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Adsorption of Radioactive Ions $^{137}Cs^+$, $^{85}Sr^{2+}$, and $^{60}Co^{2+}$ on Natural Magnetite and Hematite

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Abstract

Natural magnetite and hematite have been used as granular sorbents for $^{137}Cs^+$, $^{85}Sr^{2+}$, and $^{60}Co^{2+}$ at tracer concentration levels in aqueous solutions of constant pH (range 2–10) at 25°C. The kinetics of adsorption, up to the first 60 to 90 min, followed a first-order equation. At pH 6–8 about 50% Cs, 30% Co, and 18% Sr is removed from the solution with magnetite and 78% Co with hematite. The difference in the sorption capabilities of magnetite and hematite is discussed in terms of crystal structures of these oxides.

INTRODUCTION

The use of inorganic oxides, particularly magnetite, as an inexpensive bed filter for removal of radioactive ions from aqueous solutions in nuclear plants was suggested long ago (*1–4*). Milonjić et al. (*5–10*) investigated the thermodynamics of adsorption of Cs^+, Co^{2+}, Ce^{3+}, and the processes of sorption and desorption of H^+ and OH^- ions on the liquid–solid interfaces.

The present paper reports data on the kinetics of sorption of $^{137}Cs^+$, $^{85}Sr^{2+}$, and $^{60}Co^{2+}$ on natural magnetite and hematite. These two sorbents have different sorption capabilities with respect to the same adsorbate ions. An approximative and simplified first-order kinetic expression has been used to interpret the adsorbate depletion in the liquid phase at low coverage of the sorbent surface.

EXPERIMENTAL

Natural magnetite (Fe_3O_4), supplied by the Baljevci mine, Serbia, and hematite (α-Fe_2O_3) from the Smederevo metallurgy plant, were ground, sieved, and a 0.095–0.125 mm fraction was selected as a granular adsorbent. Both adsorbents were repeatedly washed with distilled water, then dried at 110°C for 24 h and stored. They were analyzed chemically, their structure was identified by x-ray analysis, and their specific surface area was determined with a Ströhlein area meter using a single point nitrogen adsorption method. The following results were obtained.

Surface area (m^2/g). Magnetite: 2.0 ± 0.1. Hematite: 2.3 ± 0.1

Structure (by x-ray analysis). Magnetite: octahedral crystals, inverse spinel type. Hematite: corundum type (α-Fe_2O_3), presence of γ-Fe_2O_3 not observed.

Main impurities (mass%). Magnetite: 3.92 Si, 0.42 Al, 0.86 Ca, 0.60 Mg, 0.12 Ni, <0.01 Co. Hematite: 0.07 Si, <0.01 Al, 0.01 Ni, 0.02 Co, other elements below 0.01.

In all kinetic and equilibrium experiments, 0.200 g of the sorbent was equilibrated with 10.0 cm^3 of aqueous solution containing the radioactive cation at tracer level, carrier free, 1×10^{-9} mol $^{137}Cs/dm^3$, 2×10^{-10} mol $^{60}Co/dm^3$, 6×10^{-12} mol $^{85}Sr/dm^3$, in plastic stoppered vials. The following procedure was used. Before adding the radioactive tracer, the solution was adjusted to the required pH using HNO_3 or hydrazine, and after 1 h of equilibration with the oxide sorbent, 0.010 cm^3 of an almost neutral solution of the radioisotope was added and the kinetic run started. The pH value of the solution was again measured after attaining equilibrium. The vials were agitated using a mechanical shaker in thermostated air at 25 ± 0.5°C. At various time intervals small liquid samples were taken from the vials and their relative radioactivity (counts per minute and per unit volume) was measured in a well-type gamma-scintillation counter. Separate experiments have shown that the adsorption of radioisotopes on the wall of vials and the adsorption of hydrazine on the oxide sorbents are negligible. Each kinetic run provided the relative activity of the solution at different elapsed time intervals. We shall denote A_0, A_t, and A_e the relative radioactivities of the solution at zero time, at time t, and at equilibrium, respectively. Thus, the percent amount adsorbed can be expressed as

$$\%\text{ adsorption (at time } t\text{):}\quad 100(A_0 - A_t)/A_0$$
$$\%\text{ adsorption (at equilibrium):}\quad 100(A_0 - A_e)/A_0$$

The results obtained are the mean values of at least two independent experimental runs. An overall adsorption measurement error is estimated to be not greater than 3%.

