Sorption of transition metal cations on natural heulandite

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The cation exchange equilibrium in the systems of natural heulandite—binary aqueous solutions of NaCl, $NiCl_2$, $CuCl_2$, $ZnCl_2$, and $MnCl_2$ was studied. The corrected coefficients of the selectivity ($k^a{}_{M/Na}$) and thermodynamic constants ($K_{M/Na}$) of the cation exchange of Na^+ cations for transition metal cations were determined. The selectivity of the cation exchange on natural heulandite increases in the following order: $Ni^{2+} < Cu^{2+} < Zn^{2+} < Na^{2+} < Mn^{2+}$.

Key words: natural heulandite, transition metals, cation exchange; selectivity.

It has been shown previously[1,2] that the cation exchange of Na^+ for K^+ and Cs^+ in natural heulandite is accompanied by considerable strains in the aluminosilicate cage, and the selectivity of the exchange of alkaline metal cations increases in the following order: $Li^+ < Na^+ < K^+ < Cs^+$.

In this work, the results of the application of X-ray diffractometry and thermography for the study of the properties of Ni^{2+}-, Cu^{2+}-, Zn^{2+}-, and Mn^{2+}-forms of natural heulandite are presented. We studied the selectivity of the sorption of transition metals from binary solutions by the sodium-substituted form of heulandite, *i.e.*, the cation exchange according to the equation

$$1/2\ M^{2+} + \bar{N}a^+ = 1/2\ \bar{M}^{2+} + Na^+, \qquad (1)$$

where the phase of heulandite is designated by the dash.

Experimental

Natural zeolite tuff containing up to 80 % heulandite from the Pegasskoe deposit (Kemerovo district) was used. Natural heulandite of the composition $(Na_2O)_{0.05}(K_2O)_{0.10-0.15} \times (CaO)_{0.60-0.65}(MgO)_{0.15-0.25} \cdot Al_2O_3 \cdot (8.5-9.0)SiO_2 \cdot nH_2O$ was studied.

The total dynamic ion-exchange capacity of natural heulandite determined by the known procedure[3] was 2.20±0.02 mg-equiv./g. To determine the ion-exchange capacity in the sorption of transition metals, a weighed sample of the Na^+-form of heulandite[3] was placed on an ion-exchange column, and a 0.005 *M* aqueous solution of MCl_2 ($M^{2+} = Zn^{2+}, Cu^{2+}, Ni^{2+}$, and Mn^{2+}) was passed through the column until the outlet concentration became equal to the initial concentration of the solution.

Diffractograms of monocationic forms of heulandite were recorded on a Dron-2 diffractometer (Cu-radiation, Ni-filter, current 22 mA, voltage 30 kV).

The differential thermal analysis (DTA) was carried out on an MOM derivatograph (Hungary) using a platinum-platinumrhodium thermocouple and heating a sample to 1000 °C at a rate of 10 °C per min.

The selectivity of the cation exchange from aqueous solutions containing two electrolytes was studied by the static method[1] at 298 K and the ionic strength of the solution of 0.1 mol L^{-1}. Concentrations of the cations Ni^{2+}, Cu^{2+}, Zn^{2+}, and Mn^{2+} in solution were determined by complexonometry.[4,5]

The corrected selectivity coefficients of the cation exchange (reaction (1)) were calculated by Eq. (2)

$$k^a_{M/Na} = \frac{\bar{x}_M^{1/2}\ x_{Na}}{\bar{x}_{Na}\ x_M^{1/2}} \cdot \frac{f^2_{\pm NaCl}}{f^{3/2}_{\pm MCl_2}}, \qquad (2)$$

where $k^a{}_{M/Na}$ is the corrected selectivity coefficient of the cation exchange of Na^+ (initial form) for M^{2+}; $\bar{x}_M$, $\bar{x}_{Na}$, and x_M, x_{Na} are the molar fractions of the M^{2+} and Na^+ cations in heulandite and solution, respectively; and $f_\pm$ is the mean rational activity coefficient calculated by the Debye—Hückel equation (Eq. (3)).

$$\log f_\pm = -\frac{A|z_1 z_2|\sqrt{\mu}}{1 + Ba\sqrt{\mu}} \qquad (3)$$

Here $A = 0.511$, $B = 0.3281$, $a = 4.5$ Å, z_1 and z_2 are the charges of the cation and anion, respectively, and μ/mol L^{-1} is the ionic strength of the solution.

