

## CHEMICAL-METALLURGICAL PROCESSES OF ADVANCED PROCESSING OF CRUDE ORE AND TECHNOGENIC AND SECONDARY RAW MATERIALS

# Kinetics of the Sorption of Heavy-Metal Ions by a Sorbent Obtained from Boric Acid Production Waste

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**Abstract**—The results of studies of kinetic regularities of sorption of heavy-metals ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Mn}^{2+}$ ) by a sorbent based on calcium hydrosilicate (hereinafter referred to as silicate sorbent) produced from manmade waste formed during the processing of the boron-containing mineral raw materials (boron–gypsum) have been presented.

**Keywords:** calcium hydrosilicate, boron–gypsum, silicate sorbent, sorption, heavy-metal ions, sorption kinetics

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## INTRODUCTION

Environmental contamination by heavy metals as a result of the operation of various industries is an urgent problem that requires the development of ecologically safe and inexpensive sorption materials for detoxification of contaminated objects.

Among versatile inorganic sorbents applied for decontamination of aqueous media from heavy-metal ions, a special group includes natural and synthetic silicates and composite sorbents on their basis. The high efficiency of various silicates ( $n\text{CaO} \cdot m\text{SiO}_2$ ) and hydrosilicates ( $n\text{CaO} \cdot m\text{SiO}_2 \cdot p\text{H}_2\text{O}$ ) during their application as ecologically safe sorbents for the decontamination of aqueous solutions from heavy-metal ions has been demonstrated in numerous works performed in this country and abroad (Table 1). The authors of [1–13] shown in Table 1 studied the process of the sorption of different heavy-metal ions by calcium silicates and hydrosilicates of specific compositions and structures. The mechanism of the interaction of heavy-metal salts with calcium silicates has also been studied.

Earlier, the studies of sorption properties of calcium silicates produced from waste formed during the processing of boron-containing mineral raw materials (boron–gypsum) were performed at the Institute of Chemistry Far Eastern Branch of the Russian Academy of Sciences for the first time. It was established that calcium silicates were efficient sorbents of heavy-metal ions [14–19].

The most important sorbent properties that characterize its efficiency are known to be the sorption capacity value and the sorption equilibrium attainment time. In view of this, it is of interest to study kinetic regularities of sorption of heavy-metal ions using a material based on calcium silicates (hereinafter referred to as a silicate sorbent) produced from man-made waste formed during the processing of boron-containing mineral raw materials (boron–gypsum), which was the objective of the present work.

## EXPERIMENTAL

### *Synthesis of Calcium Hydrosilicate (Silicate Sorbent)*

In order to obtain a sorbent based on calcium hydrosilicate, waste of boric acid manufacturing was used (boron–gypsum with the main components contents: 32.2 wt %  $\text{SiO}_2$ , 28.4 wt %  $\text{CaO}$ , 31.3 wt %  $\text{SO}_3$ , and 2.7 wt %  $\text{Fe}_2\text{O}_3$ ). Calcium sulfate dehydrate and amorphous silica are the main components of boron–gypsum. The boron–gypsum specific surface area is equal to 12.9  $\text{m}^2/\text{g}$ . Boron–gypsum was mixed with a solution of analytical-grade potassium hydroxide. The synthesis was carried out in an autoclave under a pressure of 1.7 atm (temperature 118°C) for 3 h. After this time period, the obtained mixture was removed from the autoclave, the precipitate was washed with distilled water heated up to 60–70°C, separated from the solution by filtering through a Blue Ribbon filter, and dried at 85°C for several hours. The target product output was controlled on the quantity of the reacted potassium hydroxide.

**Table 1.** Calcium silicates used for the sorption of heavy-metal ions

Sorbent	Sorbed ions	Literature
Xonothlite $\text{Ca}_6[\text{Si}_6\text{O}_{17}](\text{OH})_2$ and wollastonite $\text{Ca}_6\text{Si}_6\text{O}_{18}$	$\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Sr}^{2+}$ , $\text{Co}^{2+}$ , $\text{Mn}^{2+}$	1
Wollastonite $\text{Ca}_6\text{Si}_6\text{O}_{18}$	$\text{Ni}^{2+}$ , $\text{Cu}^{2+}$	2.3
11 Å tobermorite $\text{Ca}_{10}[\text{Si}_{12}\text{O}_{31}](\text{OH})_6 \cdot 8\text{H}_2\text{O}$	$\text{Ni}^{2+}$ , $\text{Co}^{2+}$	4
Xonothlite, wollastonite, tobermorite	$\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Co}^{2+}$ , $\text{Mn}^{2+}$	5
Xonothlite and tobermorite	$\text{Ni}^{2+}$ , $\text{Co}^{2+}$	6
Calcium hydrometasilicate CSH(I)	$\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Mn}^{2+}$	7–9
Composite sorbent based on calcite, calcium silicate, and silica gel	$\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cr}^{3+}$	10
Tobermorite	$\text{Pb}^{2+}$ , $\text{Cd}^{2+}$	11–13

