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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Isotherm of Exchange of Sodium and Copper Cations on Ferrimanganese Concretions

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Abstract—Isotherm of ion exchange of Cu^{2+} and Na^{+} cations on ferrimanganese concretions was studied. The ion exchange is described by an equation similar to that of the Langmuir isotherm. The limiting sorption and apparent ion-exchange constant were calculated.

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Copper(II) compounds are found in wastewater from ore-dressing factories, plants manufacturing electrolytic copper, galvanic shops of various plants, and artificial fiber factories; mine water may contain copper(II) in amounts of micrograms to grams per liter.

As a rule, acid wastewater and waste technological solutions formed in metal processing contain cations of nonferrous metals in amounts exceeding the maximum permissible concentrations (MPC) and are presently purified by the reagent method. Treatment of wastewater with alkaline reagents makes it possible, in most cases, to diminish the content of ions to values that allow discharge of purified water into sewerage system of settlements or into water basins serving as household or community water sources. However, in those cases when a deeper purification of wastewater is necessary, e.g., for its discharge into fishery basins, use of only alkaline reagents fails to produce the necessary effect [1].

As an alternative technique for deeper purification to remove heavy metal cations serve sorption and ion exchange, which enable recovery of nonferrous metals from wastewater with various salt compositions to diminish their concentration to MPC, 0.1 mg l^{-1} for fishery basins.

A promising natural sorbent for purification of wastewater and waste technological solutions are ferrimanganese concretions (FMCs) [2, 3].

FMC deposits widely occur over the bottom area of the Gulf of Finland of the Baltic Sea, being mostly found at the sea bottom surface [4].

Two types of deposits can be distinguished in the Gulf of Finland. Deposits of the first type are situated at depths of 60 m and more in the southern and northern parts of the Gulf of Finland. In these deposits, concretions are represented by spherical formations with grain sizes of 1–2 to 30 mm (predominant diameter 1–16 mm), strength of 100 kPa (1 kg cm^{-2}), and density of 1.6 g cm^{-3}. Rough estimates of the concretion resources in this region give 25–30 million tons, which corresponds to a continental deposit of medium profitability.

Another deposit lies at smaller depth of 25–30 m in Kopor'e Bay. Here, the predominant concretion diameter is 3–5 mm, more rarely 15–30 mm. In the summer of 2000, first 2500 tons of a concretion-bearing material were recovered from a depth of about 30 mm in Kopor'e Bay in the course of prospecting works [5].

The technology of FMC mining has been developed at St. Petersburg Mining Institute [5]. The possibility is studied of utilization of worked-out concretions by the pyrometallurgical method at metallurgical plants by techniques involving recovery of nonferrous metals: manganese, copper, cobalt, and nickel [6, 7].

Studies of the material composition of FMCs have shown that the main part of the ore component is represented by iron and manganese hydroxides, and nonferrous metals are isomorphically bound to minerals of manganese and iron. A characteristic feature of FMCs is their hygroscopicity resulting from the developed surface of the material (porosity 58%). The ecologically pure FMC material has the form of ready-for-use rounded

Table 1. Chemical composition of concreation from Kopoe'e Bay

Component	Content	Average content according to [3]
	wt %	
Total Mn in terms of MnO_2	35.87	33.80
Fe_2O_3	36.23	20.19
Sr	0.263	0.0027
Cu	0.339	0.0034
Pb	0.449	0.0034
Zn	0.074	0.0057
SiO_2	–	17.87
Al_2O_3	–	4.49
P_2O_5	–	2.70

grains with a granulometric composition suitable for use in bulk filters.

Table 1 presents the basic chemical composition of concretions from Kopor'e Bay, found by the X-ray fluorescence technique, in comparison with that reported in [3].

The specific surface area of the FMCs is 43.81 $m^2 g^{-1}$ [9], and their capacity for iron(II), 46.34 to 123.56 g kg^{-1} against 3.25 g kg^{-1} for the imported analog [9]. Granulation of FMCs with bentonite clays makes the capacity of modified concretions 2–3 time higher, which is due to an increase in the specific surface area upon grinding and granulation with the binder.

The large resources, comparatively high specific surface area and sorption capacity, and possibility of utilization or regeneration make use of FMCs in purification technologies economically feasible.

The isotherm of exchange of sodium and copper ions on the FMC surface was studied.

Because natural samples of ferrimanganese concretions contain various exchange cations, the FMC were converted prior to experiments to the sodium form, because sodium ions are displaced with any cations [8].