RESULTS AND DISCUSSION

In Fig. 1 are shown the experimental results obtained with magnetite sorbent, and in Fig. 2 with hematite. The adsorption kinetics is presented as percent adsorption against the elapsed time interval, at constant pH of the solution. One can note that equilibrium is attained in about 3–5 h, and the adsorption differs considerably for different adsorbate ions. Thus, the adsorption of Cs^+ is much higher than the adsorption of Co^{2+} and Sr^{2+} when magnetite is the sorbent, whereas in the case of hematite sorbent

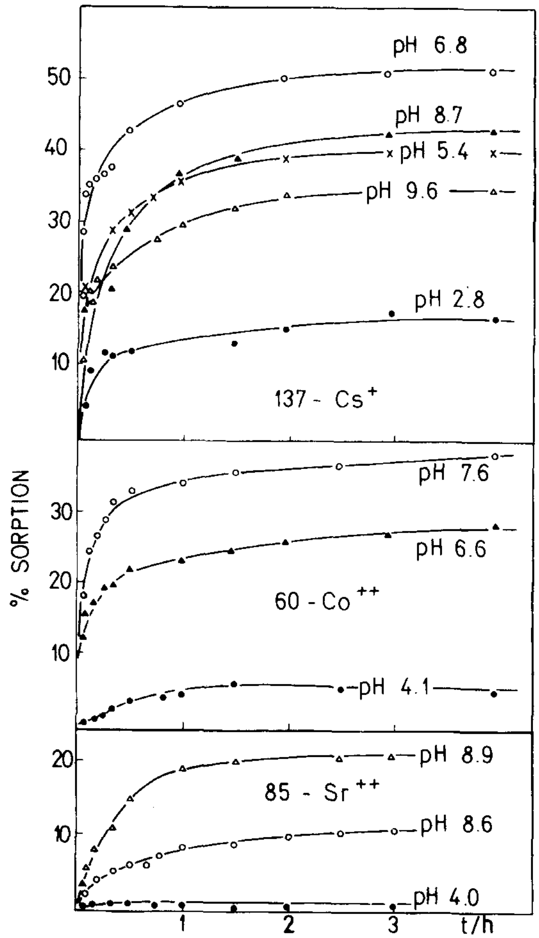

FIG. 1. Adsorption percent of $^{85}Sr^{2+}$, $^{60}Co^{2+}$, and $^{137}Cs^{+}$ on magnetite vs time, 25°C. Liquid/solid ratio 10 cm^3/0.200 g. Tracer concentration of radioactive cations, 1 × 10^{-9} mol ^{137}Cs/dm^3, 2 × 10^{-10} mol ^{60}Co/dm^3, and 6 × 10^{-12} mol ^{85}Sr/dm^3.