### Experiments on the Sorption Kinetics

Experiments were carried out on the sorption kinetics under static conditions from aqueous solutions of cobalt, cadmium, zinc, nickel, copper, and manganese chlorides with stirring using an RT 15 Power magnetic stirrer (IKA WERKE, Germany). Solutions of respective salts of the above metals in pre-set concentrations were prepared by dissolving accurately weighed samples in distilled water. Sorbent samples of 0.05 g were placed into a series of test tubes and added with 20 mL of aqueous solutions of salts of respective metals to an initial concentration of ions of 200  $\mu\text{g}/\text{mL}$  and stirred for different lengths of time (1–300 min). In some specific time periods, the solution was separated from the sorbent by filtration, and the concentrations of respective ions in it were determined. The parameters of experiments carried out to study kinetic sorption regularities are shown in Table 2.

The sorption capacity ( $A_s$ , mmol/g) of the silicate sorbent was calculated according to the formula

$$A_s = \frac{(C_{\text{init}} - C_{\text{eq}})V}{m}, \quad (1)$$

where  $C_{\text{init}}$  is the initial concentration of the metal ion in solution, mmol/L;  $C_{\text{eq}}$  is the equilibrium concentration of the metal ion in solution, mmol/L;  $V$  is the solution volume, L; and  $m$  is the sorbent weight, g.

The degree of removal of the metal ions ( $\alpha$ , %) was calculated from the formula

$$\alpha = \frac{(C_{\text{init}} - C_{\text{eq}})}{C_{\text{init}}} \times 100\%. \quad (2)$$

The kinetics data on the sorption of metal ions were analyzed in accordance with kinetic models of pseudo-first and pseudo-second orders [20, 21]. The kinetic equation of the pseudo-first order (the Lagergren's equation):

$$\frac{dA_t}{dt} = k_1(A_e - A_t), \quad (3)$$

**Table 2.** Experimental parameters at studies of kinetic regularities of sorption of heavy-metal ions by the silicate sorbent produced from boron–gypsum

Sorbed ion	Sorbate	Initial metal concentration, mmol/L	S : L ratio	Sorption duration, min
$\text{Zn}^{2+}$	$\text{ZnCl}_2$ , analytical grade, GOST Russian State Standard 4529–78	2.7	1 : 400	1–300
$\text{Ni}^{2+}$	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , chemically pure grade, GOST Russian State Standard T 4038–79	3.4	1 : 400	1–300
$\text{Cu}^{2+}$	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , pure grade, GOST Russian State Standard 4167–74	3.0	1 : 400	1–300
$\text{Cd}^{2+}$	$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ , analytical grade, GOST Russian State Standard 4330–76	1.8	1 : 400	1–300
$\text{Co}^{2+}$	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , analytical grade, GOST Russian State Standard 4525–77	3.6	1 : 400	1–300
$\text{Mn}^{2+}$	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , analytical grade, GOST Russian State Standard 612–75	3.5	1 : 400	1–300

where  $k_1$  is the rate constant for the sorption within the scopes of the pseudo-first order model and  $A_e$ ,  $A_t$  are the sorption capacities in the equilibrium state and at the moment  $t$ , respectively. In the linear integral form under initial conditions ( $A_t = 0$  at  $t = 0$  and  $A_t = A_t$  at  $t = t$ ), the equation can be written as

$$\log(A_e - A_t) = \log A_e - \frac{k_1}{2.303} t. \quad (4)$$

The kinetic model of the pseudo-second order

$$\frac{dA_t}{dt} = k_2(A_e - A_t)^2, \quad (5)$$

where  $k_2$  is the rate constant for the sorption within the scopes of the pseudo-second order model.

Equation (5) can be transformed as follows:

$$\frac{t}{A_t} = \frac{1}{k_2 A_e^2} + \frac{1}{A_e} t. \quad (6)$$

### Analytical Methods

The concentration of potassium hydroxide was determined by the method of acid–base titration using 0.1 N HCl solution prepared from the titrimetric standard as a titrant.