An air-dry FMC sample with a grain size of 0.25 ± 0.10 mm was soaked in a 5% solution of NaOH for 5 days under permanent agitation. The alkali solution was daily replaced with a fresh one. The completeness of FMC conversion to the sodium form was judged from whether or not a constant value of the activity of Na^+ cations was

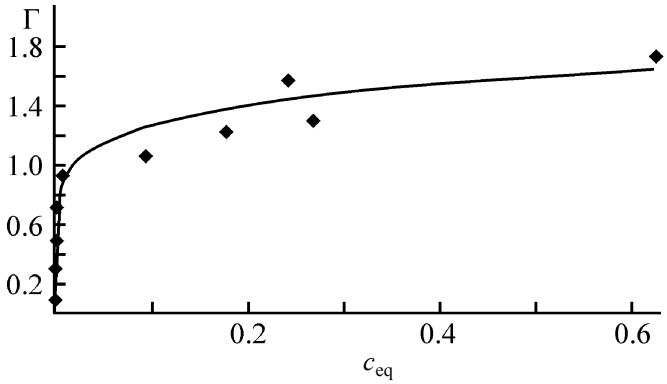

Fig. 1. Isotherm of sorption of copper cations on the FMC surface. (Γ) Sorption of copper cations, mol kg^{-1}, and c_{eq} equilibrium concentration of copper cations, M.

reached upon treatment of FMC with an alkaline solution. The activity of Na^+ ions in alkaline solutions upon a contact with FMS was measured with an ion-selective electrode and an Anion ion-meter. After that the FMC was many times washed with water to pH 7–8 of the water extract and dried to air-dry state.

The ion exchange was studied with model aqueous solutions of $CuSO_4$ with concentrations of 0.01–0.8 M in terms of copper at 298 K. The sorption Γ (mol kg^{-1}) of copper(II) cations was determined under static conditions at a liquid-to-solid volume-to-mass ratio V/m = 10 ml g^{-1} and a 5-g portion of FMC from the difference of the concentrations of the initial (c_0) and equilibrium (c_{eq}) solutions by the formula

$$\Gamma = (c_0 - c_{eq})\frac{V}{m},$$

A copper(II) sulfate solution with pH 4–5 was mixed with a weighed portion of FMC with a magnetic stirrer at a rate of 400 rpm to equilibrium state. The equilibrium corresponding to a constant solution concentration was attained in 5–6 h; in experiments, the time of phase contact was set to be no less than 10 h.

After an experiment, equilibrium concentrations of sodium ions were measured in a solution separated with a "blue-band" filter. The concentration of Cu^{2+} cations was determined by two independent methods: with ion-selective electrodes and by titration with Trilon B in the presence of murexide till a change of the solution coloration to violet [10].

Table 2 lists the initial and equilibrium concentrations of copper ions (c_0 and c_{eq}), equilibrium concentrations of sodium ions (c_{Na^+}), ionic strengths of solution (I),

Table 2. Results of experiments on ion exchange of Na^+ for Cu^{2+}

S_0, M	S_{eq}	S_{Na^+}	I	G, mol kg^{-1}	$1/G$, mol^{-1} kg	$\gamma_{\pm}$ Na_2SO_4	$CuSO_4$
0.01	4.972×10^{-9}	0.020	0.030	0.100	10	0.759	0.502
0.03	7.153×10^{-6}	0.060	0.090	0.300	3.334	0.576	0.296
0.05	2.280×10^{-5}	0.100	0.150	0.500	2.001	0.507	0.232
0.07	2.860×10^{-4}	0.139	0.210	0.697	1.434	0.465	0.197
0.10	7.500×10^{-3}	0.185	0.307	0.925	1.082	0.423	0.164
0.20	9.407×10^{-2}	0.212	0.694	1.059	0.944	0.345	0.111
0.30	1.770×10^{-1}	0.246	1.077	1.230	0.813	0.309	0.090
0.40	2.699×10^{-1}	0.260	1.470	1.302	0.768	0.286	0.078
0.80	6.270×10^{-1}	0.346	3.027	1.730	0.578	0.238	0.055

amounts of sorption (Γ), inverse amounts of sorption of Cu^{2+} ions (1/Γ), and tabulated [11] average ion activity coefficients for Na_2SO_4 and $CuSO_4$ ($\gamma_{\pm}$).

