibrium constant becomes equivalent to the distribution coefficient  $R_d$  defined as the ratio of the solute concentration on the solid phase to that on the liquid phase.

In line with the above derivation, the distribution coefficient may be related to the change in Gibbs free energy,  $\Delta G$ , by the following equation:

$$\Delta G = \Delta G^\circ + RT \ln R_d \quad (8)$$

where  $\Delta G^\circ$  is the standard Gibbs free energy change,  $R$  is the ideal gas constant, and  $T$  is the absolute temperature.

At equilibrium no change in Gibbs free energy occurs and the above equation reduces to:

$$\Delta G^\circ = -RT \ln R_d \quad (9)$$

Gibbs free energy change can also be written in terms of the enthalpy change,  $\Delta H^\circ$ , and the entropy change,  $\Delta S^\circ$ , as given below:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

Combining Eqs (9) and (10) the following expression results

$$\ln R_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

### Results and discussion

The kinetic results of cobalt sorption on kaolinite and chlorite indicate that saturation was reached in about one day of contact in both cases as illustrated by Figs 2a and b, respectively. The error bars represent calculated uncertainties resulting from weight, volume and activity measurements using the standard propagation of errors relationships.

The rapid uptake of cobalt ions might be indicative of fast adsorption steps resulting from sorption at the surface sites of the clay minerals used.

The values of the distribution coefficient,  $R_d$ , as a function of different loadings and temperatures are given in Table 1 for the sorption of Co(II) ions on kaolinite and chlorite.

The relationship between the bulk concentration of the adsorbate and the amount adsorbed on the solid

phase at a certain temperature can be described by adsorption isotherms. The Freundlich type isotherm at a certain temperature may be described as:

$$[C]_s = k[C]_l^n \quad (12)$$

where  $[C]_s$  is the amount of ionic species adsorbed on the solid matrix at equilibrium (meq/g),  $[C]_l$  is the concentration of the cation in solution at equilibrium (meq/ml),  $k$  and  $n$  are Freundlich constants. Freundlich type isotherm plots for the sorption of cobalt ions on kaolinite and chlorite are shown in Figs 3a and b, respectively. It is seen that Freundlich type isotherms provide an adequate description of the sorption behavior in all cases.

The results of least square fits to the experimental data are given in Table 2. In both cases, the  $n$  values seem to be independent of temperature, whereas the  $k$  values show a significant increase in the case of sorption of Co(II) ions on chlorite and no increase with increasing temperature in the case of Co(II) ions sorption on kaolinite. It is suggested that higher value of  $k$  indicates higher sorption affinity for the ion in solution, whereas a higher value of  $n$  indicates higher sorption intensity.<sup>3</sup> At the limit when  $n=1$ , the adsorption is said to be linear and the constant  $k$  becomes equivalent to  $R_d$ .

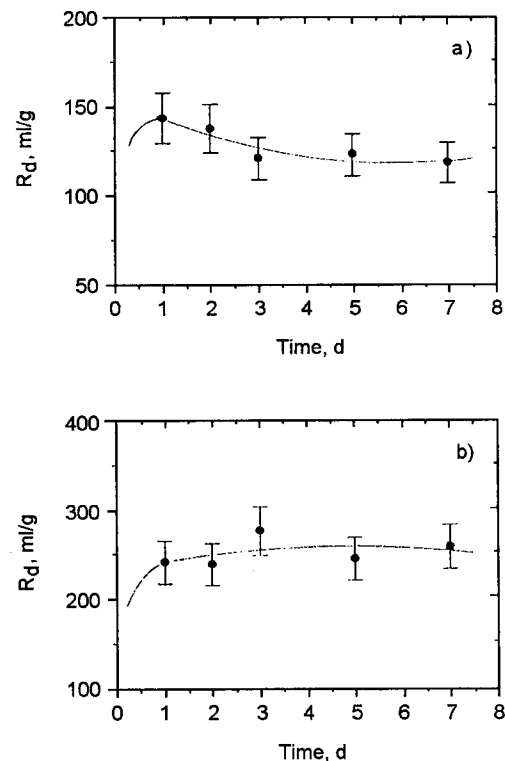


Fig. 2. Change in  $R_d$  as a function of time for the sorption of cobalt (initial concentration =  $1 \cdot 10^{-3}$  meq/ml) on kaolinite (a) and on chlorite (b)

Table 1. Variation of  $R_d \pm \Delta R_d$  (in ml/g) as a function of temperature and initial concentration for the sorption of cobalt ions on kaolinite and chlorite