The precipitates' X-ray images were recorded using a D8 ADVANCE automatic diffractometer with the sample rotation in  $\text{CuK}\alpha$  radiation. The X-ray diffraction analysis was carried out using the EVA search program with the PDF-2 powder database.

The specific surface area of the samples was determined by the method of low-temperature nitrogen adsorption using a Sorbtometer–M device.

The  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mn}^{2+}$  ions contents in the solutions were determined by the method of atomic–absorption spectrometry (AAS) using a SOLAAR M6 double-beam spectrometer (Thermo, United States) on the analytical lines at 240.7, 228.8, 213.9, 232.0, 324.8, and 279.5 nm, respectively.

## RESULTS AND DISCUSSION

According to X-ray diffraction analysis, the obtained calcium hydrosilicate is X-ray amorphous. Aside from the amorphous phase, the crystalline phases of unreacted semi-hydrate and dihydrate of calcium sulfate were found in the composition of the synthesized sample. Under the above conditions, the output of the target product (calcium hydrosilicate) was equal to 88.9%. The results of annealing the sample during the transformation of the amorphous calcium hydrosilicate into the crystalline phase of wolastonite of the triclinic modification, which was corroborated by the XRD data of the sample after annealing at 900°C. Furthermore, the phases of water-free calcium sulfate and quartz are present in

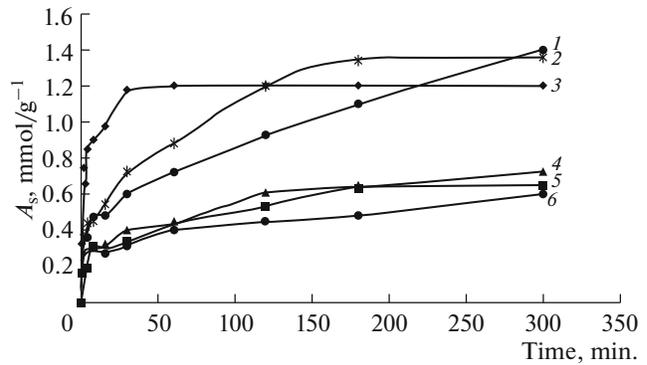


Fig. 1. Kinetic curves of the sorption of heavy-metal ions by the silicate sorbent: (1)  $\text{Co}^{2+}$ , (2)  $\text{Ni}^{2+}$ , (3)  $\text{Cu}^{2+}$ , (4)  $\text{Zn}^{2+}$ , (5)  $\text{Cd}^{2+}$ , (6)  $\text{Mn}^{2+}$ .

the sample upon annealing. The specific surface area of the material under study was equal to 46  $\text{m}^2/\text{g}$ .

Figure 1 shows the kinetic curves of the sorption of heavy-metal ions by the produced silicate sorbent.

These dependences show differences in the kinetics of sorption by the silicate sorbent. The equilibrium in the metal ions distribution between the sorbent and the solution is attained within 30 min for  $\text{Cu}^{2+}$  ions, within 60 min for  $\text{Mn}^{2+}$  ions, within 120 min for  $\text{Zn}^{2+}$  ions, and within 180 min for  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  ions. For  $\text{Co}^{2+}$  ions, the duration of the experiment (300 min) was insufficient to attain the equilibrium. However, the degree of removal of  $\text{Co}^{2+}$  ions within 300 min is rather high and attains 97.2%. One should take into account that the real time of interaction between the sorbent and the sorbate is 5–10 longer considering the duration of precipitates filtration through a Blue Ribbon filter. Under the equilibrium conditions, the values of the sorption capacity of the silicate sorbent toward  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cd}^{2+}$  ions are equal to 1.2, 0.4, 0.6, 1.35, and 0.63  $\text{mmol/g}$  corresponding to degrees of removal of 97.8, 28.6, 55.6, 99.3, and 87.8%, respectively.