Figure 1 shows an isotherm of sorption of Cu^{2+} cations on the FMC surface, constructed using the data from Table 2. Measurements of the equilibrium concentration of sodium ions with an ion-selective electrode confirmed that the exchange of sodium cations for copper cations is equivalent. The isotherm in Fig. 1 is described by the Freundlich equation $\Gamma = 1.763\ c_{eq}^{0.142}$ with a correlation factor $R^2 = 0.97$.

A thermodynamic description of the exchange of Cu^{2+} and Na^+ ions was made on the assumption of an ideal solid phase, i.e., with the activity coefficients of ions in the sorbed state disregarded. The method of linearization of an analogue of the Langmuir equation, suggested in [12], was used. The mass action law for the reaction of ion exchange

$$2Na_s^+ + Cu_{aq}^{2+} \rightleftharpoons 2Na_{aq}^+ + Cu_s^{2+}$$

has the form

$$K = \frac{\Gamma_{Cu^{2+}} a_{Na^+}^2}{\Gamma_{Na^+}^2 a_{Cu^{2+}}}, \qquad (1)$$

where K is the apparent exchange constant; $\Gamma_{Cu^{2+}}$ and Γ_{Na^+}, amounts of sorption of the ions (mol kg^{-1}); and a_{Na^+} and $a_{Cu^{2+}}$, activities of the ions in solution (mol kg^{-1}). The limiting sorption of the ions, Γ_∞ (equiv kg^{-1}), is given by

$$\Gamma_\infty = \Gamma_{Na^+} + 2\Gamma_{Cu^{2+}}$$

where the amounts of sorption of the ions are expressed in moles per kilogram.

Equation (1) can be brought to the form

$$K = \frac{\Gamma_{Cu^{2+}}[Na^+]^2 \gamma_{\pm(Na_2SO_4)}^2}{\Gamma_{Na^+}^2\ [Cu^{2+}]\ \gamma_{\pm(CuSO_4)}}$$

$$= \frac{\Gamma_{Cu^{2+}} c_{Na}^2\ \gamma_{\pm(Na_2SO_4)}^2}{(\Gamma_\infty - 2\Gamma_{Cu^{2+}})^2 c_{eq}\ \gamma_{\pm(CuSO_4)}}. \qquad (2)$$

Equation (2) was transformed to formula (4), similar to the equation of the Langmuir isotherm (3):

$$\Gamma = \Gamma_\infty \frac{K a}{1 + K a}, \qquad (3)$$

$$\sqrt{\Gamma_{Cu^{2+}}} = \Gamma_\infty \frac{\sqrt{K c_{eq}}}{c_{Na^+}\sqrt{\frac{\gamma_{\pm(Na_2SO_4)}^2}{\gamma_{\pm(CuSO_4)}}} + 2\sqrt{\Gamma Cu^{2+}\ K c_{eq}}}. \qquad (4)$$

The linear form of the equation looks like

$$\frac{1}{\Gamma_{2+}} = \frac{2}{\Gamma_\infty} + \frac{c_{Na^+}\dfrac{\gamma_{\pm(Na_2SO_4)}}{\sqrt{\gamma_{\pm(CuSO_4)}}}}{\Gamma_\infty \sqrt{K \Gamma_{Cu^{2+}} c_{eq}}}, \qquad (5)$$

which is similar to the linear Langmuir equation:

$$\frac{1}{\Gamma} = \frac{1}{\Gamma_\infty} + \frac{1}{\Gamma_\infty K a}.$$

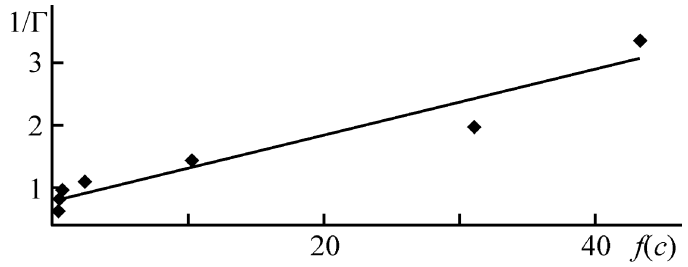

Fig. 2. Linear form of the isotherm of ion exchange of Na^+ and Cu^{2+} cations. (1/Γ) Inverse amount of sorption of copper ions kg mol^{-1}.