The thermodynamic equilibrium constants of the cation exchange ($K_{M/Na}$) were calculated by Eq. (4).

$$\ln K_{M/Na} = \int_0^1 \ln k^a_{M/Na} d\bar{x}_M \qquad (4)$$

Results and Discussion

When Na^+ cations are exchanged for heavy alkaline metal cations, a tendency for the formation of ionic pairs between ionogenic groups of heulandite and sorbed cations is observed. This results in the dehydration of the ionogenic groups of heulandite and a considerable distortion of its crystalline lattice. The DTA curves of the

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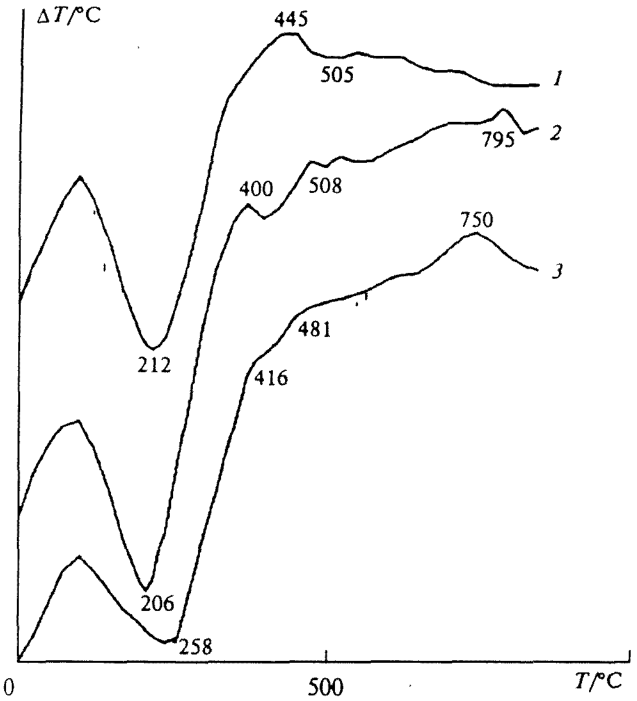

Fig. 1. DTA curves of Na$^+$- (*1*), Zn^{2+}- (*2*), and Cu^{2+}-forms (*3*) of natural heulandite.

heulandite samples studied are presented in Fig. 1. It follows from Fig. 1 that the sorption of transition metal cations by the Na$^+$-form of heulandite does not change the form of the DTA curves. The interplanar distances and relative intensities of the reflections for the cation-substituted forms of natural heulandite are presented in Table 1. As seen from the data in Table 1, the reflections of the Na$^+$-, Zn^{2+}-, and Cu^{2+}-forms of heulandite correspond to the interplanar distances (d = 9.0, 7.90, 5.25, 5.10, 4.67, 3.97, 3.92, 3.18, 3.12, 2.99, and 2.80 Å), which are close to the main reflections of heulandite.[6] The intensity of the line of 9.0 Å is virtually retained, and in our opinion it is an indicator for the content of water in heulandite.[2]

It is known[7] that the maximum ion-exchange capacity is not achieved for the sorption of two-valent cations by clinoptilolite, erionite, and mordenite. The determined values of the ion-exchange capacity (*EC*) of the Na$^+$-form of heulandite with respect to the studied cations are the following:

Cation	Na$^+$	Ni^{2+}	Cu^{2+}	Zn^{2+}	Mn^{2+}
EC/mg-equiv. g^{-1}	2.20	1.40	1.68	1.72	1.70

It is seen that the exchange capacity for the sorption of two-valent transition metal cations by heulandite is lower than the total dynamic ion-exchange capacity. It is likely that the decrease in the capacity is caused by the fact that some sorption centers of heulandite are inaccessible for transition metal cations, because they are sorbed in the partially hydrated state.