Initial concentration, meq/ml	$R_d \pm \Delta R_d$ , ml/g							
	303 K	Co <sup>2+</sup> on kaolinite			Co <sup>2+</sup> on chlorite			
		313 K	323 K	333 K	303 K	313 K	323 K	333 K
$3.7 \cdot 10^{-2}$	66±8	78±9	89±10	190±17	144±14	208±18	272±23	301±25
$3.7 \cdot 10^{-3}$	86±9	106±11	114±11	258±22	286±24	354±30	447±35	519±40
$3.7 \cdot 10^{-4}$	105±11	157±14	299±25	471±37	334±27	388±31	481±38	540±42

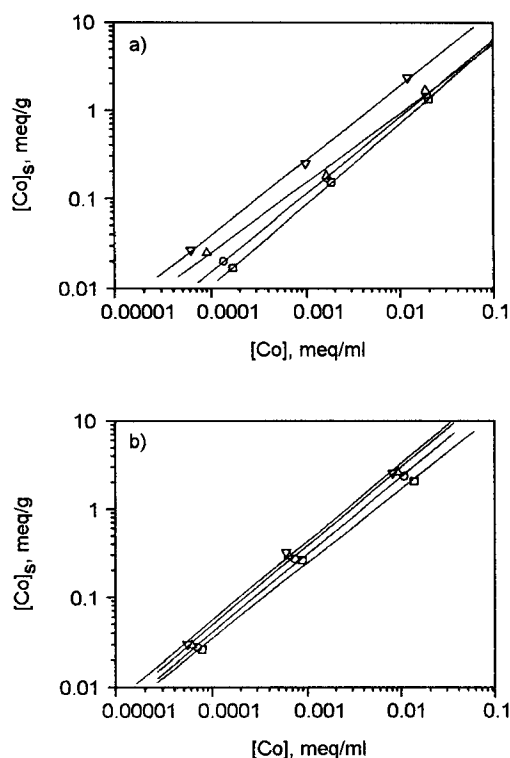


Fig. 3. Freundlich isotherm plots for the sorption of cobalt on kaolinite (a) and on chlorite (b) at different temperatures,  $\square T = 30^\circ\text{C}$ ,  $\circ T = 40^\circ\text{C}$ ,  $\Delta T = 50^\circ\text{C}$ ,  $\nabla T = 60^\circ\text{C}$

The higher affinity of the  $\text{Co}(\text{II})$  ions towards chlorite may be explained by the fact that the structure of chlorite is subject to more isomorphous substitutions than that of kaolinite, which yields a larger negative charge on the surface of chlorite and thereby increases the tendency of sorption of the positively charged cobalt ions. Another factor is that chlorite possess a larger CEC than kaolinite, thus a larger number of exchangeable cations are available for exchange with  $\text{Co}(\text{II})$  ions. Here, one should also note that the extent of solvation of any cation will determine its tendency towards exchanging with another cation, and that the charge density of a cation in

solution will determine the extent that the cation can overcome the diffusion resistance and reach the sorption sites. In the earlier study performed at our laboratories to study the effect of loading on sorption of  $\text{Co}(\text{II})$  on kaolinite with initial concentrations ranging  $7.67 \cdot 10^{-4}$ – $7.67 \cdot 10^{-8}$  meq/ml, it was found that Freundlich type isotherms were obeyed well with higher  $k$  values than was obtained in this study indicating higher sorption affinity of  $\text{Co}(\text{II})$  ions at smaller initial concentrations.<sup>1</sup>

If  $R_d$  is approximated to an equilibrium constant under the operating experimental conditions, Arrhenius plots, that is the change of  $\ln R_d$  values with reciprocal temperature, can be plotted according to Eq. (11).

Table 2. Parameters for the Freundlich type isotherm fits to the data for the sorption of cobalt ions on chlorite and kaolinite at different temperatures

Temperature, K	Co(II) on chlorite		Co(II) on kaolinite	
	$k$ , meq/g	$n$	$k$ , meq/g	$n$
303	78	0.84	45	0.90
313	126	0.87	44	0.86
323	170	0.88	33	0.77
333	186	0.88	85	0.83

Table 3. The average values of the thermodynamic parameters  $\Delta H^\circ$  (kJ/mol) and  $\Delta S^\circ$  (kJ/mol K) in the adsorption of  $\text{Co}(\text{II})$  on chlorite and kaolinite obtained in this work

Cobalt on mineral	$\Delta H^\circ$ , kJ/mol	$\Delta S^\circ$ , kJ/mol K
Co(II) on chlorite	17±3	0.102±0.007
Co(II) on kaolinite	33±7	0.14±0.03

Table 4. Variation of  $\Delta G^\circ \pm \text{S.D.}$  (kJ/mol) as a function of temperature for the sorption of cobalt ions on kaolinite and chlorite

Temperature, K	$\Delta G^\circ \pm \text{S.D.}$ , kJ/mol	
	Co <sup>2+</sup> on kaolinite	Co <sup>2+</sup> on chlorite
303	-11 ± 1	-14 ± 1
313	-12 ± 1	-15 ± 1
323	-13 ± 1	-16 ± 1
333	-16 ± 1	-17 ± 1