The dependence of the inverse amount of sorption of copper ions, $1/\Gamma Cu^{2+}$, on the argument

$$f(c) = \frac{c_{Na^+}\dfrac{\gamma_{\pm(Na_2SO_4)}}{\sqrt{\gamma_{\pm(CuSO_4)}}}}{\sqrt{\Gamma_{Cu^{2+}} c_{eq}}},$$

shown in Fig. 2, is approximated with a linear equation

$$\frac{^{aq}}{\Gamma_{Cu^{2+}}} = 0.755 + 0.054 f(c)$$

with a correlation factor $R^2 = 0.94$. Hence the following parameters were calculated: limiting sorption of copper ions, $\Gamma_\infty = 65$ equiv kg^{-1}; apparent ion-exchange constant, $K_{Na^+/Cu^{2+}} = 49.73$; and Gibbs energy of exchange of copper ions for sodium cations on the FMC surface, $\Delta G = -9.683$ kJ mol^{-1}.

The limiting sorption of strontium cations on the FMC surface is $\Gamma_\infty = 0.97$ equiv kg^{-1} [13], which is 1.73 times smaller than the limiting sorption of nickel ions (1.68 equiv kg^{-1}) and 2.73 times smaller than that of copper ions (2.65 equiv kg^{-1}). This is due to the smaller landing site area for Cu^{2+} ions. The specific surface area of FMC ($S_{sp} = 43.81$ m^2 g^{-1} [9]) and the limiting sorption of copper cations (1.325 mol kg^{-1}) were used to estimate the landing site area for Cu^{2+} ions:

$$S_M = \frac{S_{sp}}{\Gamma_\infty N_A} = \frac{43.81 \times 10^3}{1.325 \times 6.02 \times 10^{23}}$$

$$= 5.49 \times 10^{-20} R^2,$$

where N_A is the Avogadro number.

The radius of a sorbed Cu^{2+} cation was calculated to 132 pm. This value exceeds the crystallographic radius of Cu^{2+} by Bokii (80 pm) [11] and is smaller than the radius calculated by the Stokes equation (326 pm):

$$r_{ap} = \frac{|z|F^2}{6\pi N_A \eta \lambda^0},$$

where z is the charge of the copper cation; F, Faraday constant; η, viscosity of water; and λ_0, limiting equivalent electrical conductivity of the copper cation.

The experimentally determined radius of the copper cation should be regarded as an average effective radius of partly dehydrated Cu^{2+} ions. The resulting value of the Cu^{2+}_{aq} radius on the FMC surface is smaller than the radii of Sr^{2+}_{aq} and Ni^{2+}_{aq} cations adsorbed on FMC (213 and 166 pm, respectively) [13].

This circumstance indicates that, because of the stronger polarizing effect, the Cu^{2+}_{aq} cation is dehydrated to a greater extent and is more firmly bound to FMC than the Sr^{2+} and Ni^{2+} cations.

Cations can be arranged, on the basis of the Gibbs energies of ion exchange, in order of increasing displacement capacity (which correlates with the increase in the ionic potential z/r_{aq} of the cations, where z is the charge, and r_{aq}, radius of partly dehydrated cations sorbed on FMC), as follows:

	Na^+	<	Sr^{2+}	<	Ni^{2+}	<	Cu^{2+}
ΔG°_{298}, kJ mol^{-1}	–		–0.74		1.93		–9.68
$\frac{z}{r_{aq}} \times 10^3$, g m^{-1}	5.46		9.39		12.05		15.2

As r_{aq} for the Na^+ cation is taken the radius of hydrated cation by Stokes (equal to 183 pm [11].

Because the ionic potential of Cu^{2+} cations is higher, they will displace Na^+, Sr^{2+}, and Ni^{2+} cations from the FMC surface in the exchange reaction.

CONCLUSIONS

(1) It was demonstrated that the isotherm of ion exchange of Na^+ and Cu^{2+} cations on ferrimanganese concretions is described by a modified Langmuir equation and can be represented in the linear form with a correlation factor $R^2 = 0.94$.

(2) The apparent ion-exchange constant ($K = 49.73$) and the Gibbs energy of exchange of copper ions for sodium ions on the surface of ferrimanganese concretions ($\Delta G^\circ_{298} = -9.683$ kJ mol^{-1}) were found. The landing

site area for copper cations was estimated to be 5.49×10^{-20} m^2; the radius of the sorbed ion, 132 pm, points to its firmer binding to the ferrimanganese concretion, compared with Sr^{2+} and Ni^{2+} cations.

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