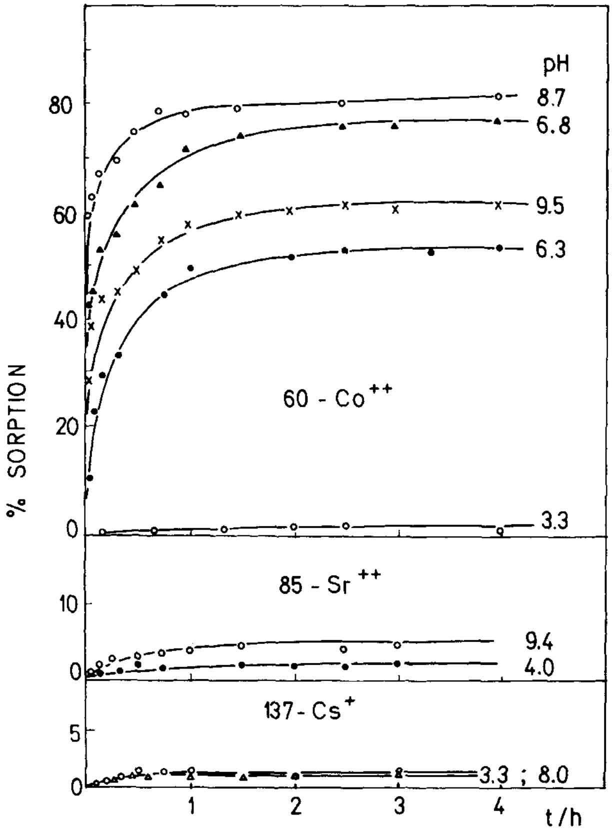

FIG. 2. Adsorption percent of $^{85}Sr^{2+}$, $^{60}Co^{2+}$, and $^{137}Cs^{+}$ on hematite vs time. Other data as in Fig. 1.

the sorption of Co^{2+} is high but the sorption of Cs^{+} and Sr^{2+} very low. Obviously, the affinity of magnetite and hematite toward the same adsorbate ion is quite different (compare Co^{2+} at pH 6.6 in Fig. 1 and at pH 6.8 in Fig. 2, also Cs^{+} in Figs. 1 and 2). In the fourth column of Table 1 are the values of percent adsorption at equilibrium. One can note the influence of pH on the adsorption. The adsorption increases with increasing pH up to a maximum value which is usually attained between pH 7–9. This fact indicates that the sorption of H^{+} ions competes strongly with the sorption of adsorbate cations.

The following interpretation of the kinetic data is suggested. We assume, as a first approximation, that the surface of the solid is quasi-homogeneous

TABLE 1

Sorption Kinetics for Tracer Concentration of Adsorbate Ions, 10.0 cm^3 Solution Equilibrated with 0.200 g Adsorbent at 25°C, Constant pH

Adsorbent	Adsorbate	pH of solution	Adsorption (removal) at equilibrium (%)	Eqs. (4)–(7)[a]		
				$k \times 10^4$ s^{-1}	$k_s' \times 10^4$ s^{-1}	$k_d \times 10^4$ s^{-1}
Magnetite (Fe_3O_4)	$^{137}Cs^+$	2.8	18.4	1.8	0.3	1.5
		5.4	41.7	4.0	1.7	1.3
		6.8	52.2	4.1	2.2	2.0
		8.7	42.8	3.6	1.5	2.0
		9.6	35.6	3.8	1.4	2.5
	$^{60}Co^{2+}$	4.1	≈6	≈5	≈0	≈4
		6.6	30.6	2.1	0.6	1.5
		7.6	39.8	6.8	2.7	4.1
	$^{85}Sr^{2+}$	4.0	≈0	[b]	[b]	[b]
		8.6	18.5	3.4	0.6	2.8
		8.9	22.8	5.5	1.2	4.2
Hematite (α-Fe_2-O_3)	$^{60}Co^{2+}$	3.3	≈0	[b]	[b]	[b]
		6.3	53.0	4.3	2.3	2.0
		6.8	78.3	4.2	3.4	0.8
		8.7	80.2	6.4	5.4	1.0
		9.5	62.9	5.0	3.1	1.8
	$^{85}Sr^{2+}$	4.0	≈0	[b]	[b]	[b]
		9.4	≈5	≈4	≈0	≈4
	$^{137}Cs^+$	3.3	≈0	[b]	[b]	[b]
		8.0	≈0	[b]	[b]	[b]

[a] Estimated accuracy of the rate constants: ±(5–8)%.

[b] Owing to low adsorption, application of Eq. (7) is unreliable.