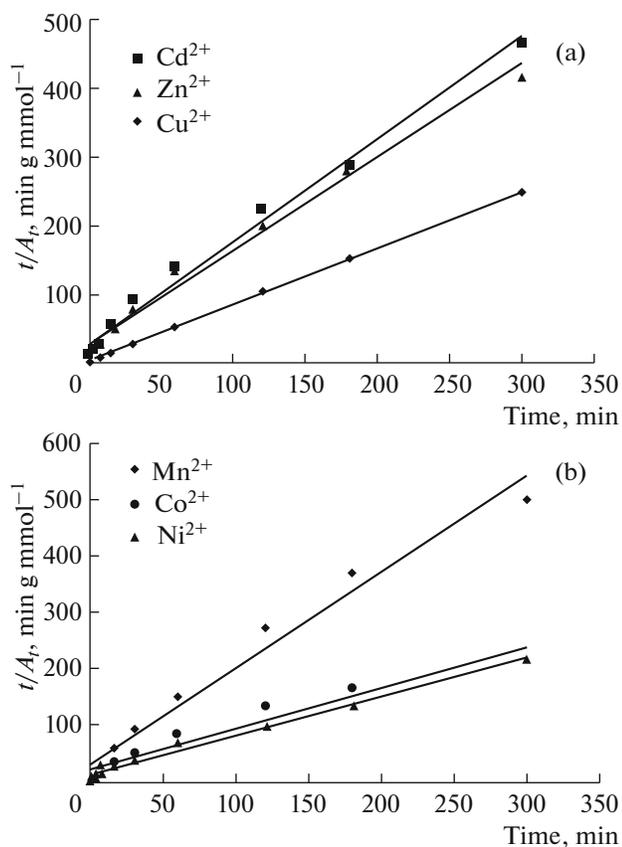
The apparent pseudo-rate constants ( $k_1$  and  $k_2$ ) and corresponding squares of correlation coefficients ( $R^2$ ) that indicate the correctness of the relation to kinetic models of pseudo-first and -second orders are shown in Table 3.

As can be seen from the data of Table 3, in almost all cases (except  $\text{Co}^{2+}$ ), the kinetics of the sorption of heavy-metal ions by the silicate sorbent under study is described most adequately by the pseudo-second order model, which is indicated by the corresponding correlation coefficients. However, in some cases (sorption of  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  ions), the difference between the correlation coefficients for models of the pseudo-first and -second orders is insignificant. The

**Table 3.** Results of processing kinetic curves of the sorption of heavy-metal ions by silicate sorbent using models of chemical kinetics

Metal ion	Kinetic model			
	pseudo-first order		pseudo-second order	
	$k_1, \text{min}^{-1}$	$R^2$	$k_2, \text{g mmol, min}$	$R^2$
$\text{Cu}^{2+}$	0.68	0.9484	0.49	0.9999
$\text{Mn}^{2+}$	1.07	0.9642	0.12	0.9741
$\text{Zn}^{2+}$	0.7	0.9845	0.083	0.9855
$\text{Ni}^{2+}$	0.2	0.9215	0.041	0.9879
$\text{Cd}^{2+}$	0.69	0.9359	0.1	0.9876
$\text{Co}^{2+}$	0.03	0.9880	0.03	0.9506

kinetics of the sorption of  $\text{Co}^{2+}$  is described most adequately by the pseudo-first order model. The linear dependences obtained from the experimental data in



**Fig. 2.** Dependences of relative values of the sorption capacity at moment  $t$  over time in accordance with the experimental data on sorption of heavy-metal ions by the silicate sorbent: (a)  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ; (b)  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ .

accordance with the pseudo-second order equation are shown in Fig. 2.

## CONCLUSIONS

The kinetics of the sorption of heavy metals ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Mn}^{2+}$ ) by a sorbent based on calcium hydrosilicate produced using an autoclave method from manmade waste formed during the processing of boron-containing mineral raw materials (boron–gypsum) has been investigated.

It has been established that the equilibrium in the distribution of metal ions between solution and sorbent is achieved within 30 min for  $\text{Cu}^{2+}$  ions, 60 min for  $\text{Mn}^{2+}$  ions, 120 min for  $\text{Zn}^{2+}$  ions, and 180 min for  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$  ions. For  $\text{Co}^{2+}$  ions, the duration of the experiment (300 min) is insufficient to achieve equilibrium. However, the degree of removal of  $\text{Co}^{2+}$  ions within 300 min is sufficiently high and achieves 97.2%.

It has been demonstrated that, in almost all cases (except  $\text{Co}^{2+}$  ions), the kinetics of the sorption of heavy-metal ions by the studied silicate sorbent is described most adequately by the pseudo-second order model. On the other hand, the kinetics of the sorption of  $\text{Co}^{2+}$  is described most adequately by the pseudo-first order model.

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