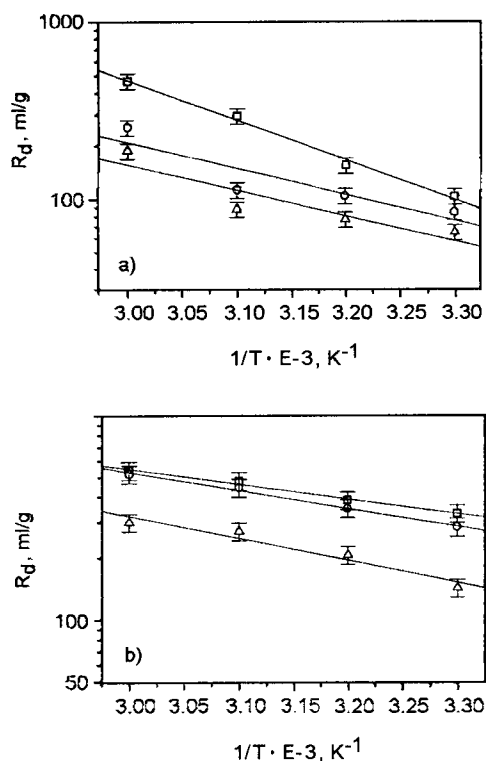


Fig. 4. Variation of  $\log R_d$  as a function of temperature for the sorption of cobalt on kaolinite (a) and on chlorite (b) at various initial ion concentrations (meq/ml):  $\Delta$   $3.70 \cdot 10^{-2}$ ,  $\circ$   $3.70 \cdot 10^{-3}$ ,  $\square$   $3.70 \cdot 10^{-4}$

Arrhenius plots for the sorption of  $\text{Co(II)}$  ions on chlorite and kaolinite are shown in Figs 4a and b, respectively. Changes in enthalpy of sorption,  $\Delta H^\circ$  (kJ/mol), and in entropy of sorption,  $\Delta S^\circ$  (kJ/mol K), under the specified experimental conditions were calculated from the slopes and intercepts of least square fits to the experimental data and are given in Table 3. These values represent averages of different concentrations, while the uncertainties represent standard deviations (S.D.).

The endothermic nature of sorption of  $\text{Co(II)}$  on chlorite and kaolinite is indicated by the positive values of the enthalpy changes,  $\Delta H^\circ$ . Similar behavior of  $\text{Co(II)}$  on alumina and oxide surfaces were reported by other authors.<sup>4,5</sup> The increase of sorption of  $\text{Co(II)}$  ions on both clay types with increasing temperature may be attributed to a negative temperature coefficient of its solubility or steep simultaneous decrease of real adsorption of solvent.<sup>4</sup> The increase may also be due to the acceleration of some originally very slow adsorption steps or even due to the creation of some new active centers on the solid surface.<sup>3</sup>

$\text{Co(II)}$  ions are well known for making aqua-hydrated cations in water. For cations that are solvated well in water, another possible explanation is suggested for the endothermic behavior.<sup>6</sup> Adsorption requires that such ions to a certain extent be denuded of their hydration sheath so that their migration toward the sorption interface is facilitated. The dehydration process of ions requires energy and this energy is assumed to exceed the exothermicity of the ions attacking the surface. The implicit assumption here is that after adsorption, the environment of the metal ions is less aqueous than it was in the solution state. The removal of water from ions is essentially an endothermic process, and as more heat is supplied by increasing the temperature of adsorption more dehydrated cations will be available and thus the extent of sorption is expected to increase.

The positive values of the entropy changes,  $\Delta S^\circ$ , might suggest that  $\text{Co(II)}$  ions sorbed on chlorite and kaolinite surfaces are relatively immobile and the displaced ions from the solid surface are greater in number than the adsorbed  $\text{Co(II)}$  ions, which means that two monovalent ions may be exchanged for a single  $\text{Co(II)}$  ion.<sup>4</sup> The positive entropy change together with the endothermicity yield a spontaneous process.

The free energy of specific adsorption,  $\Delta G^\circ$  (kJ/mol) was calculated for different concentrations at each temperature utilizing Eq. (9).

The calculated values of  $\Delta G^\circ$  for the  $\text{Co(II)}$  adsorption on chlorite and kaolinite at all four temperatures are given in Table 4. The spontaneity of the sorption process is indicated by the negative  $\Delta G^\circ$  values for both of the adsorption cases. It is also obvious that the spontaneity of sorption increases as temperature increases leading to higher coverages at higher temperatures.

The magnitude of the energy of sorption is in the 8–16 kJ/mol range which is the energy range for ion exchange type reactions.<sup>7</sup> This suggests that the mechanism of  $\text{Co(II)}$  ion sorption on chlorite and kaolinite is principally ion exchange.

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