(with uniformly distributed isoenergetic sites). The sorption–desorption process is reversible and can be described by the Langmuir type of equation:

$$d\theta_t/dt = k_s c_t(1 - \theta_t) - k_d\theta_t$$

Here, θ_t is the fraction of the surface covered by the adsorbate whose concentration in the solution is c_t (both θ_t and c_t refer to the elapsed time t), k_s is the second-order rate constant for sorption, and k_d the first-order rate constant for desorption. It has been shown that the exact solution of the above differential equation gives an expression which contains implicitly the equilibrium constant $K = k_s/k_d$ (*9*), and therefore it is not convenient for our case. However, at very low adsorbate concentration (for example, at the tracer level and/or the beginning of the sorption process), one can assume that $\theta << 1$, and write the above equation in simplified form:

$$d\theta_t/dt = k_s c_t - k_d \theta_t \tag{1}$$

The surface coverage θ_t is proportional to the difference $c_0 - c_t$, i.e., the depletion of the adsorbate concentration. Hence,

$$\theta_t = f(c_0 - c_t); \qquad d\theta_t/dt = -f(dc_t/dt) \tag{2}$$

Here, c_0 is the adsorbate concentration at zero time, and f (dm^3/mol) is a constant. Equations (1) and (2) give

$$-dc_t/dt = (k_s' + k_d)c_t - k_d c_0 \tag{3}$$

$$k_s' = k_s/f$$

At equilibrium, $(dc_t/dt) = 0$ and $c_t = c_e$ (c_e is the equilibrium adsorbate concentration). Therefore, one obtains

$$(k_s' + k_d)c_e = k_d c_0 \tag{4}$$

Equations (3) and (4) give

$$-(dc_t/dt) = k(c_t - c_e) \tag{5}$$

$$k = k_s' + k_d \tag{6}$$

After integration of Eq. (5), one obtains a simple first-order kinetic expression:

$$\ln(c_t - c_e) = -kt + \text{constant} \tag{7}$$

The integration constant is calculated from the condition $c_t = c_0$ when $t = 0$. Hence,

$$\text{constant} = \ln(c_0 - c_e)$$

Since the adsorbate concentrations c_0, c_t, and c_e are proportional to the relative radioactivities of the solution A_0, A_t, and A_e, we have interpreted the kinetic data using Eq. (7) and plotted $\ln(A_t - A_e)$ vs t. The values of k, obtained with the least-squares method, are listed in the fifth column of Table 1. Several plots are presented in Fig. 3.