Table 1. Diffractograms of the cation-substituted forms of natural heulandite

Na$^+$-form		Cs$^+$-form[2]		Cu^{2+}-form		Zn^{2+}-form	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
9.07	6	—	—	9.02	5	8.97	5
7.90	3	—	—	7.89	1	7.89	1
6.66	2	—	—	6.60	1	6.65	1
5.25	2	—	—	5.21	2	5.23	4
5.13	2	5.15	1	5.09	1	5.09	1
4.67	2	—	—	4.67	2	4.66	3
3.97	7	3.97	4	3.97	10	3.96	10
3.92	4	3.92	2	3.90	8	3.91	8
3.56	1	3.56	1	3.54	2	3.54	2
3.43	3	3.43	2	3.41	3	3.41	2
3.18	3	3.18	2	3.16	3	3.16	3
3.13	2	3.13	1	3.12	1	3.12	1
2.99	4	3.01	3	2.99	3	2.98	2
2.81	2	2.81	1	2.79	2	2.79	2
2.75	1	2.75	2	2.74	2	2.74	2

The isotherms of the cation exchange Na$^+$/M^{2+} are presented in Fig. 2. It follows from Fig. 2 that the logarithms of the corrected selectivity coefficients of the cation exchanges depend linearly on the counterion composition of heulandite. The correlation coefficients of the dependence of $\ln k^{a}_{M/Na}$ on $\bar{x}_M$ for the exchanges Na$^+$/Mn^{2+}, Na$^+$/Zn^{2+}, Na$^+$/Cu^{2+}, and Na$^+$/Ni^{2+} are

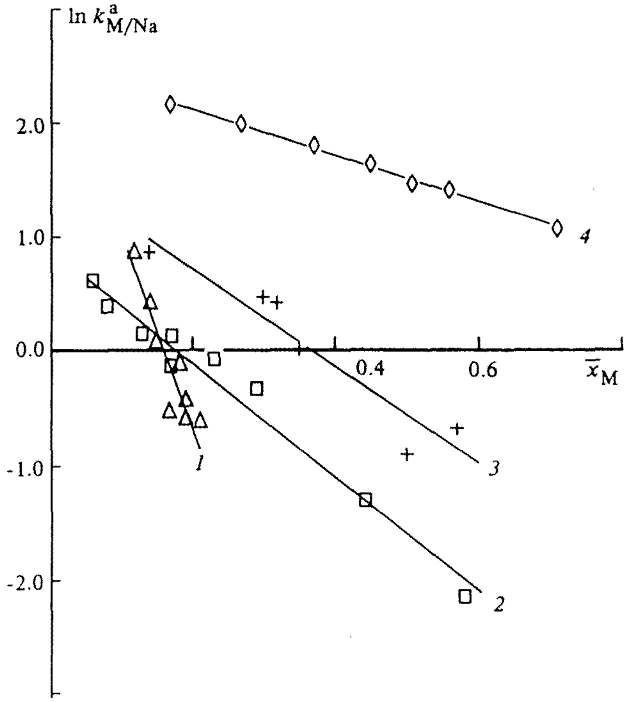

Fig. 2. Dependence of the selectivity coefficients of the cation exchange on the counterion composition of heulandite: *1*, Ni^{2+}/Na$^+$; *2*, Cu^{2+}/Na$^+$; *3*, Zn^{2+}/Na$^+$; *4*, Mn^{2+}/Na$^+$.

Table 2. Thermodynamic constants ($K_{M/Na}$) of the cation exchange of transition metals on the Na^+-form of natural heulandite and hydration energies (ΔG_h)* of the cations

M^{2+}	ΔG_h /kJ mol^{-1}	$K_{M/Na}$
Ni^{2+}	2055	0.0037
Cu^{2+}	2055	0.19
Zn^{2+}	2005	0.60
Mn^{2+}	1879	4.48

* Literature data.[8]

equal to 0.99, 0.95, 0.99, and 0.93, respectively. It is likely that the linearity of the functions reflects an insignificant role of the mutual effect of different counterions on the ion exchange energy in the composition range considered. The slopes of the lines are associated with the energy nonequivalence of ion-exchange centers, which make an additive contribution to the Gibbs energy of the system, when the counterion composition of heulandite changes due to the exchange of the cation pairs studied. Probably, this is a manifestation of the similarity of the Coulomb interactions of cations with ionogenic groups and the solvent.

The thermodynamic constants of the cation exchange ($K_{M/Na}$) calculated by Eq. (4) and hydration energies of the cations studied are presented in Table 2. The comparison of the values of the resulting thermodynamic constants makes it possible to present the following order of the selectivity of heulandite with respect to the metal cations studied: $Ni^{2+} < Cu^{2+} < Zn^{2+} < Na^{2+} < Mn^{2+}$. The data in Table 2 are evidence that the order of the values of the selectivity of the sorption of transition metal cations on heulandite coincides with the sequence of their dehydration.

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