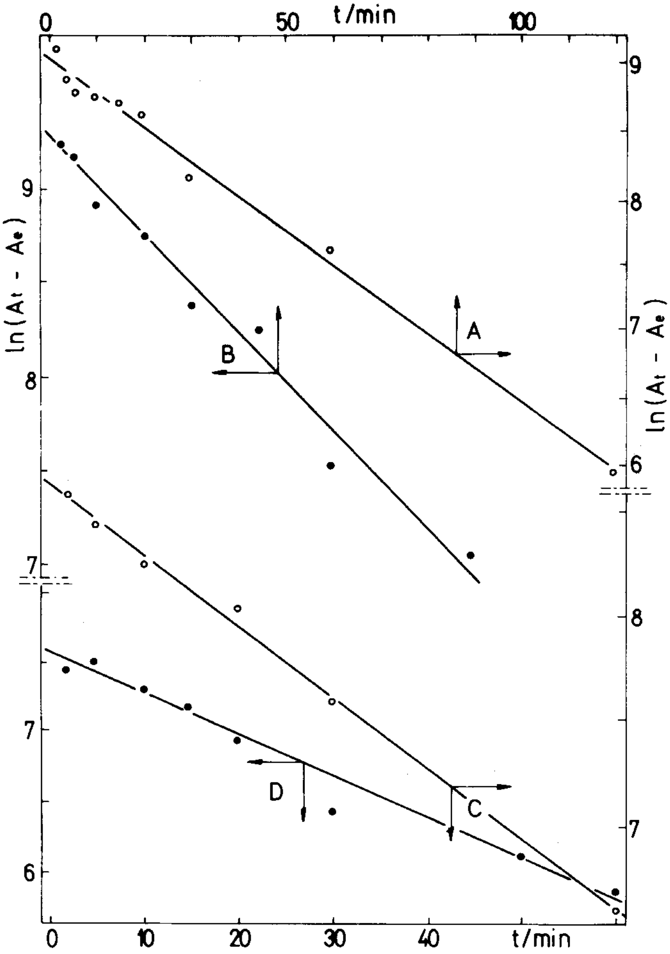

FIG. 3. Plots of ln ($A_t - A_e$) vs time applied to the sorption kinetics of (A) $^{137}Cs^+$ on magnetite, pH 6.8; (B) $^{60}Co^{2+}$ on hematite, pH 6.8; (C) $^{85}Sr^{2+}$ on magnetite, pH 8.9; (D) $^{60}Co^{2+}$ on magnetite, pH 4.1. Other data as in Fig. 1.

The simple kinetic model represented by Eq. (7) is not valid beyond the elapsed time of 60–90 minutes. At longer time intervals, deviations and scattering of results appear. Probably two phenomena interfere. First, at long time intervals, c_t is close to c_e and therefore the logarithm of their difference is prone to great error. Second, at long time intervals the basic assumptions of this simple model probably do not hold. At very low adsorption (below 3–4%) the values of c_0, c_t, and c_e are close, and again the application of Eq. (7) is hardly possible. Such cases are marked in Table 1 with superscript *b*.

The observed rate constant k has been used to calculate the rate constants k_s' and k_d. For that purpose, Eqs. (4) and (6) are used: $k_d = kA_e/A_0$, $k_s' = k - k_d$, $A_e/A_0 = (100 - \text{eq.\% ads.})/100$. The values k_s' and k_d are listed in the last two columns of Table 1.

The present data clearly show that magnetite is a good sorbent for Cs^+, but hematite, in contrast, is a poor one. The explanation for such an opposite behavior might lay in the different crystal structures of these oxides. Hematite (α-Fe_2O_3) has a corundum-type crystal structure. The oxide ions O^{2-} form a hexagonally close-packed array with Fe^{3+} ions occupying the octahedral interstices (*11*). Magnetite (Fe_3O_4) is a mixed Fe(II)–Fe(III) oxide which forms black octahedral crystals of specific "inverse spinel" structure, with all Fe^{2+} ions in octahedral interstices, whereas the Fe^{3+} ions are half in tetrahedral and half in octahedral interstices of a cubic close-packed array of oxide ions. The electrical conductivity of the crystals is 10^6 times that of hematite, which is probably due to valence oscillation between Fe^{2+} and Fe^{3+} sites (*11*). It seems that the interaction of the large Cs^+ ions with the oxide ions on the surface of magnetite is more favorable than the corresponding interaction on the surface of hematite. Moreover, the repulsive positive field of Fe^{3+} ions in hematite is stronger than the corresponding repulsive field of Fe^{2+} ions in magnetite. The consequence of both effects is that magnetite adsorbs Cs^+ ions well but hematite does not.

In the case of Co^{2+}, hematite is a better sorbent than magnetite (compare the fourth column in Table 1, pH 6.6 for magnetite and pH 6.3 for hematite). We propose two conjectures which might give a possible explanation: a) Co^{2+} might form a mixed oxide $Fe_2^{III}Co^{II}O_4$ on the surface. Of course, the process could operate on the surfaces of both oxides, but more intensely on hematite than on magnetite since the Fe^{3+} content of the former oxide is higher. In that case, both oxides adsorb Co^{2+}, but hematite should be the better sorbent. b) The slightly higher value of the specific surface area of hematite could be a reason for the higher Co^{2+} sorption. However, the relative low values of the specific surface areas of both oxides, as well as the unsatisfactory accuracy of the Ströhlein method used, do not allow a more precise analysis.

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